

Article

Minero-Petrographic Characterization of Chianocco Marble Employed for Palazzo Madama Façade in Turin (Northwest Italy)

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Abstract: The study of ancient marble plays an important role in the interpretation of historical and archaeological sites 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 the Piedmont region (Northwest Italy) and employed for the Palazzo Madama façade. A multi-analytical study based on petrographic (optical and scanning electron microscopy), electron microprobe, cathodoluminescence 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, such as the façade of the 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 (Penninic 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 maintenance of 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 as applied to cultural heritage highlights how the study of the genesis and characteristics of ornamental stones is primarily a geological matter, and has to be solved by 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 decoration, 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 [2–4]. 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 the ease of cleaning, marble has been widely employed in valuable buildings, from Roman times to the end of the eighteenth century [5].

One of the most prestigious buildings in Turin is certainly the Palazzo Madama (Figure 1a), a 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 a symbol of power until the sixteenth century, when it was replaced by the Palazzo Reale as seat of the Duke 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 configured. 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 in contradictory and partially wrong conclusions in the attribution of the stones employed over the centuries [10,11].



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

For this reason, and because of many recent conservation issues, the conservation and restoration foundation "La Venaria Reale", in collaboration with the Foundation Torino Musei and under the supervision of the Superintendence of Archeology, Fine Arts and Landscape for the Metropolitan City of 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 char.

2. Geological Setting

In the central area of the Susa Valley (NW Italy), the metamorphic stratigraphic cover of the Dora Maira Massif crops out and includes marbles. The Dora Maira Massif belongs to the Penninic Domain of the Western Alps (Figure 2a); it is a continental crust unit. It was involved in the Alpine orogeny

(about 50 Ma ago) which resulted in pervasive metamorphism and deformation. The Dora Maira Massif is predominantly made up of Palaeozoic micaschists, gneiss, and rare slices of dolomitic marbles which derived from the Alpine metamorphism of Triassic to Early Jurassic carbonate sediments. The Alpine metamorphism developed under eclogitic conditions in a first event, when peak pressures (P) and temperatures (T) were reached, a retrograde metamorphic event under greenschist facies conditions followed. [12]. Historically, Susa Valley marbles have been distinguished as “Foresto and Chianocco marbles” on the basis of their extraction site [13,14]. In fact, 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.

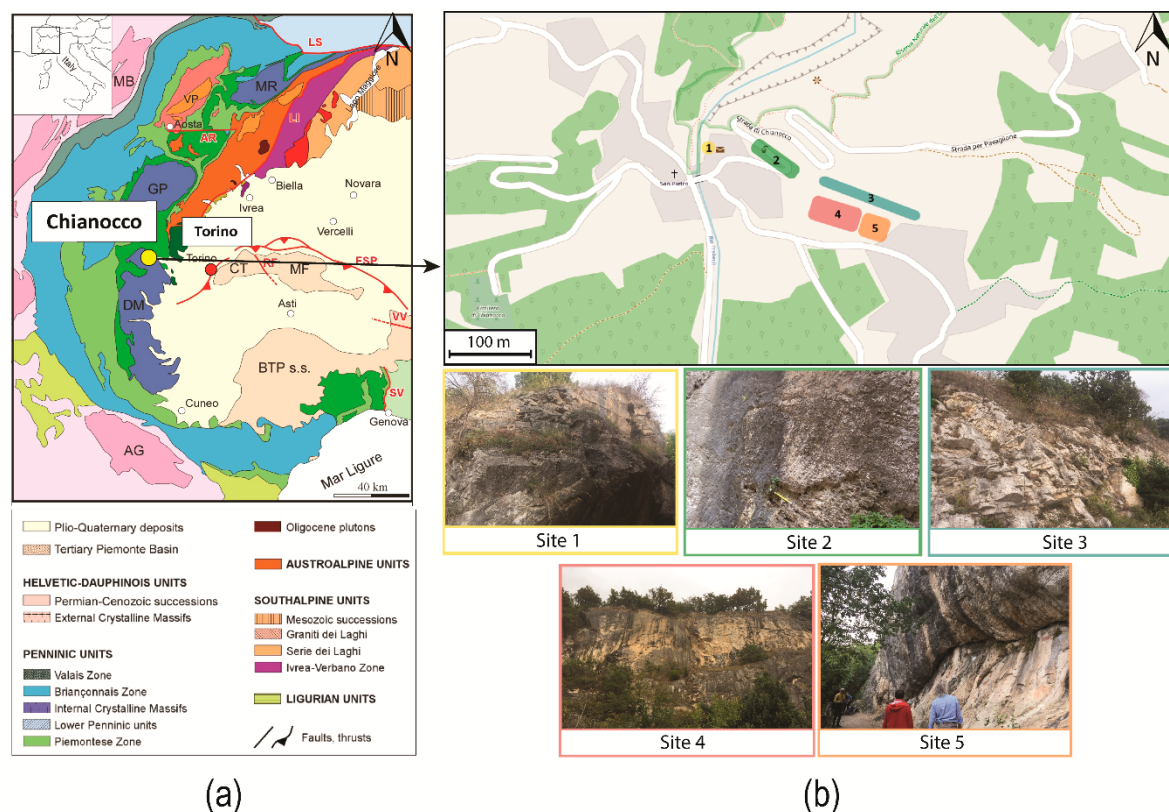


Figure 2. The Chianocco municipality: (a) Geological setting of the Piedmont region and location of the Chianocco municipality; (b) Location of the five quarry sites in the Chianocco municipality.

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 buildings, monuments and artefacts constituted in marble (a precious material most used and traded in antiquity) a multi-analytical approach is necessary [15–18].

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. 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 the 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 Department 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).

Determination of major elements was performed using a scanning electron microscope (SEM; JEOL JSM-IT300LV) combined with an energy-dispersive X-ray spectrometer (EDX), with a silicon drift detector (SDD) from Oxford Instruments, installed at the Dipartimento di Scienze della Terra of the University of Turin. The following operative conditions were adopted: an accelerating voltage of 5 kV, a counting time of 50 s, a process time 5 µs and working distance of 10 mm. The measurements were performed in high vacuum conditions. A cobalt standard was analyzed for correction and calibration both in energy and in intensity of EDX acquired spectra. Enabling spectra visualization and elements recognition was done by the Microanalysis Suite Oxford INCA Energy 300. A ZAF data reduction program was used for spectra quantification. Astimex Scientific Limited standards were used to obtain full quantitative analyses. All the analyses were formula recalculated using the MINSORT computer program [19]. Representative polished thin sections of the marble were analyzed using the SEM-EDS system, with backscattered electron (BSE) and X-ray signals and it permitted us to define the chemistry of selected minerals. In the BSE images the brightness signal is sensitive to differences among mean atomic number showing different grey levels for different phases (i.e., calcite and dolomite). In fact, the minerals with higher mean atomic numbers (e.g., calcite) are brighter than the ones with lighter forming elements (e.g., dolomite). In addition to carbonates, mica crystals have also been analyzed; a representative selection of mica composition is reported in Table 1. Lastly, mass spectroscopy for the determination of stable isotope ratios was used. The stable isotope analyses (i.e., $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$) have been performed on calcite and dolomite for the studied marble types. The protocol reported in McCrea (1950) [20] was applied. An amount of 10 mg of powdered 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 Finnigan 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

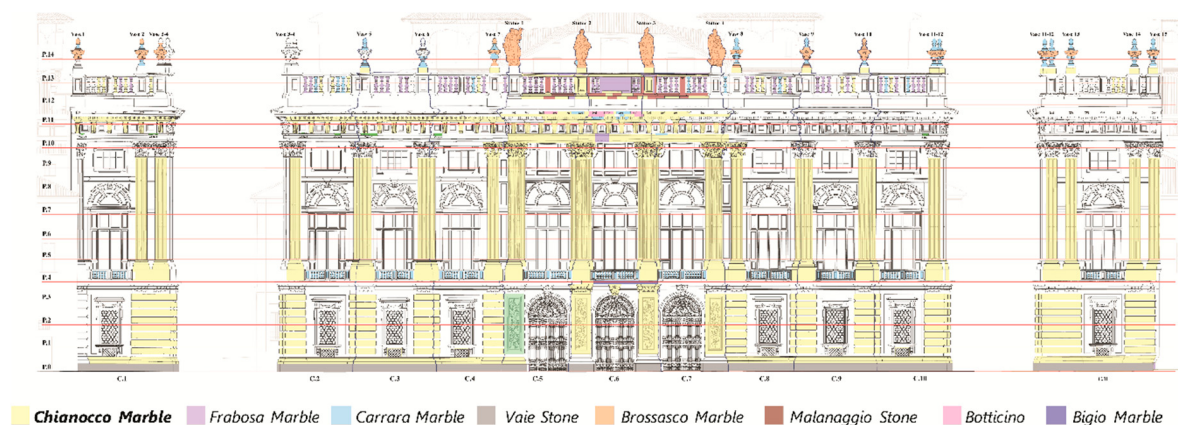
The façade of Palazzo Madama can be considered one of the masterpieces of the architect Filippo Juvarra. Classical and baroque decorative themes coexist; in fact, Juvarra designed a piano nobile with arch-headed windows linked to a mezzanine overhead by a colossal order of pilasters in a composite style. The central three arches are emphasized by the relief offered by the columns attached to the façade. The façade was surmounted by a spectacular balustrade decorated with vases and statues in white marble.

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, and Vaje stone), and in the restorations of the façade through time (Carrara marble, Prali marble, Botticino limestone, and Malanaggio stone) (original and restoration stones shown in Table 2).

Table 1. Representative SEM-EDS analysis of white mica from Palazzo Madama façade samples and Chianocco quarries recalculated on the basis of 22 Ox.

Sample	Façade						Quarry					
							Site 3			Site 2–4		
Analysis Number	Ph 1	Ph 2	Ph 3	Ph 4	Ph 5	Ph 6	Ph 7	Ph 8	Ph 9	Ph 10	Ph 11	Ph 12
SiO ₂	56.57	56.22	57.4	57.28	56.94	57.21	59.67	54.21	56.57	53.01	59.18	59.25
Al ₂ O ₃	26.83	27.39	25.8	26.05	26.42	26.06	22.64	30.89	26.77	32.52	23.24	23.32
FeO	0	0	0	0	0	0	0	0	0	0	0	0
MgO	5.45	5.35	5.75	5.66	5.61	5.78	7.37	3.79	5.34	3.42	6.99	6.95
CaO	0	0	0	0	0	0	0	0	0	0	0	0
Na ₂ O	0	0	0	0	0	0	0	0	0	0.72	0	0
K ₂ O	11.15	11.04	11.05	11.01	11.03	10.95	10.31	11.11	11.32	10.33	10.59	10.48
Total	97.05	96.27	96.86	97	95.77	96.05	95.98	96.47	97.03	95.62	96.07	95.9
Si	7.08	7.03	7.17	7.16	7.12	7.15	7.42	6.79	7.09	6.63	7.37	7.37
Al IV	0.92	0.97	0.83	0.84	0.88	0.85	0.58	1.22	0.92	1.37	0.63	0.63
Al VI	3.04	3.07	2.97	2.99	3.01	2.98	2.74	3.34	3.04	3.42	2.78	2.79
Fe	0	0	0	0	0	0	0	0	0	0	0	0
Mg	1.02	1	1.07	1.05	1.05	1.08	1.37	0.71	1	0.64	1.3	1.29
Ca	0	0	0	0	0	0	0	0	0	0	0	0
Na	0	0	0	0	0	0	0	0	0	0.18	0	0
K	1.78	1.76	1.76	1.76	1.76	1.75	0	1.77	1.81	1.65	1.68	1.66

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

In particular, Chianocco marble was employed for the entire marble decoration of the façade, including 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 balustrade. 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 balustrade [10,11], has not been found at the Palazzo Madama.

All kind of stone materials, both original and restoration ones, were exploited in the Piedmont region, except for Carrara marble, that crops out in Tuscany, and Botticino limestone that crops out in Lombardy.

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.

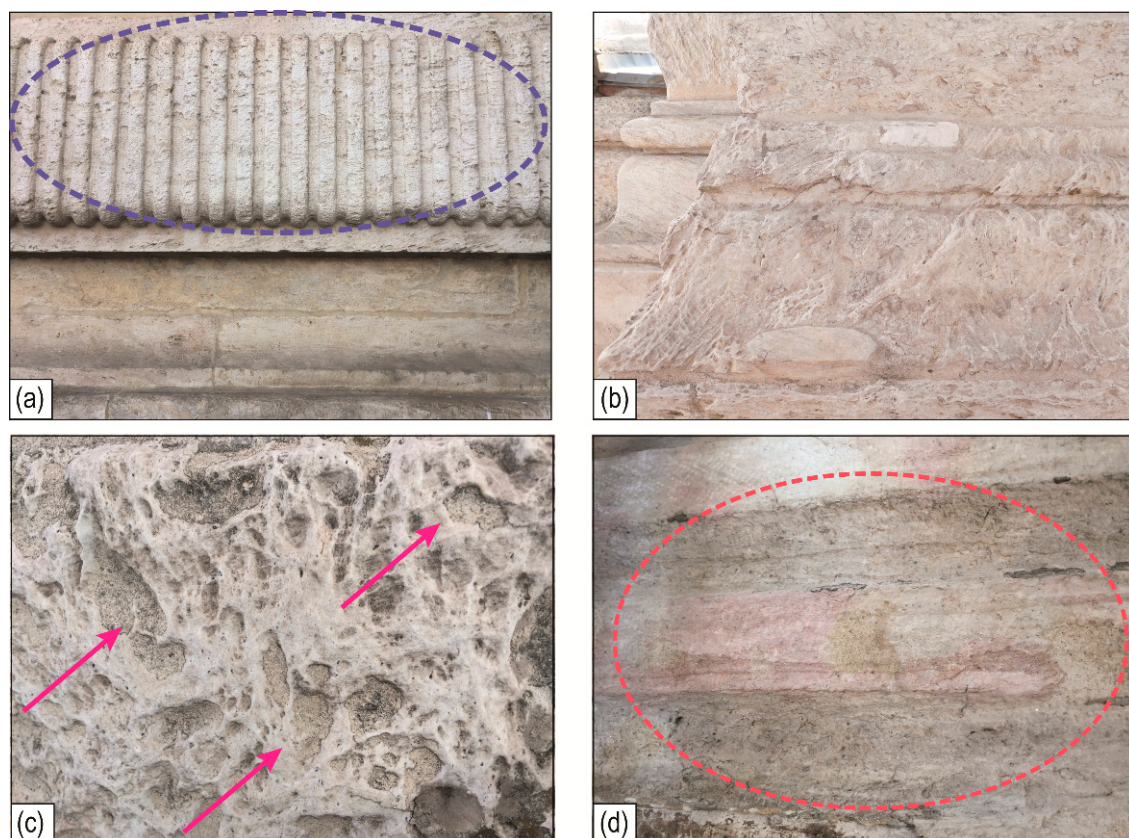


Figure 4. Characteristics of Chianocco marble macroscopically observed on the Palazzo Madama façade: (a) Slab of the façade with a strongly vacuolar texture; (b) Brecciated fabric with a pervasive vein network observed on a base of column of the façade; (c) Presence of mortars in the pores of the stone; (d) Detail of the reddish alteration of the column of the façade.

Table 2. The Palazzo Madama façade: (a) Original stone materials of architectural elements of the Palazzo Madama façade; (b) Replacement stone materials of the architectural elements of the Palazzo Madama façade.

(a)	Original Stones	Use	(b) Replacement Stones	Replacement of	
				Chianocco Marble	Brossasco Marble
	Chianocco marble	Columns, pilasters, ashlar, 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 (?)	

Table 2. Cont.

(a)	Original Stones	Use	(b)	Replacement Stones	Replacement of	
					Chianocco Marble	Brossasco Marble
	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 Bardiglio marble	Elements of the great summit balustrade Elements of lower balustrade	

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 *cagneules*, a historical Alpine term to indicate brecciated carbonate rocks with a vacuolar structure [22].

5. The Chianocco Marble

5.1. Petrography

Petrographic analyses have been conducted on façade samples and on outcrop ones. Specimens from the façade were not sampled directly in situ but they consist of fragments detached from the summit balustrade. Outcrop samples were collected from five sites in the surroundings of Chianocco village (Figure 2b) and four of them (Site 1, 2, 4, 5) resulted as analogous to the façade marble. Conversely, the marble of Site 3 is very massive, fine-grained, white to gray and foliated at 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 is grano-blastic characterized by a 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. A potassium mica, characterized by high Si content (fengitic in composition) and a sodium mica (paragonite) was detected in this marble according to SEM-EDS analyses. This mineral assemblage is indicative of high pressure—low temperature metamorphic conditions. Potassium mica shows a strong zoning characterized by a compositional change in Si content between 6.63 and 7.37 atoms per formula unit (p.f.u.) on the basis of 22 O_x. (Table 1). Sodium mica is characterized by a compositional change in Si content between 5.98 and 6.14 atoms per formula unit (p.f.u.) on the basis of 22 O_x. (Table 3). This implies that the mica has grown under metamorphic conditions of high pressure, typical for the Dora Maira Massif [12]. The zoning of phengite can be ascribed to the effects of partial retrogression of phengite towards muscovite during the second metamorphic event that involved the Dora Maira Massif, which took place in low pressure conditions (Figure 5b–d).

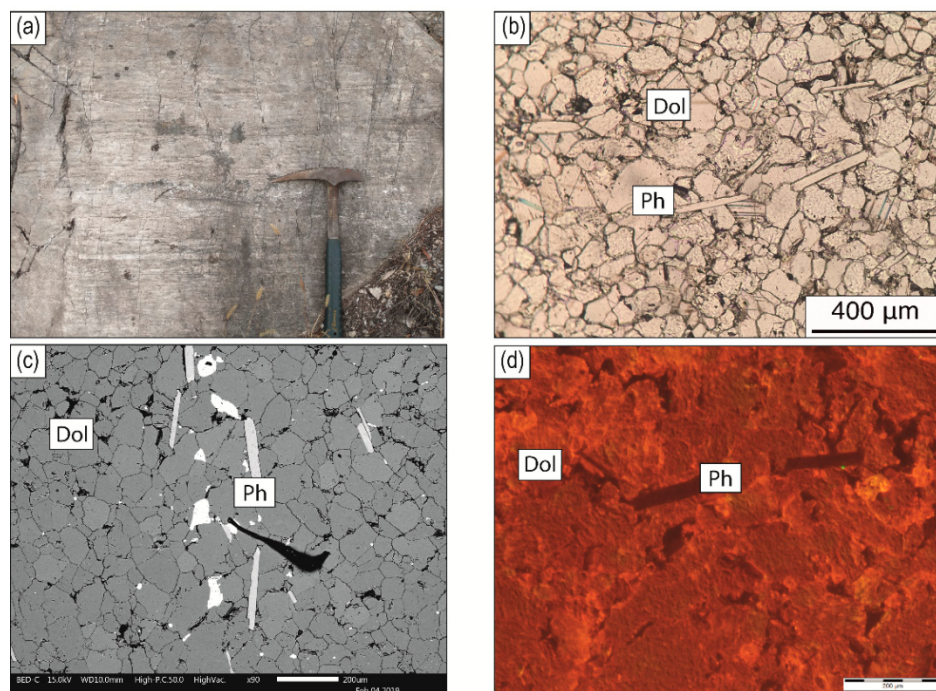


Figure 5. Petrography of the marble of Site 3: (a) Macroscopic aspect of the marble at Site 3; (b) Photo of optical microscope with only a polarizer, in which dolomite and phengite crystals are indicated; (c) SEM backscattered image. Dolomite crystals are dark grey and phengite ones are light-grey; (d)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

Table 3. Representative SEM-EDS analysis of paragonite from Chianocco massive marble (Site 3).

Sample	Quarry (Site 3)			
Analysis Number	<i>Pg 1</i>	<i>Pg 2</i>	<i>Pg 3</i>	<i>Pg 4</i>
SiO ₂	50.57	49.11	50.13	49.64
TiO ₂	0.00	0.00	0.00	0.00
Al ₂ O ₃	40.67	42.04	41.07	41.53
FeO	0.00	0.00	0.00	0.00
MgO	0.62	0.00	0.48	0.00
CaO	0.00	0.28	0.00	0.00
Na ₂ O	7.50	8.17	7.73	7.90
K ₂ O	0.00	0.00	0.00	0.00
Total	95.53	96.06	96.78	96.38
Si	6.14	5.98	6.09	6.06
Al IV	1.86	2.02	1.91	1.95
Al VI	3.96	4.01	3.97	4.03
Fe	0.00	0.00	0.00	0.00
Mg	0.11	0.00	0.09	0.00
Ca	0.00	0.04	0.00	0.00
Na	1.77	1.93	1.82	1.87
K	0.00	0.00	0.00	0.00

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

Conversely the Chianocco marble (Sites 1, 2, 4, and 5) 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–f). Calcite fills mm-large veins with commonly sharp edges. Crystals are equant, limpid and show an overall dull brown CL colour (Figure 6e).

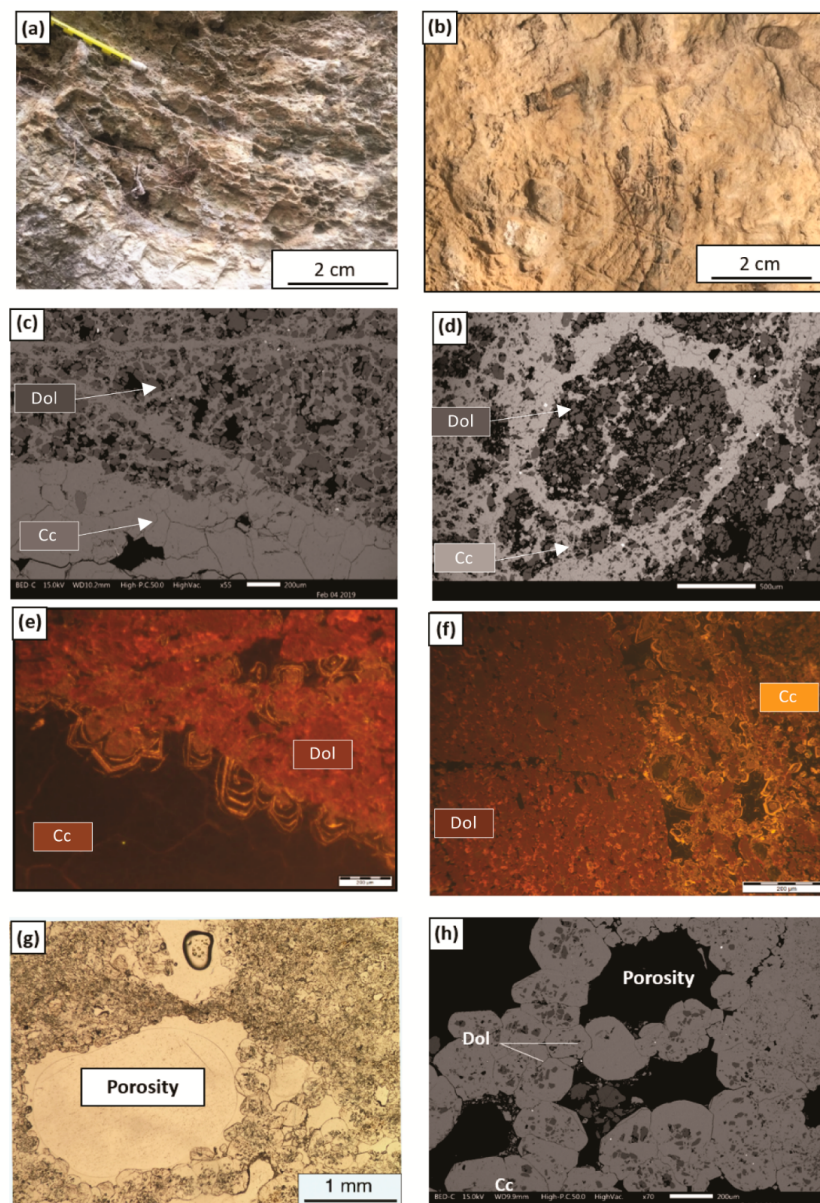


Figure 6. Petrography of Chianocco marble: (a, b) Macroscopic aspect of Chianocco marble; (c) SEM backscattered image where calcite veins are clearly visible; (d) SEM backscattered image where cataclastic structure is evident; (e) Cathodoluminescence image where in a calcite vein a zoning is recognizable 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 microscope image with only a polarizer, with evident vacuolar texture; (h) SEM backscattered image where the voids are surrounded by calcite septa that originally separated the dolomite clasts.

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).

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

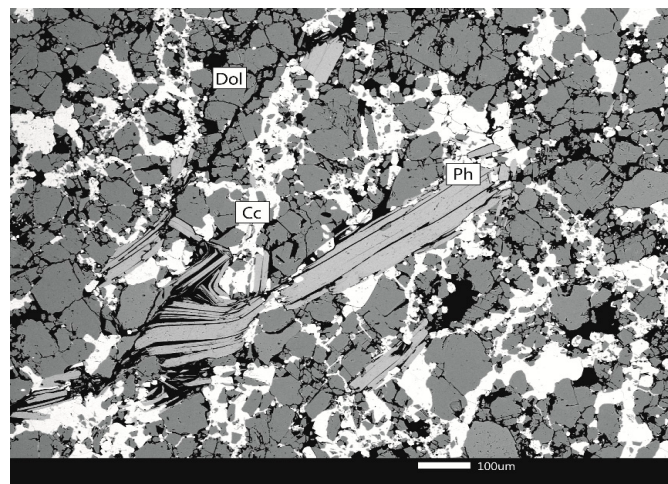


Figure 7. SEM backscattered image of Phengite crystal broken and folded.

The white mica of façade and quarry samples, analyzed by SEM-EDS, plots in the field of phengite and displays a high content of silicon, and index of crystallization at high pressures (Table 1, Figure 8). More in detail, the Si amount, expressed as atoms per formula unit (p.f.u.) based on 22 oxygens, varies between 7.03 and 7.17 for façade samples, and between 6.63 and 7.42 for quarry samples and falls in the field of high pressure. The Mg content is between 1.00 and 1.08 atoms p.f.u. for façade samples and between 0.64 and 1.37 for quarry samples, whereas Fe was always absent, consistently with the carbonate system composition. The composition of phengite of Palazzo Madama samples partially corresponds to the mica of quarry marbles (Figure 8a). Notably the micas of historical quarry samples show a wider range of variation in the Si/Al ratio.

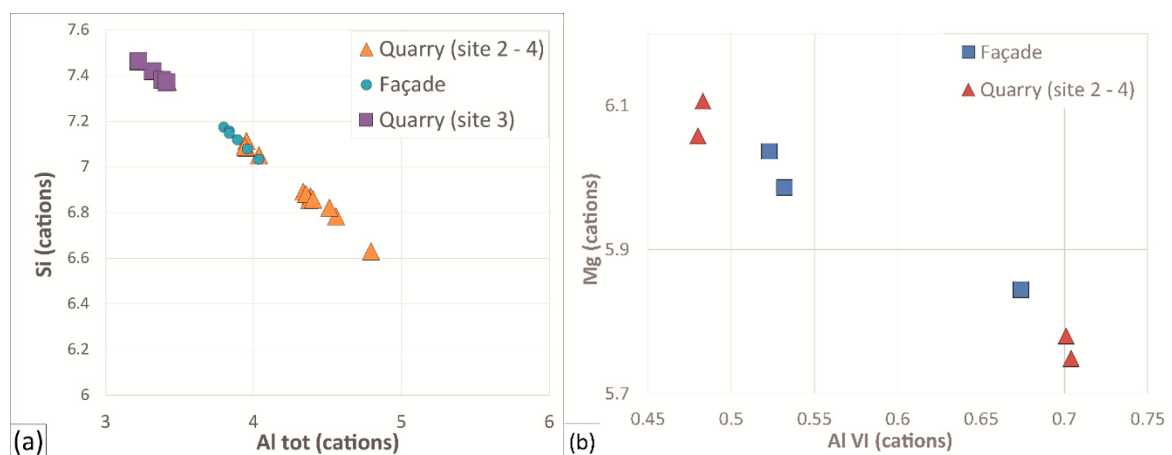


Figure 8. The Palazzo Madama façade and Chianocco quarry: (a) Si-Al tot classification diagram for white mica of the Chianocco marble from the Palazzo Madama façade and Chianocco quarry; (b) Mg-AlVI classification diagram for phlogopite of the Chianocco marble from the Palazzo Madama façade and Chianocco quarry.

Phlogopite, which is characterized by a much higher Mg:Fe ratio than biotite, was also found. Phlogopite only rarely occurs in marbles and therefore it can be used to characterize the marble variety of the Palazzo Madama façade from the mineralogical point of view. Phlogopite blasts occur rarely in the samples from the Chianocco quarries; Table 4 and Figure 8b show representative SEM-EDS analyses of phlogopite.

Table 4. Representative SEM-EDS analysis of phlogopite from the Palazzo Madama façade samples and Chianocco quarries recalculated on the basis of 22 O_x.

Façade				Quarry (Site 2–4)			
<i>Phl 1</i>	<i>Phl 2</i>	<i>Phl 3</i>	<i>Phl 4</i>	<i>Phl 5</i>	<i>Phl 6</i>	<i>Phl 7</i>	<i>Phl 8</i>
46.17	46.51	46.21	47.55	47.27	46.33	46.88	46.46
0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
14.87	13.42	13.62	12.67	12.68	14.66	14.41	13.32
0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
28.79	29.61	29.30	29.77	29.81	28.34	28.30	30.01
0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
0.00	0.00	0.37	0.00	0.00	0.00	0.00	0.00
8.92	9.12	9.21	10.01	8.86	8.63	9.06	8.80
96.84	97.00	96.55	96.70	93.69	95.02	96.68	96.62
6.29	6.36	6.33	6.46	6.44	6.34	6.39	6.34
1.71	1.64	1.67	1.54	1.56	1.66	1.61	1.66
0.67	0.52	0.53	0.49	0.48	0.70	0.70	0.48
0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
5.84	6.04	5.99	6.03	6.06	5.78	5.75	6.11
0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
0.00	0.00	0.10	0.00	0.00	0.00	0.00	0.00
1.37	1.39	1.41	1.67	1.35	1.31	1.38	1.34

Finally, some samples are characterized by a red zone in calcite veins due to the presence of iron oxides inside calcite crystals (Figure 9a,b). This phenomenon is visible on the macroscopic scale in Site 4 (Figure 9c); the rock on the outcrop is similarly reddish as the column of the façade already mentioned (Figure 4d).

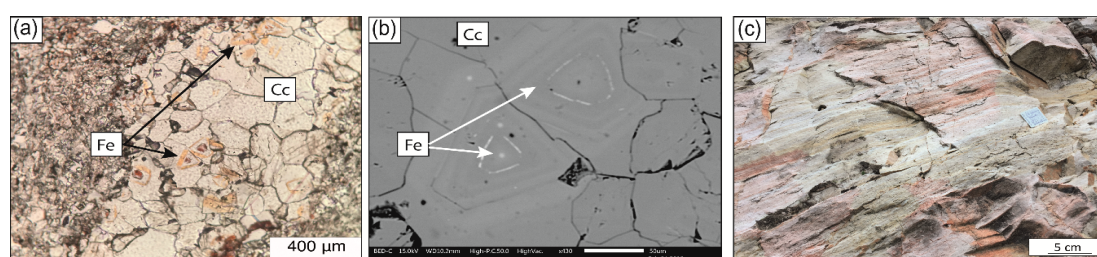


Figure 9. Reddish alteration phenomena: (a) Red zones in calcite veins observed by optical microscope with only a polarizer; (b) SEM backscattered image where zones of iron oxides in calcite crystals are visible; (c) Reddish alteration phenomena visible at the Site 4 quarry.

SEM-EDS analysis also revealed in some areas superficial gypsum with spherical and “rose” morphology (Figure 10a). Also, intergranular gypsum was found (Figure 10b,c).

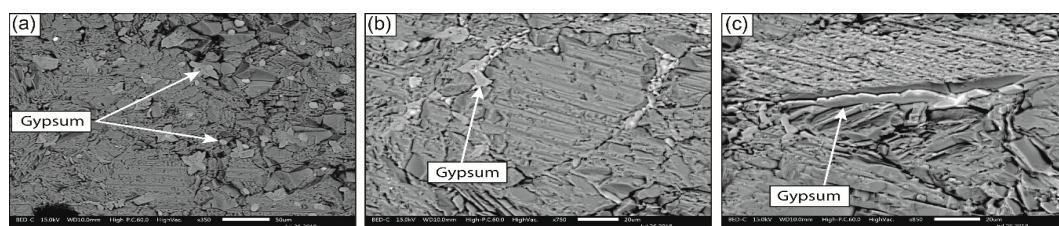


Figure 10. SEM backscattered image with superficial gypsum present in façade samples: (a) Spherical and “rose” morphology gypsum; (b,c) Intergranular gypsum.

5.2. C-O Stable Isotope Analysis

C-O stable isotope analyses have been carried out on two selected samples of Chianocco marble where the characteristic brecciated structure is best represented. One consists of a piece detached from the Palazzo Madama façade and the other comes from Site 4, in the surroundings of Chianocco, village where the rock results are analogous to the façade marble. Values of $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ have been determined on calcite and dolomite of both samples. The results, referred to as the PDB standard, are plotted in Table 5 and Figure 11 where data from the literature [18], concerning the massive dolomitic marble, are also reported for comparison. These analyses were not aimed to be a complete archaeometric characterization and provenance of Palazzo Madama marble but only to verify the genetic relationships of calcite and dolomite which, on the basis of petrographic observations, are clearly not in equilibrium. Although the data set is not statistically highly significant, two points are relevant: 1) Isotopic data of dolomite samples coming from the façade and from Chianocco quarries compare well with data referred to the massive dolomitic marble of Chianocco and Foresto quarries [18] with $\delta^{18}\text{O}$ values ranging between -7.06 and -6.00 and $\delta^{13}\text{C}$ ranging from 0.79 to 1.30 ; 2) Calcite is significantly more depleted in ^{18}O than dolomite, showing values of -9.2 and -10.8 ‰ PDB i.e., with a shift of up to -4.8 ‰ PDB from dolomite to calcite in the same sample. This establishes marked differences in physico-chemical features of the fluids (temperature, nature and composition of fluids) and thus contrasting geological settings in which dolomite and calcite formed. In particular, the dolomite portion of the rock records the Alpine metamorphic overprint of Triassic sediments whereas the calcite portion is likely due to post-metamorphic evolution of the marble after exhumation and interaction with meteoric waters.

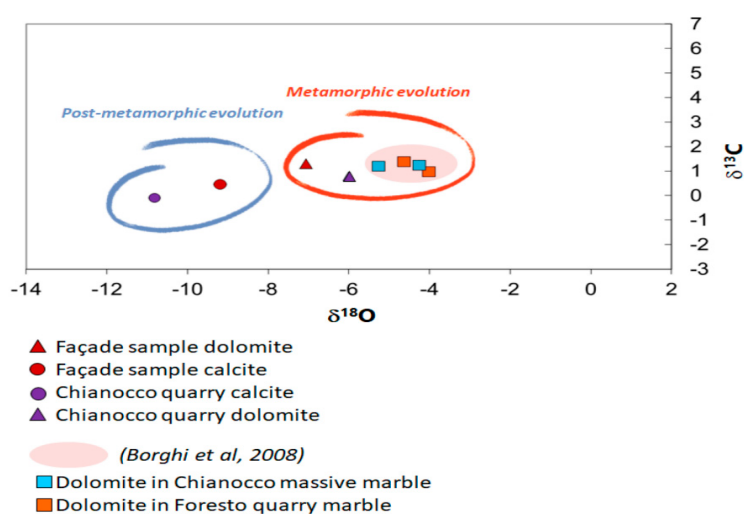


Figure 11. The $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ diagram of calcite and dolomite of the investigated Chianocco marble. The isotopic reference of Chianocco and Foresto dolomite according to Borghi et al., 2008 is also reported.

Table 5. Calcite and dolomite stable isotope (C, O) data of the Palazzo Madama façade sample and Chianocco quarry sample.

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

6. Model Evolution

The petrographic study of the quarry and façade samples allowed us to define a model of the evolution of the rock from its formation to its employment. This model is articulated in six steps as shown in Figure 12, starting from deposition of the dolostone, through Alpine metamorphism and brittle deformation and brecciation to superficial partial dissolution, with only the very last step being related to the recent exposure of the stone to atmospheric agents as a facing of the Palazzo Madama. In the following, each step will be commented on in detail.

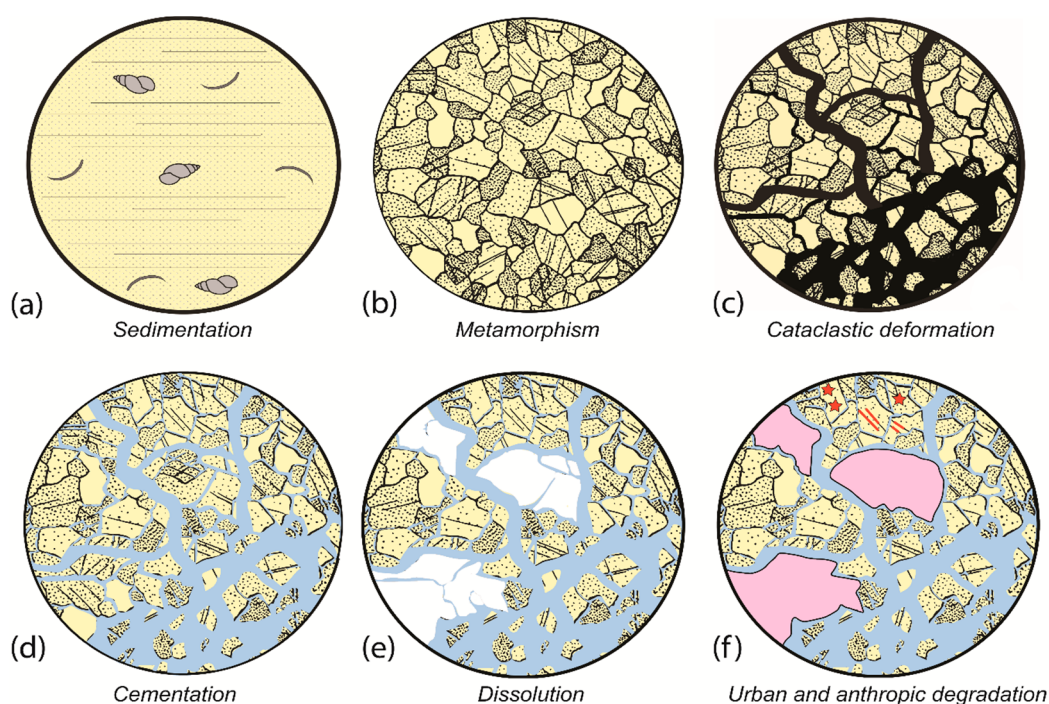


Figure 12. Representation of the model evolution of Chianocco marble from its formation to its employment: (a) Original dolostone; (b) Dolomitic marble; (c) Brittle deformation indicated by black fractures; (d) Cementation indicated in light blue color (tectonic carbonate breccia with a complex and pervasive 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 was 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 phengite indicates 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 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 $\delta^{18}\text{O}$ 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 (possibly the 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

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 massive 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.

7. Conclusions

A multidisciplinary geological approach was applied to the façade of the Palazzo Madama, one of the most important historical monuments in Turin and a UNESCO World Heritage site, which has been recently affected by environmental degradation. A detailed architectural-petrographic relief and minero-petrographic and isotopic analyses were carried out comparing quarry samples coming from the historic sites of exploitation with selected fragments detached from the façade. The main results may be summarized as follows:

- 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 reddening, 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 the 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 issues 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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