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Minero-petrographic characterization of Chianocco Marble employed for Palazzo Madama façade in Turin (NW Italy)

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Abstract: The study of ancient marbles plays an important role in the interpretation of an historical and archaeological site and gives interesting information about building materials used in ancient times and their trade routes. The present work focuses on Chianocco Marble that represents one of the most important ancient white marbles for Cultural Heritage exploited in Piedmont region (NW Italy) and employed for Palazzo Madama façade. A multi-analytical study based on petrographic (optical and scanning electron microscopy), electron microprobe and stable isotope analyses was carried out on these marbles in order to perform an archaeometric study.

Chianocco Marble was used in Turin during the baroque era by the Savoy architect Filippo Juvarra (1678 - 1736) in historical buildings, as the façade of Palazzo Madama, the plinth of the façade of the town Cathedral and the columns (now plastered) of the portico of Piazza San Carlo. This stone is a dolomitic rock belonging to the Mesozoic cover of the Dora Maira Massif (Pennidic Unit). It shows a vuggy fabric characterized by a vacuolar texture due to tectonic brecciation and subsequent selective dissolution during subaerial exposure. This kind of research is useful to highlight the importance of the use of local stones as building materials and to investigate stone materials for the restoration and the maintenance of the historical buildings.

Keywords: Chianocco Marble; Heritage stone; Archaeometry, Western Alps, isotopic analysis, SEM-EDS.

1. Introduction

Ancient buildings, artifacts and findings are mainly made of natural and artificial materials obtained from geological resources. The development of Geosciences applied on Cultural Heritage has made it possible to highlight how the study of the nature and origin of ornamental stones is predominantly a geological matter, which cannot be solved without a geologic approach [1]. A proper characterization of these materials requires minero-petrographic studies for defining their provenance, conservation state, and application of good preservation strategies.

In Piedmont, and in particular in Turin, stone has always been largely used for both constructions and decorations, becoming one of the distinctive elements of the local architectural heritage: statues, city walls, floors, roofs, and other architectural elements, are often made of the many varieties of rocks belonging to the different geological units of the Western Alps [2,3,4]. Often, the selection of stone materials in architecture is driven by specific values and meanings attributed to the different rocks; moreover, the use of specific lithotypes can be related to aesthetic values, technical progress or even economic circumstances. Because of their easiness of lavorability, marbles have been widely employed, from Roman times to the end of XVIII century, in valuable buildings [5].

One of the most prestigious building in Turin is certainly Palazzo Madama (Figure 1a), an historical and architectural complex located in the center of the town. It is an UNESCO World Heritage site and at present is the seat of the city Ancient Art Museum. It is the testimony of two thousand years of history: originally built by the Romans as a gateway to the town, the building became first a defensive system, and then the symbol of the power until the sixteenth century, when it was replaced by the Palazzo Reale as seat of the Dukes of Savoy. With King Carlo Alberto, politics also entered Palazzo Madama: in 1848, the king placed the Subalpine Senate in the large hall on the first floor, destined to become one of the places of politics in which Italy's unity was most strongly prefigured. Considerably embellished under the regency of the two Royal Ladies also known as “Madame” (hence the name): Maria Cristina of France and Maria Giovanna Battista of Savoy, the old medieval castle was retrained by the work of Filippo Juvarra, who realized (1718-1721) the great façade which dominates the square [6,7]. He chose the Chianocco Marble, a yellowish grey marble from the Susa Valley, for coating the façade. The strong deterioration of this marble made necessary, over time, several restorations and replacements by different stone materials recalling the original one but coming from different sources [8,9]. As a consequence, many archaeometric studies carried out on the façade of Palazzo Madama resulted to be contradictory and partially wrong in the attribution of the stones employed over the centuries [10,11].

For this reason, and because of many recentconservation issues, the Conservation and Restoration Foundation “La Venaria Reale”, in collaboration with Fondazione Torino Musei and under the supervision of Soprintendenza Archeologia, Belle Arti e Paesaggio per la Città metropolitana di Torino promoted several technical and scientific investigations in order to develop a pilot project for the overall conservation and future maintenance of the historical façade (Figure 1b).

The purpose of this paper is to provide a detailed petro-architectonic survey and a minero-petrographic characterization of the Chianocco Marble also aimed to define the causes of its degradation.

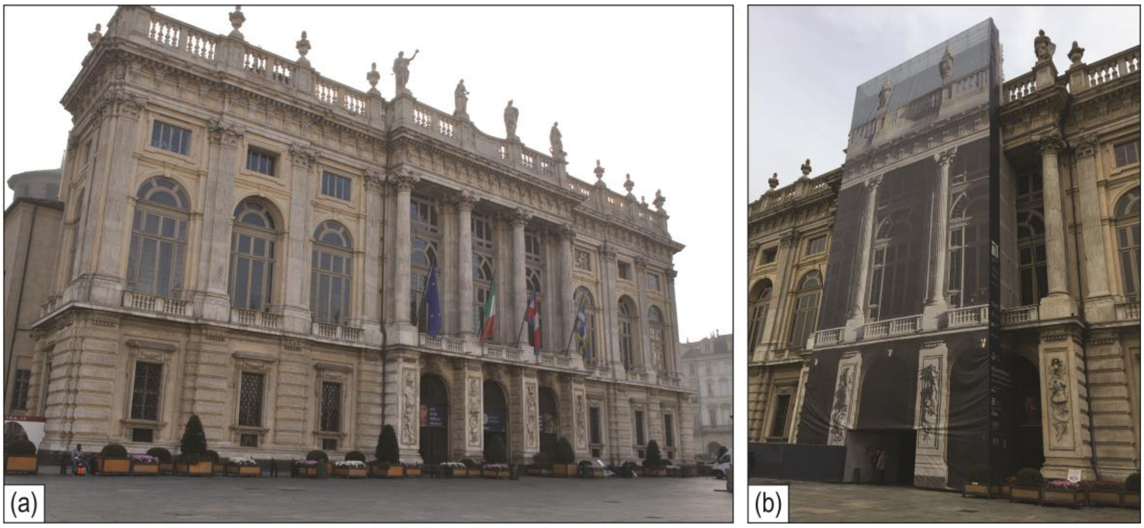

Figure 1. (**a**)View of the Palazzo Madama façade.; (**b**) Study site located in the central area of the façade.

2. Geological setting

In the central portion of the Susa Valley (north-western Italy), some marbles pertaining to the meta-carbonate cover of the Dora Maira Massif crop out. The Dora Maira Massif is a unit of continental crust belonging to the Pennidic Domain of the Western Alps (Figure 2a), which was pervasively deformed and metamorphosed during the Alpine orogeny, which occurred about 50 Ma ago. The Dora Maira Massif is predominantly made up of gneiss and micaschists of Palaeozoic age and rare slices of the original carbonate cover Triassic to Early Jurassic in age, which during Alpine metamorphism became dolomitic marbles. The Alpine metamorphic cycle resulted in a first event that developed under eclogitic conditions, during which peak pressure (P) and temperature (T) conditions were reached, followed by a retrograde metamorphic event that developed under greenschist facies conditions [12]. Historically, Susa Valley marbles have been distinguished in "Foresto and Chianocco Marbles" on the basis of their extraction site [13,14]. Actually, they are two different kind of rocks with different petrographic features resulting from different geological processes. The Foresto Marble consists of massive whitish marbles whereas the Chianocco Marble shows a vacuolar structure and a yellowish color.

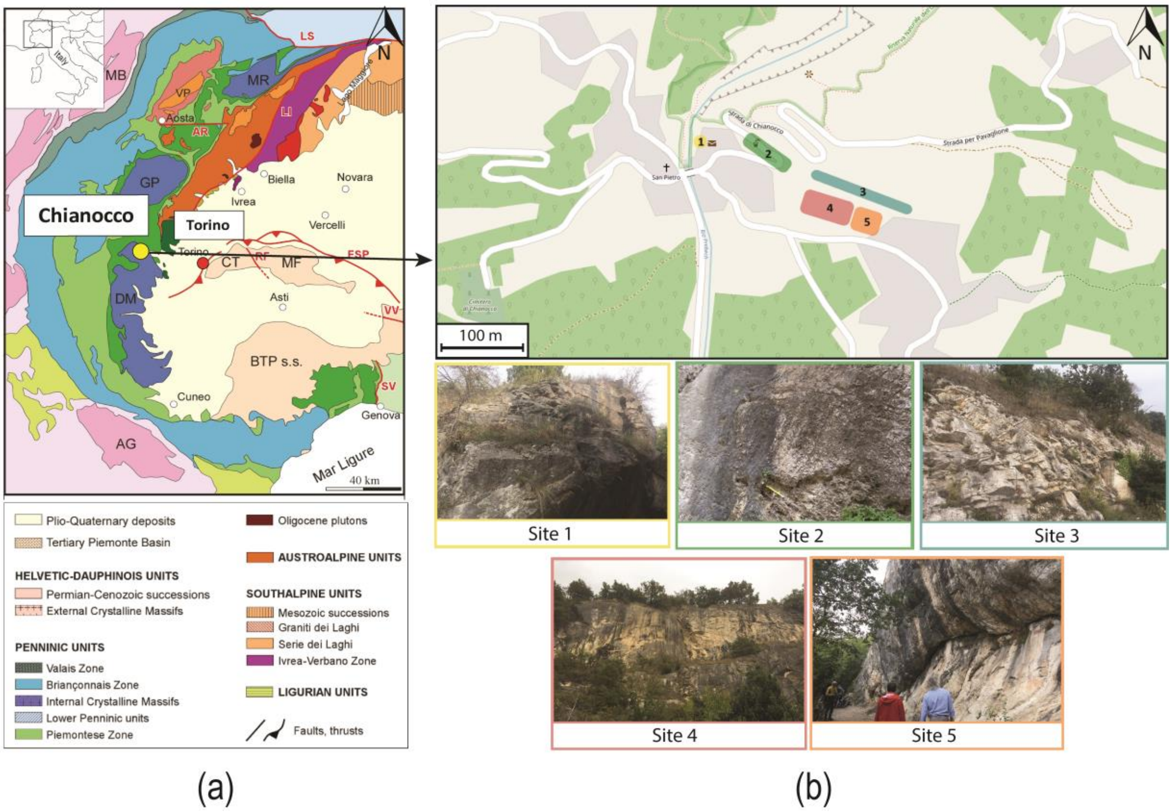

Figure 2. (**a**) Geological setting of Piedmont region and location of Chianocco municipality; (**b**) Location of the 5 quarry sites in Chianocco Municipality.

3. Materials and Methods

The support of the Earth Science Department of Turin to the study of the Palazzo Madama façade consisted in the realization of an architectural-petrographic survey of the façade, in the characterization of its lithotypes, in the diagnosis of the state of preservation, in the study of the degradation causes and in the definition of a model of the evolution of the marble of the façade from its formation to its employment.

For this kind of study related to the identification of building, monuments and artefacts made of marble, a stone material most commonly traded in antiquity and showing few macroscopic diagnostic features a multi-analytical approach is essential. [15, 16, 17, 18].

Starting from the architectonic relief of the façade, a mapping of stone materials in false color, named "petro-architectonic relief" in this paper, was achieved.

Starting from the architectonic relief of the façade, a mapping of stone materials in false color, named "petro-architectonic relief" in this paper, was achieved. The fragments detached from the façade were catalogued and, from the data collected, the most representative samples were selected for detailed studies.

In order to understand the properties of the material, the localization of the ancient quarries has been essential. Five significant sites in Chianocco Municipality were individuated and sampling work has been conducted.
Petrographic studies on uncovered thin sections (30 μm thick) were carried out by optical microscopy and cathodoluminescence (CL) at the Earth Sciences Dept. of the University of Turin.
CL observations were performed on polished thin sections using a CITL 8200 mk3 equipment (operating conditions of about 17 kV and 400 μA).

A Scanning Electron Microscope (JEOL JSM-IT300LV) equipped with an energy-dispersive X-ray spectrometer (EDX), with a SDD (a silicon drift detector from Oxford Instruments), hosted at the Earth Science Department of the University of Turin, was used for the determination of major elements. The experimental conditions include: accelerating voltage 15 kV, counting time 50 s, process time 5 μs and working distance 10mm. The measurements were conducted in high vacuum conditions. The EDX acquired spectra were corrected and calibrated both in energy and in intensity thanks to measurements performed on cobalt standard introduced in the vacuum chamber with the samples. The Microanalysis Suite Oxford INCA Energy 300, that enables spectra visualization and elements recognition, was employed. A ZAF data reduction program was used for spectra quantification. The resulting full quantitative analysis is obtained from the spectra, using natural oxides and silicates from Astimex Scientific Limited_ as standards. All the analyses were formula recalculated using the MINSORT computer program [19].

Finally, mass spectroscopy for the determination of stable isotope ratios were carried out. The stable isotope analyses (i.e., $\delta^{13}C$ and $\delta^{18}O$) have been carried out on calcite and on dolomite for the studied marble types. The protocol reported in McCrea (1950) [19] was followed. In particular, a quantity of 10 mg of powered calcite or dolomite was reacted with 100% orthophosphoric acid under vacuum conditions. The oxygen and carbon isotopic composition produced by CO_2 was analyzed using a Finningan MAT 250 mass spectrometer. The results are expressed as an isotopic ratio in relation to the PDB standard [21], following the convention defined by the International Atomic Energy Agency.

4. The Palazzo Madama façade

The façade of Palazzo Madama can be considered one of the masterpieces of Filippo Juvarra architect. Classical and baroque decorative themes coexist; in fact, Juvarra designed a high-ceilinged piano nobile with arch-headed windows, which is linked to a mezzanine above it by a colossal order of pilasters of a composite style. Each pilaster stands on a sturdy and formal fielded channel-rusticated base against the ashlar masonry of the ground floor. The central three arches are accentuated by the bolder relief offered by full columns attached to the façade, which is returned inward behind them to afford a vast glass-fronted central interior space like a glazed loggia. A spectacular balustrade decorated with vases and statues in white marble surmounts the façade.
Juvarra's design choice consists in that the façade assumes the function of a transparent grid and through it the interior decorative development can be perceived, in a resulting composition based on the passage of light. Juvarra desired a completely open loggia but weather conditions in Turin had forced him to protect the interior with the screen of large glazed windows [6,7].
The petro-architectonic relief (Figure 3) resulted in the false color representation of the different categories of materials used originally (Chianocco Marble, Brossasco Marble, Frabosa Marble, Vaje Stone) and in the restorations of the façade through time (Carrara Marble, Prali Marble, Botticino Limestone, Malanaggio Stone). In particular, Chianocco Marble was employed for the entire marble decoration of the façade, included bas relief and ornaments, Brossasco Marble for the statues and the vases of the apex and Vaje Stone for the base of the building. Frabosa Marble was used for some pillars and the slab in the summit balaustrade. The Carrara Marble, light gray in color, was employed for an extensive replacement that involved both parts originally made of Brossasco Marble and Chianocco Marble elements. Prali Marble was used for the first pillar on the left observing the façade and Malanaggio Stone replaces numerous elements (pillars, bases and cornices) of the central part of

the large summit balustrade. Botticino Limestone was employed for elements of the cornice and of the upper part of the facade and slabs of the balcony between the third and fourth column.
It is worth noting that, the Gassino Stone, reported by previous authors as a replacement material for the capitals, ledge and balaustrade [10, 11], has not been found at Palazzo Madama.
All kind of stone materials, both original and restoration ones, were exploited in Piedmont region, except for Carrara marble, that crops out in Tuscany, and Botticino limestone that crops out in Lombardy.

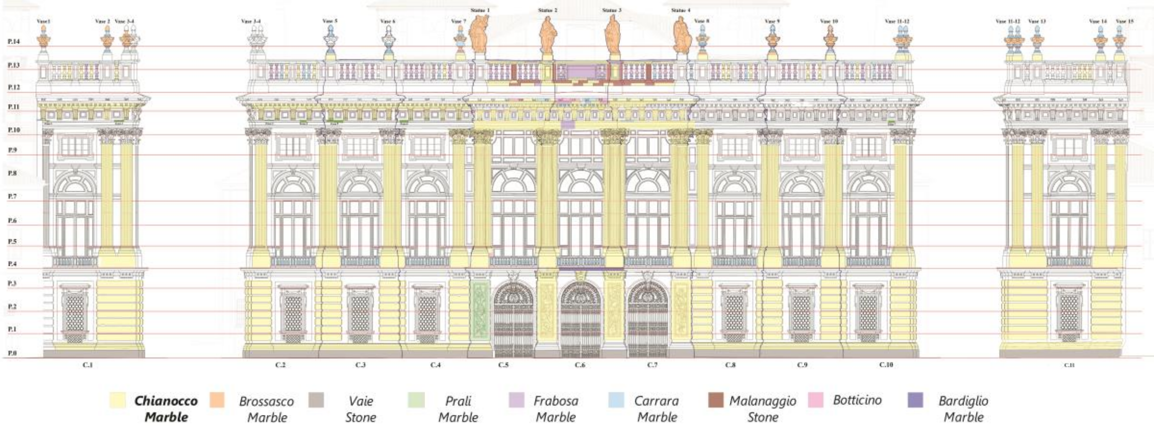

Figure 3. Petro-architectonic relief in false color representation of Palazzo Madama façade (architectural drawings courtesy of Fondazione Torino Musei-Palazzo Madama).

Original stones	Use	Replacement stones	Replacement of	
			Chianocco Marble	**Brossasco Marble**
Chianocco Marble	Columns, pilasters, ashlars, cornices, portals and summit balustrade	**Prali Marble**	Whole pillar under the first column on the left and slabs of the balcony between first and second column (?)	
Brossasco Marble	Statues and bases on the summit balustrade, balustrade on the windows of the staircase	**Carrara Marble**		Several elements of the balustrades on the large windows of the staircase and parts of the vases on the summit balustrade
Frabosa Marble	Staircase and elements of the summit balustrade	**Botticino limestone**	Elements of the cornice and of the upper part of the facade and slabs of the balcony between the third and fourth column	
Vaie Marble	Base of façade	**Malanaggio Stone**	Elements of the great summit balustrade	

Table 1. Original and replacement stone materials of architectural elements of Palazzo Madama façade.

On the façade the following characteristics of the Chianocco Marble were observed: a strongly vacuolar structure (Figure 4a), a brecciated fabric with a pervasive vein network (Figure 4b), presence of mortars in the pores (Figure 4c), a reddish alteration of the columns (Figure 4d). Moreover, the local occurrence of a white soft powder on the stone suggests sulphation processes due to acid rains. The so called Chianocco Marble therefore actually shows a more or less continuous range of fabrics and lithologies from veined marbles to a tectonic carbonate breccia characterized by a high porosity and a vacuolar appearance which is comparable to the cargneules, a historical Alpine term to indicate brecciated carbonate rocks with a vacuolar structure [22].

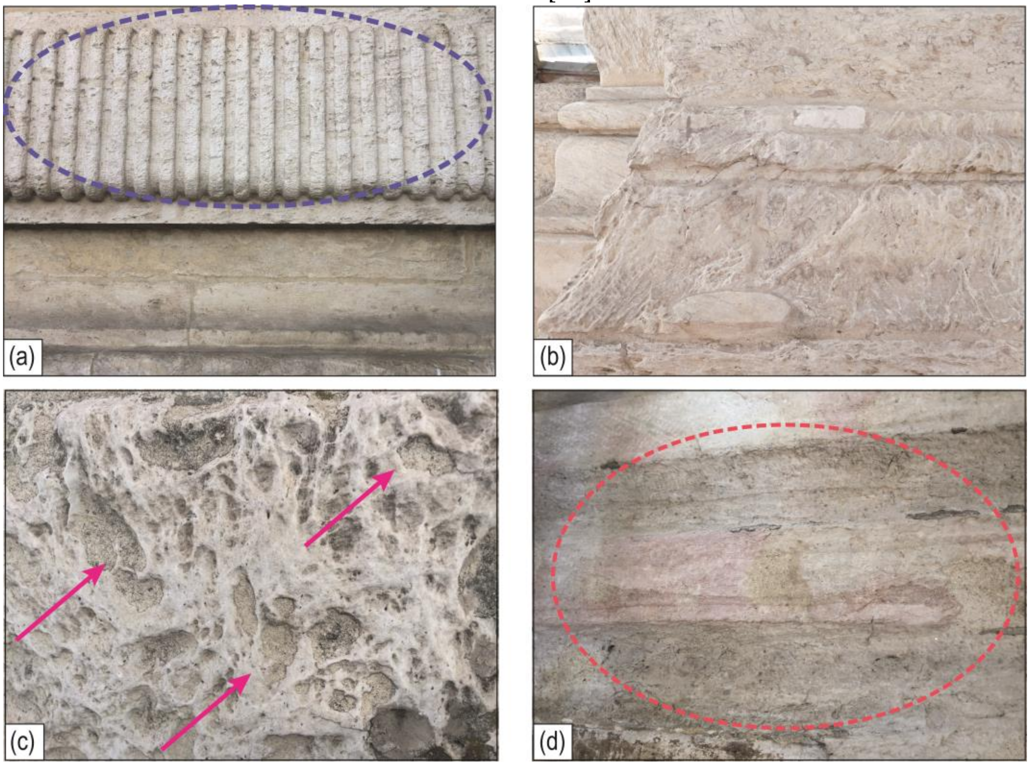

Figure 4. Characteristics of Chianocco Marble macroscopically observed on Palazzo Madama façade: (**a**) slab of the façade with a strongly vacuolar texture; (**b**) brecciated fabric with a pervasive vein network observed on a base of column of the façade; (c) presence of mortars in the pores of the stone; (d) detail of the reddish alteration of the column of the façade.

5. The Chianocco Marble

5.1. Petrography

Petrographic analyses have been conducted on façade samples and on outcrop ones. In fact, five sites were individuated in the surroundings of Chianocco village (Figure 2b) and four of them (1, 2, 4, 5) resulted analogous to the façade marble. Conversely, the marble of site 3 is very massive fine-grained, white to gray and foliated at a macroscopic observation. Similar features were not found in the marble used in the façade of Palazzo Madama.

The marble from Site 3 (Figure 5a) is characterized by a paragenesis consisting of major dolomite (Dol 80-90% in vol) and minor calcite (Cc 10-15% in vol) and some accessory minerals as quartz, white mica, apatite, rutile and opaque minerals. The rock shows a homogeneous grain ranging from homeo- to heteroblastic (average grain size 0.10-0.15 mm) grain. The texture resulted grano-blastic characterized by triple point structure; the single crystal shows lobed to irregular edges. It also has a weakly oriented texture defined by some crystals of white mica which at SEM-EDS system resulted to be Paragonite (Pg) and Phengite (Ph) in composition (Si content in Ph ranging between7.52-7.60 atoms per unit formula based on 22 atoms of oxygen). This mineral assemblage is indicative of high pressure – low temperature metamorphic conditions (Figure 5b, c, d).

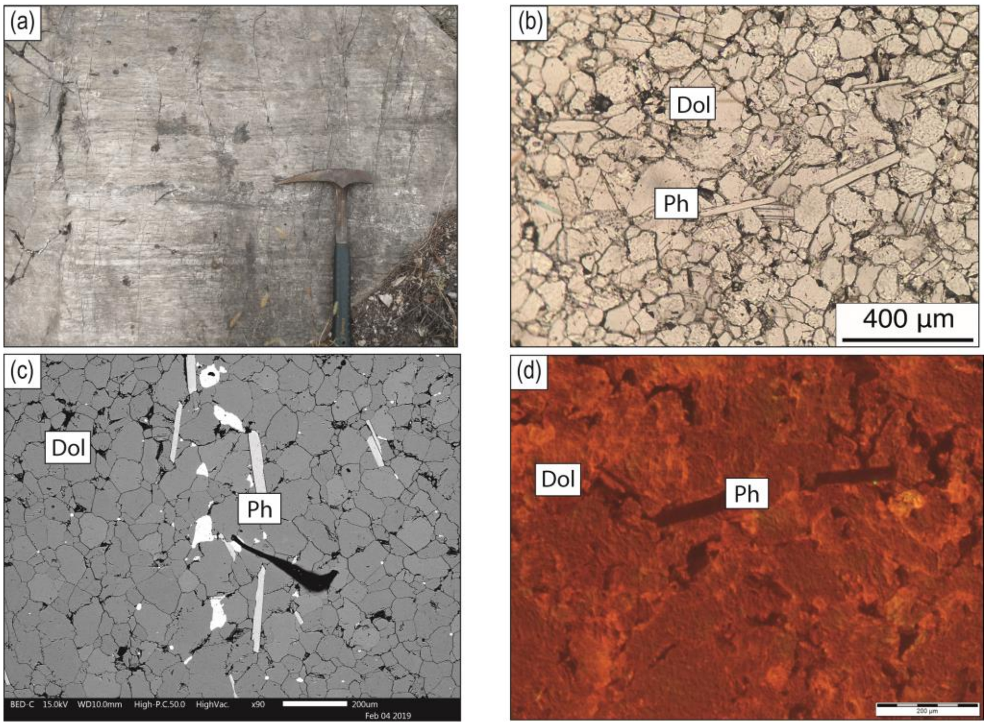

Figure 5. Petrography of marble of Site 3: (**a**) Macroscopic aspect of the marble at the Site 3 quarry; (**b**) Photo of Optical Microscope with only polarizer in which dolomite and phengite crystals are indicated. (**c**) SEM backscattered image. Dolomite crystals are dark grey and phengite ones are light-grey (**d**) Cathodoluminescence image where dolomite crystals appear red and phengite crystals brown.

Based on microscopical observations, this marble resulted strictly comparable to the Foresto marble [23].

Conversely the Chianocco Marble is characterized by a greater complexity in both structure and composition. Macroscopically it commonly shows a porous and vacuolar texture with irregularly shaped voids up to some centimeters large (Figure 6a,b). Microscopic analyses, and in particular SEM-BSE and cathodoluminescence (CL) imaging clearly show that the rock is dolomitic but calcite may be very abundant (Figure 6c,d,e,f). Calcite fills mm-large veins with commonly sharp edges. Crystals are equant, limpid and show an overall dull brown CL colour (Figure 6e). However, a zoning is recognizable with the very first portion of crystals characterized by thin bands of bright to moderate yellow (Figure 6e,f). This zoning clearly documents a crystal growth in a void in static conditions. Calcite is also present in intimate association with dolomite, clearly distinguishable in CL for the orange colour. Calcite fills spaces among irregularly shaped fragments of dolomite, from few tens of microns to some millimetres large and shows the same zoning observed in veins. This demonstrates that the Chianocco Marble is a cataclasite where the original dolomitic marble was fractured and/or comminuted into fragments of heterogeneous grain size; successively the fractures and the open spaces in the cataclasite were cemented by sparry calcite. Moreover, in some portions of the rock, calcite septa that originally separated the dolomite clasts now surround the voids (Figure 6g,h).

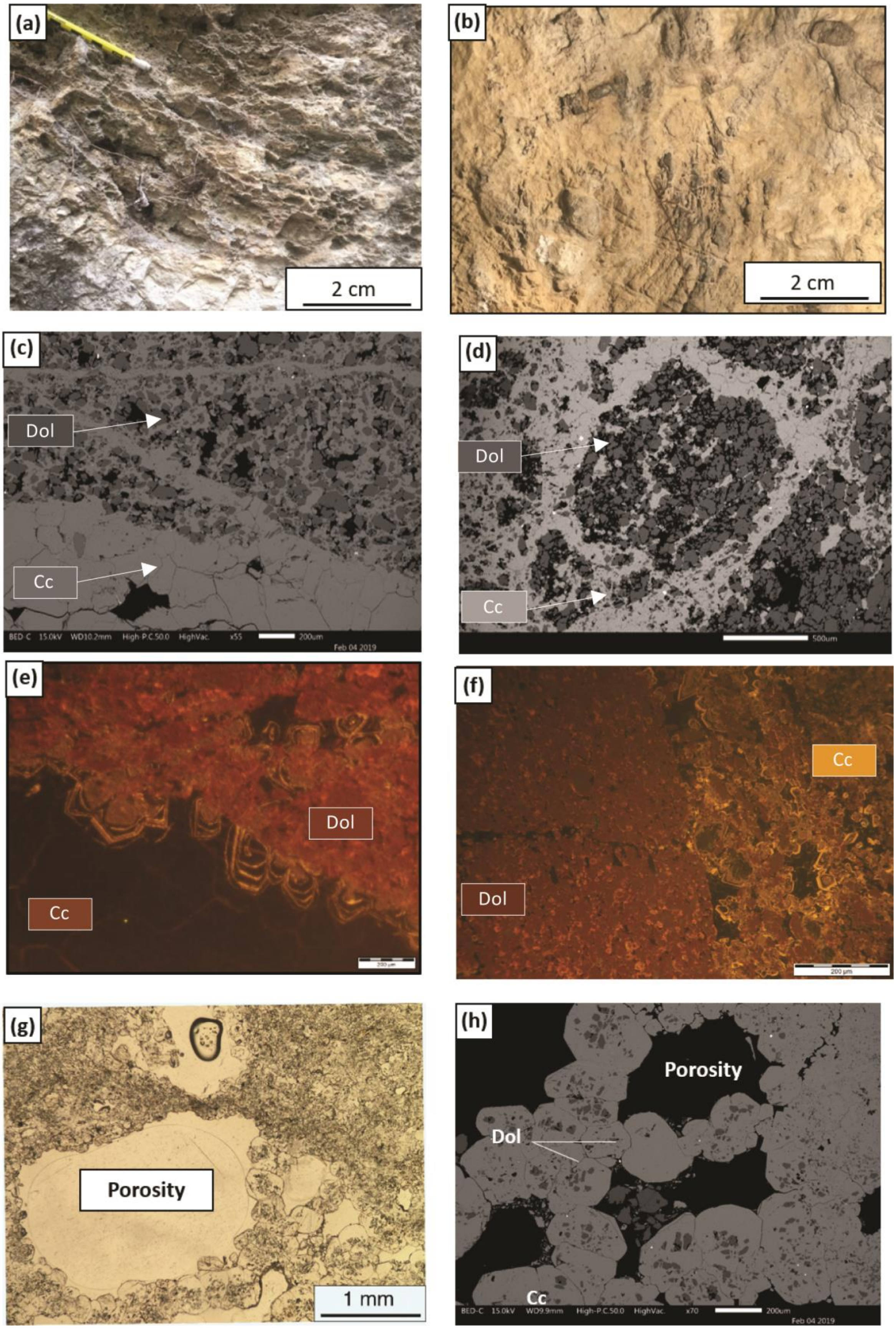

Figure 6. Petrography of Chianocco Marble: (**a**), (b) Macroscopic aspect of Chianocco Marble; (**c**) SEM backscattered image where calcite veins are clearly visible; (**d**) SEM backscattered image where cataclasite structure is evident; (**e**) cathodoluminescence image where in calcite vein a zoning is

recognizable with the very first portion of crystals characterized by thin bands of bright to moderate yellow; (**f**) cathodoluminescence image where different dolomite, in red, and calcite, in black and yellow, portions are recognizable; (**g**) optical microscopo with only polarizer image with evident vacuolar texture; (**h**) SEM backscattered image where the voids are surrounded by calcite septa that originally separated the dolomite clasts.

Phengite and phlogopite also occur in the Chianocco Marble and locally are broken and folded (Figure 7).

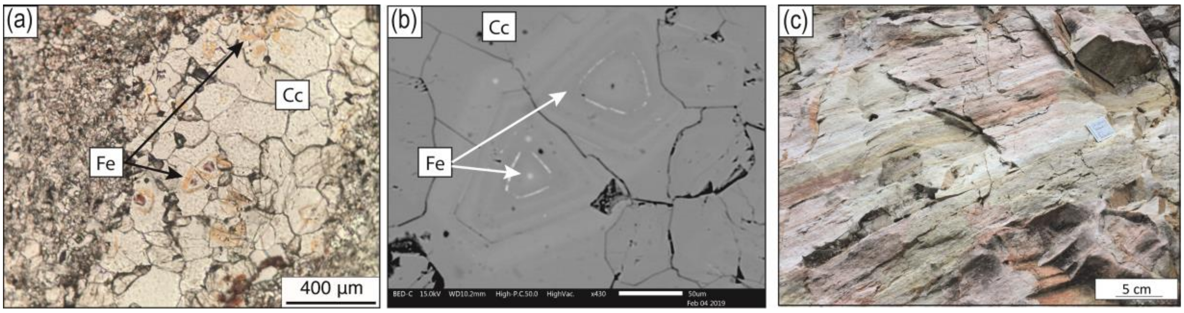

Figure 7. SEM backscattered image of Phengite crystal broken and folded.

Finally, some samples are characterized by red zone in calcite veins due to the presence of iron oxides inside calcite crystals (Figure 8a,b). This phenomenon is visible on macroscopic scale in the site 4 (Figure 8c); the rock on outcrop results reddish as the column of the façade already mentioned (Figure 4d).

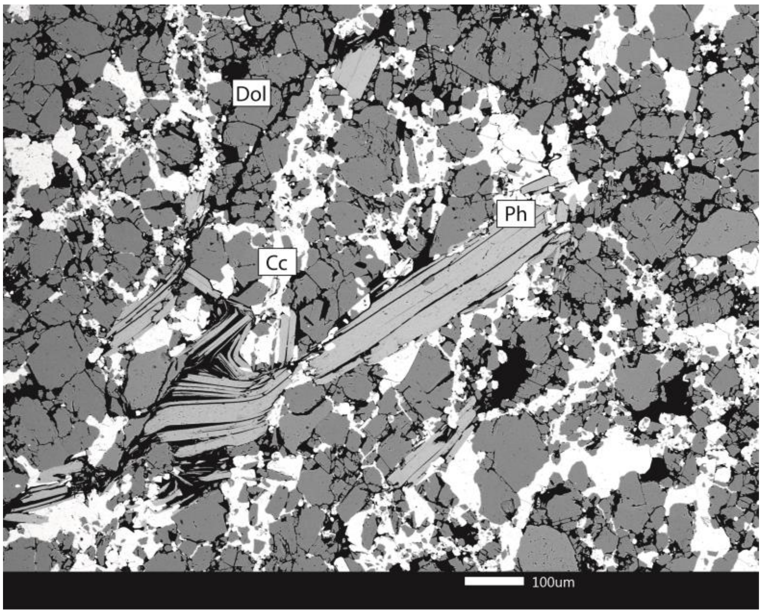

Figure 8. Reddish alteration phenomen: (**a**) Red zones in calcite veins oserved by optical microscope with only polarizer; (b) SEM backscattered image where zones of iron oxides in calcite crystals are visible; (c) Reddish alteration phenomen visible on Site 4 quarry.

SEM-EDS analysis also revealed in some areas superficial gypsum with spherical and "rose" morphology (Figure 9a). Also, intergranular gypsum was found (Figure 9b,c).

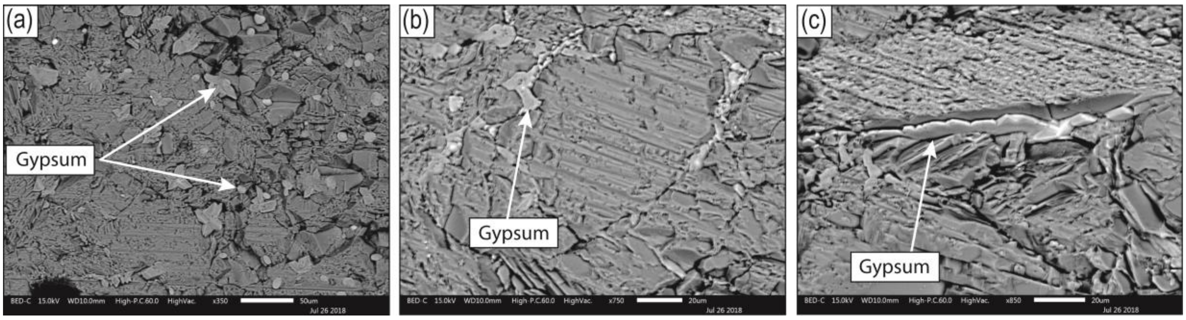

Figure 9. SEM backscattered image with superficial gypsum present in façade samples: (a) spherical and “rose” morphology gypsum; (b) and (c) intergranular gypsum.

.2. C–O stable isotope analysis

For a complete archaeometric characterization of Palazzo Madama marble, C-O stable isotope analyses have been carried out. For comparison, isotopic analyses of local marbles of the Chianocco quarries have been also reported. Values of δ[18]O and δ[13]C have been determined on both calcite and dolomite. The results, referred to the PDB standard, are reported in Table 2 and Figure 10. Isotopic data of dolomite samples coming from the façade and from Chianocco quarries compare well with data referred to site 3 of Chianocco and Foresto quarries [18] with δ[18]O values ranging between-7.06 and -6.00 and δ[13]C ranging from 0.79 to 1.30. In addition, a good correlation between calcite isotopic data of a sample from façade and a sample from Chianocco quarry can be noted with more negative δ[18]O values ranging between -10.82 and -9.20 and δ[13]C ranging from -0.10 to 0.45.
Isotopic data support petrographic observations showing that dolomite and calcite were not in equilibrium.

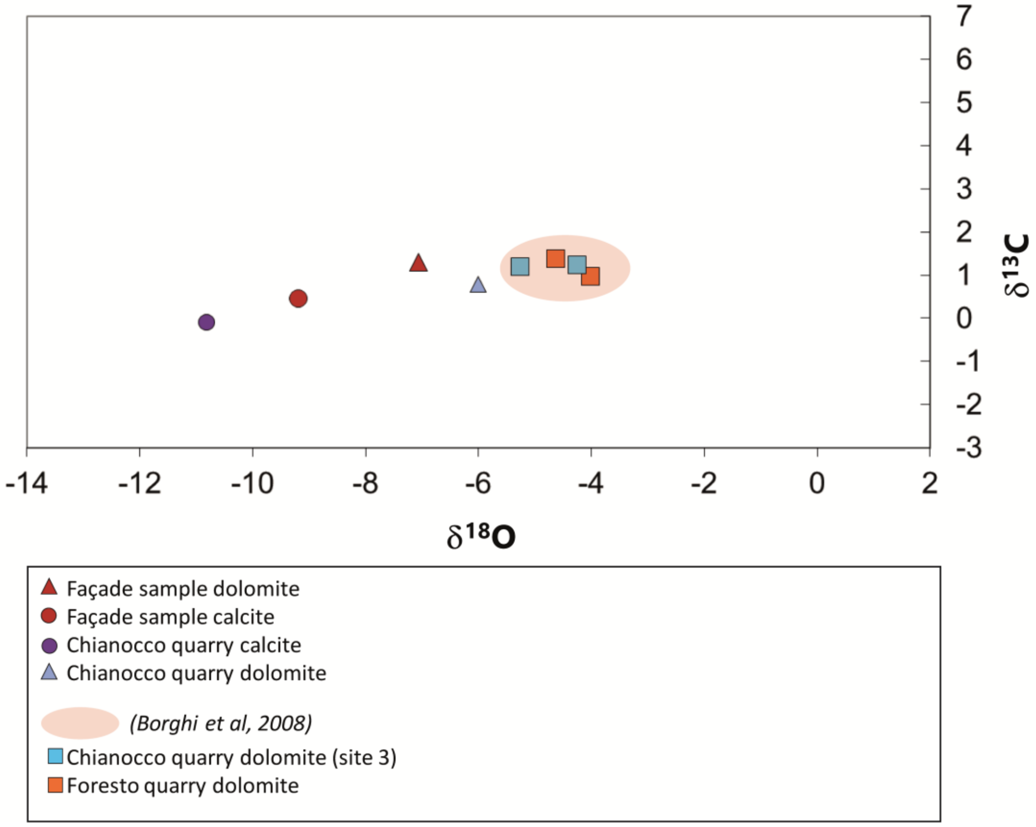

Figure 10. The δ[18]O and δ[13]C diagram of calcite and dolomite of the investigated Chianocco Marble investigated. The isotopic reference of Chianocco and Foresto dolomite according to Borghi et al, 2008 is also reported.

Sample	**Calcite**		**Dolomite**	
	$\delta^{13}C$	$\delta^{18}O$	$\delta^{13}C$	$\delta^{18}O$
Façade sample	0.45	-9.20	1.30	-7.06
Chianocco quarry	-0.10	-10.82	0.79	-6.00

Table 2. Calcite and dolomite stable isotope (C, O) data of Palazzo Madama façade sample and Chianocco quarry sample.

5. Model evolution

The petrographic study of the quarry and façade samples allowed to define a model of the evolution of the rock from its formation to its employement. This model is articulated in 6 steps as shown in Figure 11, starting from deposition of the dolostone, through alpine metamorphism and brittle deformation and brecciation to superficial partial dissolution, only the very last step being related to the recent exposure of the stone to atmospheric agents as a facing of Palazzo Madama. In the following, each step will be commented in detail.

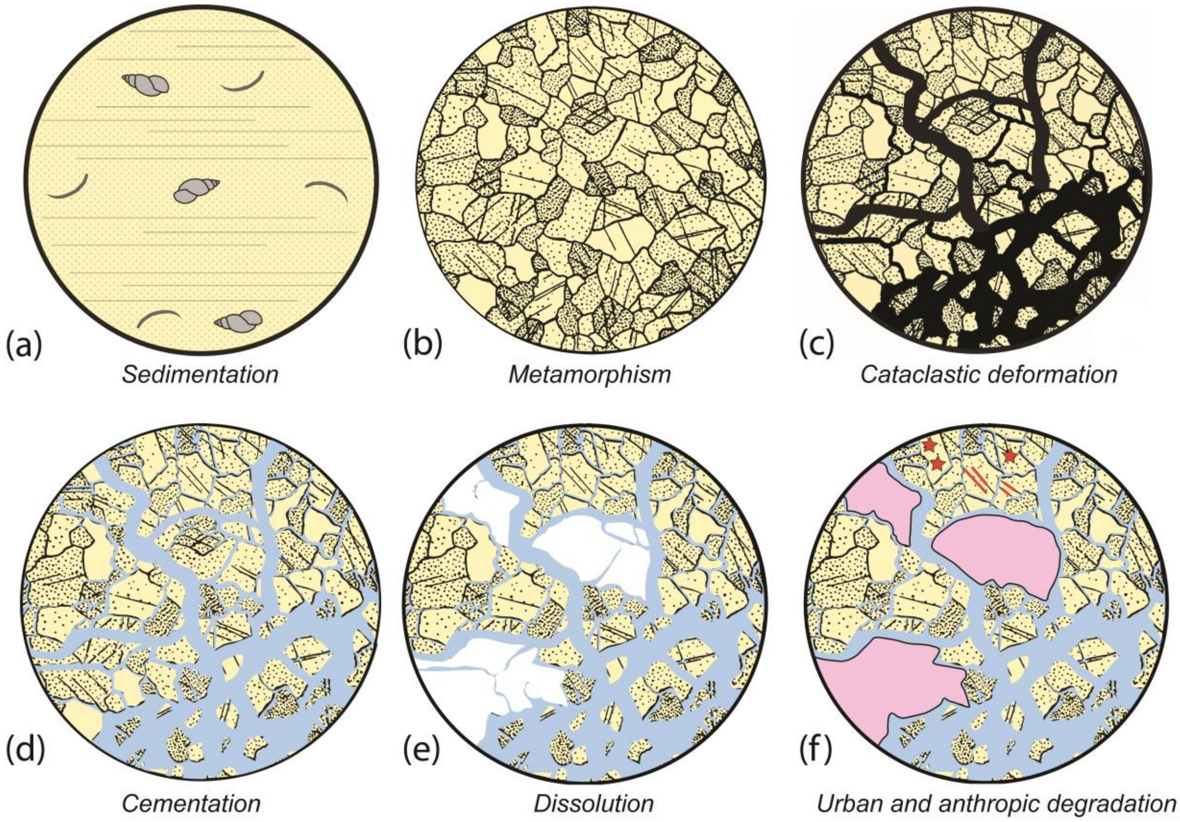

Figure 11. Representation of the model evolution of Chianocco Marble from its formation to its employement: (**a**) original dolostone; (**b**) dolomitic marble; (**c**) brittle deformation indicated in black fractures; (**d**) cementation indicated in light blue color (tectonic carbonate breccia with a complex and pervasive cataclastic fabric); (**e**) selective dissolution of dolomite marble clasts indicated in white (vacuolar texture); (**f**) mortars in the pores indicated in pink and sulphation indicated in red stars, circles and lines in the upper part of the round.

Step 1

In the Triassic, a carbonate sediment was deposited in a peritidal environment and very early dolomitized. No fossil nor sedimentary structures are preserved in the Chianocco Marble but it is clearly established in the geological literature that an extensive carbonate platform existed in the Triassic in all the units presently involved in the Alpine chain.

Step 2

During the first part of the Alpine orogenesis (Late Cretaceous-Eocene) oceanic and continental units were involved in subduction processes. The presence of phengiteindicates high pressure conditions in site 3 samples, therefore attesting that it is a marble formed in a metamorphic process in a pressure and temperature range corresponding to eclogitic facies. These characteristics reveal that these samples are comparable to the Foresto Marble, extracted since ancient times a few kilometers from Chianocco, and used in 9 BC for the Arco di Susa [23] and for the façade of the Cathedral of Turin. It is in fact a fine-grained, very compact dolomite marble.

The proximity of Foresto quarries with Chianocco lead to mistakenly merge Foresto and Chianocco Marbles in a unique lithotype.

Steps 3 and 4

In a later, post-metamorphic, stage which is not possible to date precisely, brittle deformation took place at high crustal levels, probably not far from the surface. This event caused a strong grain reduction of the dolomitic marble and its transformation into a tectonic carbonate breccia with a complex and pervasive cataclastic fabric. The $\delta^{18}O$ values of calcite veins and cement, lighter than marble dolomite, possibly document meteoric waters percolating down and feeding a fracture-related circulation system.

Step 5

A process of selective dissolution of the dolomite marble clasts explains the origin of the vacuolar texture. This process took place when the calcite-cemented breccias were exposed to weathering at or very close to the topographic surface in a very recent past (Pleistocene?) giving rise to a vacuolar structure comparable to that shown by the so called cargneules well known in the Alpine literature [22]. In some portions of the rock, calcite septa that originally separated the dolomite clasts now surround the voids.

Step 6 - Environmental and anthropic degradation

Regarding the environmental degradation, superficial sulphation of carbonate rocks is typical of degradation due to acid rains, in particular for formation of gypsum crystals with spherical and "rose" morphology. The comparison with stone samples from outcrop shows that gypsum is not present in the Chianocco Marble insofar supporting the environmental degradation hypothesis.

Moreover, Past restoration interventions carried out with not suitable materials (like cement-based mortars) contributed to accelerated deterioration.

6. Conclusions

The petrographic and isotopic study of selected specimen from Palazzo Madama façade and its comparison with quarry sample coming from the historic site of explotation allows to know the composition and the fabric of the stone material. Starting from this point its behavior, possible alteration or degradation due to environmental and / or anthropic factors since its installation until today can be deduced.

A multidisciplinary geological approach was applied to the façade of Palazzo Madama, one of the most important historical monuments in Turin and UNESCO World Heritage site, recently affected by environmental degradation. A detailed architectural-petrographic relief and minero-petrographic and isotopic analyses were carried out and led to the following main results:

- the kind of ornamental stone used and their precise distribution on the façade were defined distinguishing the original stone materials from the ones used during historical restorations;
- the originally used material, the Chianocco Marble, is still the most abundant and the one which shows the greatest degradation;

- the minero-petrographic study of the Chianocco Marble and the comparison with the same material cropping out in the historical quarries shows that some features observed on the Palazzo Madama façade such as a vacuolar structure and local reddenings, usually absent in ornamental marbles, are primary features of the rock itself and are not due to degradation in an urban context. They are conversely related to the very complex history of the rock which started in the Triassic age as deposition of a carbonate sediment, evolved through Alpine metamorphism and deformation, and finished with exposure at surface where dissolution by meteoric waters generated the vacuolar structure. Only gypsum crystals grown in voids and the application of mortars in natural voids, enhancing the physical degradation of the stone, are due to pollution and human interventions.

This research highlights the importance of geological studies in conservation issue in Cultural Heritage by defining the characteristics of stone materials, and the reasons for their degradation. In particular, this is true for local heritage stones which can be studied not only on the historical buildings but also in the provenance areas.

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