Periodico di Mineralogia (2012), 81, 3, 345-357 DOI: 10.2451/2012PM0020

PERIODICO di MINERALOGIA
established in 1930

An International Journal of
MINERALOGY, CRYSTALLOGRAPHY, GEOCHEMISTRY, ORE DEPOSITS, PETROLOGY, VOLCANOLOGY
and applied topics on *Environment*, *Archaeometry* and *Cultural Heritage*

Yellowing of a white granite pavement in urban environment: the Fe-rich patina of Piazza Cavalli, Piacenza (Italy)

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Abstract

An integrated petrographic, colorimetric and capillary water absorption study of decayed flagstones of Granito Bianco (white granite) Montorfano from Piazza Cavalli (Piacenza, Italy) can provide important clues on the formation of yellowish patina on leucocratic granites used for buildings and decorative purposes. The granitic flagstones constituting the pavement of Piazza Cavalli rest on a basement consisting of iron-rich (Fe_2O_3 = 6.53-7.37 wt%) clay bricks. After more than two centuries of exposition to the urban environment, these surfaces acquired a yellowish patina characterised by a significantly higher yellow component that do not occur on the fresh surfaces in the native quarry of Mergozzo (NW Italy). In particular, the intensity of the yellowish patina is not controlled by the modal amount of biotite, the main Fe-rich mineral of Granito Bianco Montorfano. The results of the capillary water absorption test indicate that the aged Granito Bianco Montorfano flagstones have higher water transport capability than samples recently extracted from the Mergozzo quarry. The capillary water rise is controlled by inter/intragranular porosity of the granite flagstones. In particular, iron-rich compounds preferentially occur along the pores, indicating that iron can be efficiently transported by advection from the clay brick basement towards the surface. The results of this study show that (i) external iron sources coupled with iron advection are essential to the development of a Fe-rich yellowish patina on white granites, (ii) the release of iron from femic minerals contribute to the development of rust stains, but cannot account for the yellowish patina covering large surfaces of white granite flagstones.

Key words: patina; yellowing; water capillary rise; Granito Bianco Montorfano; Piazza Cavalli; Piacenza.

Introduction

Patinas are defined as the chromatic modification resulting from natural ageing and not involving visible surface deterioration (UNI 11182, 2006). They frequently appear on surfaces of both natural rock outcrops and stones used in buildings and urban décor. Patinas differ from crusts inasmuch as the former has no appreciable thickness under naked eye inspection and covers more or less the whole exposed stone surface, whereas the latter is the accumulation of material of variable thickness. According to the ICOMOS-ISCS glossary (Vergès-Belmin, 2008), two sub-types of patina can be recognised: orange to brown Ca-oxalate patinas (Rampazzi et al., 2004; Pavía and Caro, 2006) and iron-rich patinas. The latter is generally related to the breakdown of Fe-rich minerals to form Fe-oxide "rust" stains (Siegesmund and Snethlage, 2011).

The aim of this study concerns the yellowish patina on flagstones of Granito Bianco (white granite) Montorfano constituting the pavement of Piazza Cavalli in Piacenza, northwestern Italy (Figure 1). The Granito Bianco Montorfano is a leuco- to slightly mesocratic monzogranite currently quarried on the slopes of Montorfano near the village of Mergozzo (Lago Maggiore, NW Italy). This is one of the most important stone used especially in Northern Italy for both modern and historical buildings, and monuments (Bugni et al., 2000; Cavallo et al., 2004). Granitoid rocks, widely used in the Mediterranean area for building and ornamental aims since the antiquity, are igneous rocks that may contain up to a few tens volume % of Fe-rich minerals, namely biotite and amphibole ± Fe-sulphides. These minerals can provide iron sources to the development of the iron-rich patinas. The paradox is that many light-

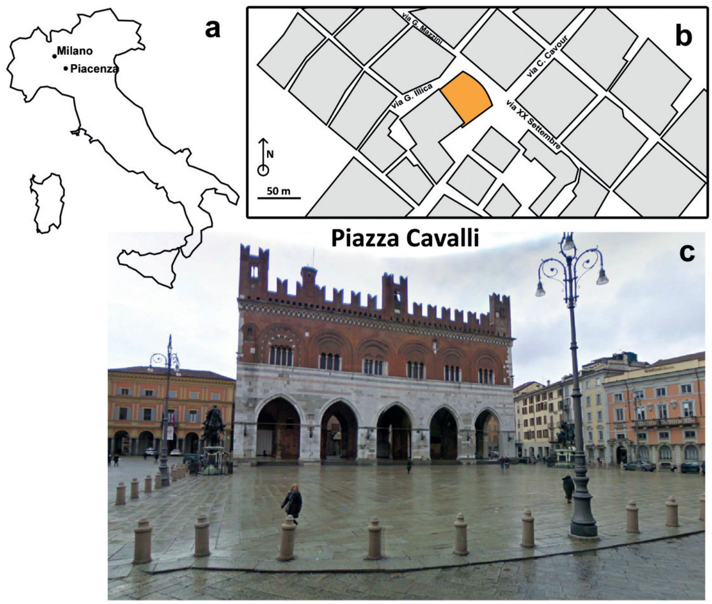

Figure 1. a) Piacenza, at about 80 Km SSE from Milan; b) localization of Piazza Cavalli; c) Piazza Cavalli, Piacenza. In the middle, the so-called "Palazzo Gotico", on the two sides the bronze sculptures of the dukes Ranuccio and Alessandro Farnese.

coloured granitoids employed since Roman times such as the leuco-tonalite known as Marmor Claudianum and the Granito di Nicotera (Antonelli et al., 2009) as well as the Elban and Mysian granites (De Vecchi et al., 2000) lack of significant yellowing. Consequently, the origin and development of natural rust on stones requires alternative explanations other than the oxidation of ferrous iron released from femic minerals.

The description of the Piazza Cavalli pavement

Since the end of the 13th century, Piazza Cavalli has been the centre of the social and political life of Piacenza, about 80 km SSE from Milano (Figure 1). The granite pavement of Piazza Cavalli has been built during the 1780s upon a 15th century clay brick flooring (Eremo, 2005). Today, the stratigraphy of Piazza Cavalli consists of (from bottom to top) (a) the clay brick basement, (b) a layer of small terracotta fragments mixed with sand, and finally (c) the uppermost granite flagstones (Figure 2; reconstructed by the data available from the Comune di Piacenza, 2008). The flagstones have variable length (locally exceeding 2 m), with an average of 8 cm of thickness and 55 cm in width respectively. The cross-section of the slabs has a tapered shape to ease the placement over the sandy layer. Most of the flagstones of Piazza Cavalli consist of Granito Bianco Montorfano white granite, with minor occurrence of Granito Rosa Baveno pink granite. The top of the slabs shows the granular texture typical of granites, consisting of medium (5-10 mm) to fine-medium (< 5 mm) interlocking minerals. Locally, dark-grey and fine-grained rounded pods, known as mafic microgranular enclaves, occur. After more than two centuries from the stonework, the surface of the white granite acquired a yellowish patina varying in colour from very light yellow to dark yellowish-brown. Some of the slabs show also the so-called “rust” stains, dark-orange halos around Fe-bearing minerals, biotite and pyrite. Interestingly, yellowish brown stripes are visible at the border of several granite flagstones, adjacent to the gaps between one tile and another (Figure 3). These strips do not display any systematic spatial relation with the occurrence of biotite, the Fe-rich black mineral.

Materials and Methods

In order to study the origin of the yellowish patina on the Granito Bianco Montorfano, five large fragments (named from PC1 to PC5) of granite flagstones have been collected from the

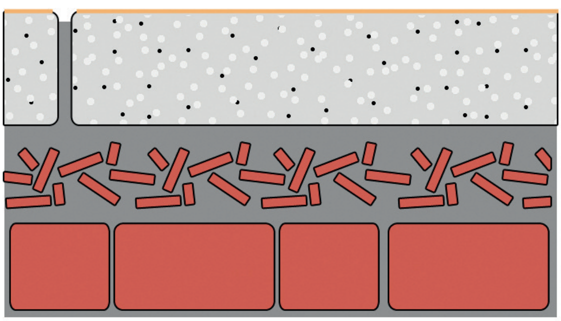

Figure 2. Stratigraphy of the Piazza Cavalli. From bottom to top (not in scale): 15th century brick basement in a sandy mortar; 10 cm-thick sandy mortar bed with earthenware pieces inside; Granito Bianco Montorfano flagstones; a few-micron thick yellowish patina.

Figure 3. A paving slab of Piazza Cavalli showing rust stripes on the edges towards the sand-filled crevices.

municipal storehouse of Piacenza. These fragments derive from damaged flagstones previously belonging to the pavement of Piazza Cavalli and recently replaced with new Granito Bianco Montorfano tiles in 2009. The sampling was aimed to obtain the whole spectrum of chromatic intensity of the yellowish patina, from very light yellow to dark yellow (Figure 4). Several smaller slabs, cores and thin section were prepared from the large granite fragments for microscopic and colorimetric analyses. Some mm-sized specimens, including both patina and the substrate, were embedded into KBr pellets to prepare cross sections to be observed under an Olympus BX51M optical microscope in both visible and UV light. In addition, eight small blocks of Granito Bianco Montorfano were collected from the active quarry of Mergozzo to investigate the extent of yellowish patina development in natural environment.

Modal analyses, i.e. the proportions of the main minerals constituting the volume of the granite, were acquired by image analysis on several cm^2 wide surfaces obtained from slabs

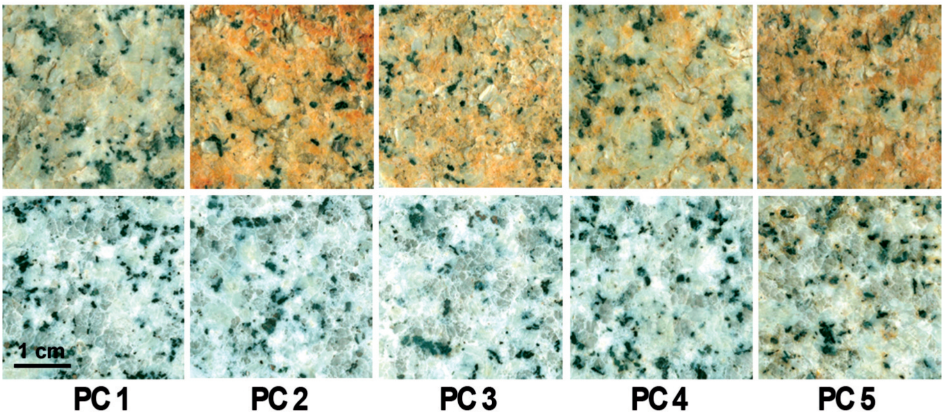

Figure 4. The yellowish patinas (top) and freshly cut surfaces (bottom) of the correspondent samples considered in this study. Images are 3.5 x 3.5 cm across.

sawn off the large fragments using the segmentation capabilities of the MULTISPEC program (https://engineering.purdue.edu/~biehl/MultiSpec). The modal analysis by image processing (compared to conventional point-counting techniques of standard petrographic ~ 27.0 mm x 45.0 mm thin sections) has the advantage to provide a far wider sampling area and thus overcome the oversampling of large minerals with respect to the small ones.

Secondary (SE) and backscattered (BSE) electrons images of the yellowish patina (sample PC2) were acquired with a FEI Quanta 200 Environmental Scanning Electron Microscope (ESEM). EDS microanalyses were collected using an X-EDS detector Oxford INCA X-sight using an accelerating voltage of 12-25 kV to optimize the beam-sample interaction volume. The analyses were carried out at the Centro Interdipartimentale Grandi Strumenti (Modena University).

Colorimetric measurements were performed under laboratory conditions on five cores (5.0 cm diameter and 1.5 cm in thickness) on both the patina and the freshly cut surface opposite to the patina. The measurements were collected during a single session with a Konica Minolta CM 2600d spectrophotometer. The white balance was obtained using the Minolta CM-A415 plate and the readings were carried out using a 8.0 mm-diameter viewing aperture, specular component included (SCI) and excluded (SCE), UV 0%, Illuminant D65 and 10° observer angle. Ten records on each surface were captured with casual criterion throughout an area of about 20 cm^2, obtaining average values of lightness L* and the colour coordinates a* (red-green component) and b* (the yellow-blue component) of the CIELAB colour space. The SCE mode resulted the more appropriated for measurements on granitic surfaces because of the sub-metallic lustre of biotite.

The capillarity water absorption test was carried out under laboratory conditions on cores (5.0 cm diameter and average thickness of 3.0 cm) drilled from the large granite fragments from the Piazza Cavalli pavement and from the small blocks collected from the quarry. The yellow patina was not present in any tested sample in order to study the intrinsic characteristic of the granite. The capillary test follows the EN 15801 (2009) procedure: the cores were placed on pads of filter papers into a closed container where demineralised water was poured until the pads reached saturation. The samples were weighed with a ACCULAB VICON balance and the water absorption coefficient and the capillary absorption were calculated within seven days.

Finally, the bulk chemical composition (major elements) of three fragments of clay bricks from the basement was determined on pressed powder pellets by X-ray fluorescence spectrometry. We

Table 1. Modal composition of the samples of Granito Bianco Montorfano from the Piazza Cavalli pavement.

Sample	PC1	PC2	PC3	PC4	PC5	G&P*
Quartz	34.7	29.1	26.6	37.5	43.0	26-54
Alkali-feldspar	38.3	53.5	37.1	39.6	30.7	24-44
Plagioclase	14.2	10.8	28.3	14.3	15.0	19-38
Biotite	6.3	3.7	7.0	3.9	4.5	2-8**
Chlorite	5.8	2.5	0.3	3.9	3.6	
Sulphides/"Rust" stains	0.6	0.3	0.9	0.8	3.3	not reported

* Modal composition for Granito Bianco Montorfano from Gandolfi and Paganelli (1974).
** Data comprise both biotite and chlorite.

used a Philips PW 1480 spectrometer equipped with a Rh tube; raw data quantification follows the correction method of Franzini et al. (1972).

Results

On the fresh surface, devoid of the yellowish patina, the samples show a "salt-and-pepper" appearance typical of the Granito Bianco Montorfano and defined by white to light grey quartz and feldspars, and black biotite. "Rust" stains around biotite and Fe-sulphides are detectable with an unaided eye and mainly occur in the fresh surface of samples PC3, PC 4 and PC5 (Figure 4). It is important to note that biotite flakes without rust halos also occur in each examined sample. A common feature visible on the fresh surfaces is the occurrence of a network of joints defined by mineral-mineral boundaries (intergranular porosity; Choquette and Pray, 1970) as well as by fractures within single grains. In thin section, the granite flagstones from Piazza Cavalli show a typical hypidiomorphic texture defined by subhedral microperthite, plagioclase, biotite (which is partially replaced by chlorite) and by anhedral quartz. Microperthite always has a turbid appearance and, locally, is rimmed by a thin albite corona. Modal analyses of the Piazza Cavalli flagstones (Table 1) indicate mineral abundances within or near the values reported in literature for the Granito Bianco Montorfano (Gandolfi and Paganelli, 1974). The modal amount of the "rust" stains, either the reddish halo around biotite and sulphides, is generally below 1.0 vol% with the exception of sample PC5 (3.3 vol%).

In cross-section (Figure 5), the yellow patina appears as a few micrometre thick ochre layer irregularly distributed over the granitic substrate. The same ochre colour crosses the substrate along the intergranular porosity. No fluorescence emission was detected by UV inspection, thus excluding the occurrence of organic matter in the patina.

Backscattered (BSE) imaging of the surface of a portion of sample PC2 showing an intense dark yellowish patina is characterised by smooth domains corresponding to quartz grains and other domains pitted by micropores located in correspondence with alkali-feldspar (Figure 6a). The micropitted texture is known as etch-pits and are more abundant on the albite rimming alkali-feldspar. The development of this microporosity is a well-documented feature of alkali-feldspars and it is likely related to dissolution-recrystallization processes during deuteric alteration of feldspar crystals (Lee et al., 1995). The intergranular porosity is highlighted by bright Fe-bearing compounds particularly visible in the bottom half of Figure 6b. Carbon, nitrogen, sulphur were not detected. Fractures, either empty

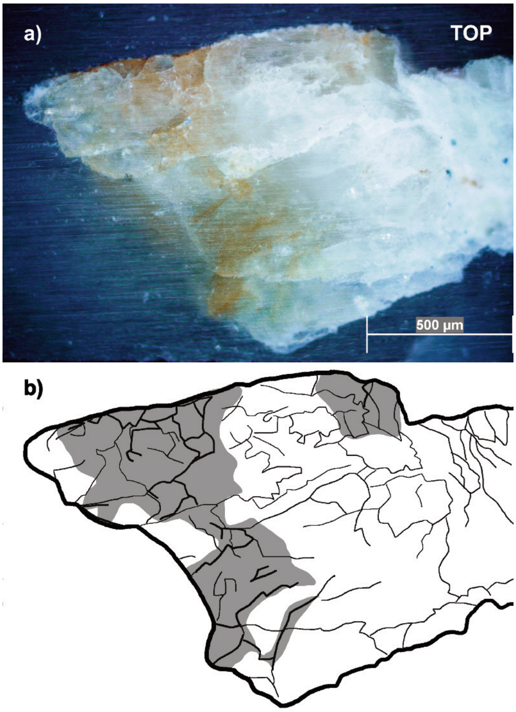

Figure 5. a) Cross section from the top of sample PC 2 down to 1mm inside the granitic substrate; b) line drawing highlighting the location of the iron-rich compounds (in grey).

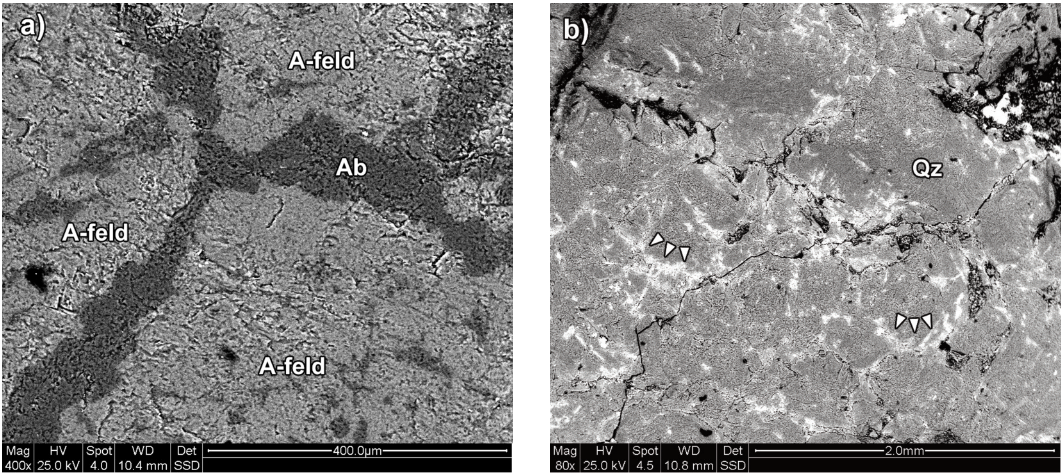

Figure 6. a) BSE image showing the micropores on feldspars. A-feld = microperthite; Ab = albite; b) BSE image showing the enrichment of iron along grain-grain contacts (arrows). Qz = quartz.

or partially filled with particulate, crosscut the mineral assemblage.

Average colorimetric values for both freshly cut and patina surfaces are reported in Table 2. The patina display an average L* (luminosity) of 65.95 ± 2.80, with similar values from the different samples. The b* coordinate (blue - yellow, -b* indicating blue and +b* yellow) is always positive and varies from 9.71 ± 1.19, measured from the pale yellowish patina on PC 1, to high positive values of 20.76 ± 1.71 for the intense ochre patina on the sample PC 2. The a* coordinate (green - red, -a* denoting green and +a* red) has low positive values comprised between 0.66 ± 0.72 and 6.09 ± 0.84. The freshly cut surfaces shows higher L*, and lower a* and b* values than the patina. Only the fresh surface of sample PC5, which is significantly affected by the presence of rust halos, has colour coordinates similar to the pale yellow patina occurring on PC1. The samples from the quarry were analysed on both the patina acquired by the exposed surfaces and on the fresh surfaces obtained in laboratory. The yellow component of the patina on the quarried samples is always lower than the patina visible on the Piazza Cavalli flagstones.

The results of the capillary water test were plotted as the mass of absorbed water per area of samples vs. the square root of time. Within the first hour of the test, a capillary wetting front rises several millimetres from the base of the cores in both the Piazza Cavalli and quarry samples (Figure 7). The absorption curves show that the Piazza Cavalli samples attain the saturation stage later than the quarried samples (Figure 8).

Discussion

Black and grey patinas and crusts on granite surfaces from natural outcrops and buildings have been already studied from NW Spain (Silva et al., 2009; Sajiurjo-Sánchez et al., 2012), Ireland and Scotland (Schiavon et al., 1995), and Portugal (Schiavon, 2002; Pereira de Oliveira et al., 2011). These studies concluded that the black/grey coatings contain Si and Al, with minor amounts of carbon, nitrogen, sulphur and variable iron

Table 2. Average (± 1σ) colour measurements.

	Sample	L*	a*	b*
Piazza Cavalli, patina	PC 1	67.7 ± 1.26	0.66 ± 0.72	9.71 ± 1.19
	PC 2	64.09 ± 1.23	6.09 ± 0.84	20.76 ± 1.71
	PC 3	69.27 ± 1.28	2.95 ± 0.81	16.49 ± 1.51
	PC 4	66.39 ± 1.25	2.27 ± 0.81	15.92 ± 1.49
	PC 5	62.27 ± 1.22	4.95 ± 0.81	18.73 ± 1.62
Piazza Cavalli, fresh	PC 1	78.27 ± 1.34	-0.35 ± 0.69	0.28 ± 0.69
	PC 2	73.72 ± 1.31	-0.31 ± 0.67	0.56 ± 0.67
	PC 3	77.45 ± 1.34	-0.3 ± 0.71	1.48 ± 0.72
	PC 4	73.05 ± 1.34	-0.4 ± 0.72	1.02 ± 0.73
	PC 5	75.54 ± 1.32	0.25 ± 0.74	4.86 ± 0.94
Mergozzo quarry, patina	3	69.32 ± 1.28	-0.65 ± 0.69	0.63 ± 0.69
	4	72.14 ± 1.30	-0.32 ± 0.76	4.70 ± 0.91
	7	78.15 ± 1.34	-0.47 ± 0.67	0.61 ± 0.68
Mergozzo quarry, fresh	3	70.52 ± 1.29	-0.89 ± 0.71	-0.89 ± 0.72
	4	64.67 ± 1.23	-0.01 ± 0.74	5.36 ± 0.95
	7	74.50 ± 1.32	-0.39 ± 0.68	0.53 ± 0.68

L* = luminosity; a* = red - green component; b* = yellow - blue component

contents. Different origins have been proposed for these coatings, from biogenic processes (Schiavon, 2000; Pereira de Oliveira et al., 2011) or reaction between granite and air pollution in urban environments (Schiavon et al., 1995).

The origin of yellowish patina on light-coloured granites, conversely, has been rarely studied. The release of iron from ferro-magnesian silicates (e.g., biotite) or Fe-sulphides (pyrite) is the preferred explanation for the appearance of "rust" stains, an explanation particularly attractive for igneous rocks such as granites and diorites, that typically contain Fe-bearing phases up to tens vol%. The leaching of iron from Fe-bearing minerals in granitic rocks can be induced either by biological activity (Figuereido et al., 1996) or by abiotic oxidation (Dorn, 1998). The former is related to the formation of Fe-Si complex compounds caused by biological attack and it only occurs in rural environment, far from urban pollution (Schiavon, 2002); the latter involves leaching of Fe-bearing minerals and subsequent oxidation on the surface to produce insoluble Fe^{3+}-bearing compounds such as goethite and/or Fe^{3+}-oxide-hydroxide. The dissolution of Fe-bearing minerals dissolution seems to be enhanced by the presence of air-borne pollutant and water (Schiavon, 2000).

The intense yellowish patina on several Granito Bianco Montorfano flagstones used for paving Piazza Cavalli is difficult to explain with the mere biotic/abiotic alteration of Fe-bearing minerals. The massive yellowish patina, visible on the whole granite surfaces, is a striking feature that is not easily reconcilable with the short range leaching of iron from minerals to the surroundings. Simple visual inspection and

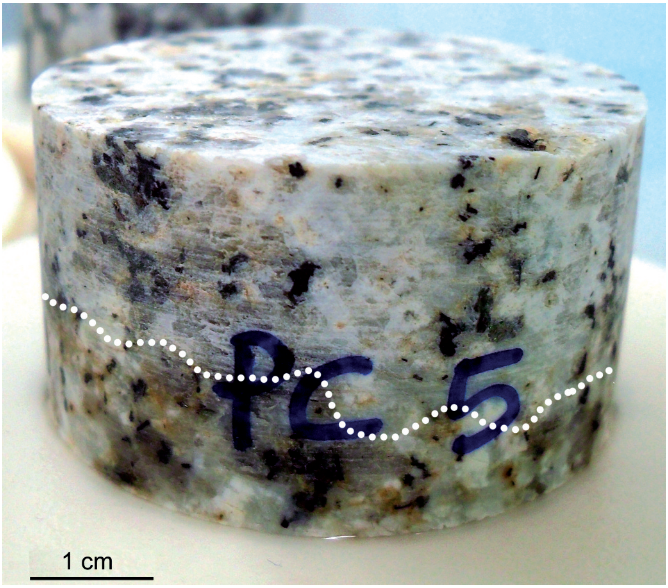

Figure 7. Capillary wetting front visible during the water absorption test for the core PC5.

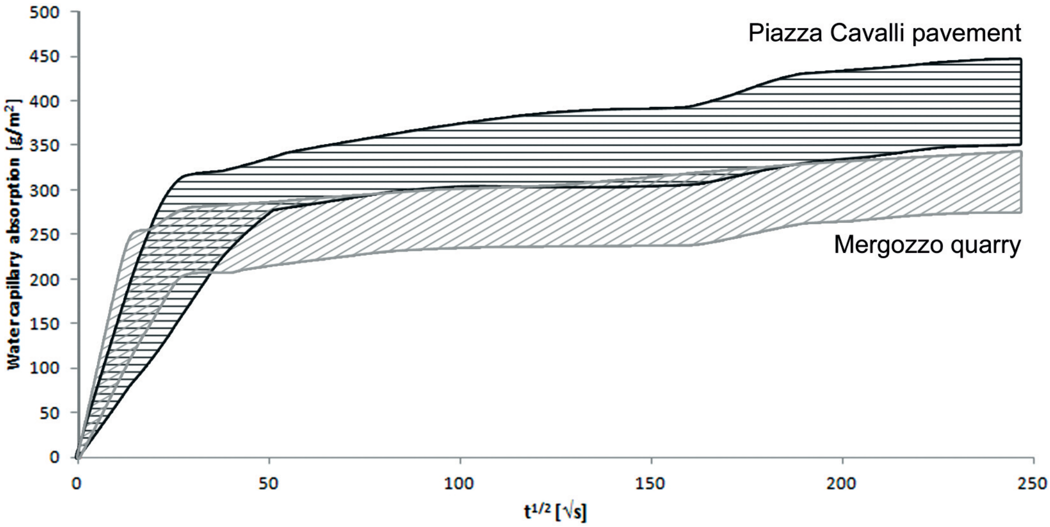

Figure 8. Comparison of capillary water absorption curves between five granite cores from Piazza Cavalli (hatched area) and eight granite samples (crosshatched area) quarried in 2010 at Mergozzo (NW Italy).

optical microscopy clearly show that most of the biotite is not rimmed by rusty halos. The petrographic data is also corroborated by the lack of a positive correlation between the b* value, which quantifies the yellow-blue chromatic component of the patina, and the modal abundance of biotite. For example, the most intense yellow component was measured on the patina covering the sample PC2 that, in turn, contains the lowest modal amount of biotite. This lack of correlation indicates that the decay of Fe-bearing minerals (oxidation of Fe^{2+} released during weathering) does not control the development of the massive yellow patina. All these first order observations show that the origin of the yellowish patina requires other iron sources, in addition to the iron supplied by the alteration of biotite, and a feasible way to transfer iron from the external source to the surface of the granite slab.

The systematic occurrence of yellow-to-orange stripes on the borders of the pavement stones suggests that the sand-filled joints can be connected with a local iron source. The stratigraphy of the Piazza Cavalli pavement is characterised by terracotta fragments mixed with sand interlayered between the granitic flagstones and the 15th century red-bricks basement. Both the terracotta fragments and the clay bricks are a potential iron source: the determined bulk iron content (expressed as Fe_2O_3, Table 3) of three fragments of clay bricks sampled from the basement is high and varies from 6.53 to 7.37 wt%. The need of an external source of iron is also supported by (1) the limited yellowing of the surface of the quarried samples, where no other iron source than femic minerals is available and (2) the inspection of several Granito Bianco Montorfano slabs disseminated throughout the historical centre of Piacenza. These latter granite flagstones, which do not rest on a clay brick basement, lack of the yellowish patina and partially covered by grey particulate (air pollutants and road dust from vehicular traffic; Dept. of Public Works of the Piacenza municipality, pers. communication).

External iron sources located up to tens of cm far from the surface poses the problem of the iron transfer from its source region to the surface. In the Piazza Cavalli flagstones the yellowing already occurs inside the volume of the stone, along grain-grain mineral boundaries that emerge on the surface (Figures 5 and 6b). The staining of the inter/intragranular porosity suggests that Fe-rich water percolates the granite matrix up to its surface. The movement of water through the Granito Bianco Montorfano (Figure 7) is quantified by the capillary water absorption coefficient AC that is higher than the Pietra d'Istria micritic limestone and similar to some of the Macigno siliciclastic sandstones (Table 4).

The capillary water absorption curves allow evaluating the role of the weathering effects on the water transport capability of the Granito Bianco Montorfano (Figure 8). The capillary rise during the first hour of elapsed time is similar for the whole sample set, with the quarried granite reaching the saturation stage earlier than the Piazza Cavalli samples. The reason of this different behaviour may be found in a different

Table 3. Bulk composition of clay brick fragments from the Piazza Cavalli basement.

Sample	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	MnO	MgO	CaO	Na_2O	K_2O	P_2O_5	LOI*	sum
PCB1A	57.2	0.72	14.1	6.53	0.16	4.78	10.8	1.41	2.25	0.16	1.98	100
PCB1B	55.3	0.78	14.6	7.09	0.17	5.15	11.2	1.36	2.31	0.17	1.87	100
PCB2	56.7	0.88	16.1	7.37	0.19	4.07	9.45	1.07	2.53	0.16	1.48	100

* Loss On Ignition (LOI) obtained by thermogravimetric methods.

Table 4. Average values (± 1σ) of the water absorption coefficient AC for different stones.

	AC [$g/m^2s^{1/2}$]	σ	Reference
Granito Bianco Montorfano, Piazza Cavalli Pavement (n = 5)	1.58	0.14	This study
Granito Bianco Montorfano, the Mergozzo Quarry (n = 8)	1.36	0.08	This study
Macigno sandstone (n = 26)	3.33	2.87	Franzini et al. (2007)
Micritic Limestone (Pietra d'Istria) (n = 6)	0.42	--	Tomašić et al. (2011)
Travertine (perpendicular to bedding)	3.94	1.48	García-del-Cura et al. (2012)

decay degree between the Piazza Cavalli and Mergozzo samples. The former have undergone more than two centuries of alteration processes, mainly physical and mechanical stresses that may have enhanced the pore connectivity. As a whole, the capillary water absorption test demonstrate that, in spite of its compactness, the Granito Bianco Montorfano (1) has a greater water absorption than other stones commonly employed in historical buildings in northern Italy (e.g., the widespread Pietra d'Istria micritic limestone) and (2) the amount of absorbed water increases with weathering.

We infer that the origin of the yellow patina requires the following steps: (a) infiltration of rainwater through the gap between adjacent flagstones, (b) uptake of Fe^{2+} from the terracotta fragments and the clay bricks underlining the granite, (c) advection of ferrous iron and its upward transport through the interconnected inter/intragranular granite pores, (d) oxidation of Fe^{2+} through abiotic reactions since microstructures and elements (C, N, S) generally related to biological activity were not found on the examined pavement stones.

Conclusions

The occurrence of patinas on stones is always of concern when there is need to design maintenance and/or restoration actions for historical monuments and the building industry (e.g., Fugazzotto and Braga, 2012). In particular, aesthetical issues may arise when decayed dimension stones with a well-developed patina have to be replaced by petrographically similar stones with fresh surfaces. In this study we showed that in the case of white granite dimension stones, exemplified by the Granito Bianco Montorfano, the development of the yellowish patina is controlled by the availability of iron-rich materials in the surrounding of the stonework and by the advection-controlled infiltration of iron through the granite pores. The iron released from the breakdown of femic minerals (biotite, amphibole, Fe-sulphides) can contribute to a limited extent to the development of the patina. The occurrence of discrete "rust" stains rimming some of these femic minerals is the result of a short-range iron leaching that do not play a major role in the formation of the massive yellow patina that may cover the whole surface of a dimension stone.

Acknowledgements

We thank Ing. Giovanni Carini and Geom. Fabrizio Rancati (Comune di Piacenza) who generously provided technical support during various stages of this work. The constructive review by Laura Gaggero and the editorial handling by Antonio Gianfagna are greatly appreciated. Andrea Natali and Emilio Catelli offered precious advices on colorimetry and sample preparations, respectively. We wish to thank Kenya Monique Brown for proofreading the manuscript. This study is part of C.P. graduation thesis at TeCoRe (Bologna University). Financial support from Comune di Piacenza and RFO (Bologna University) is acknowledged.

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Submitted, May 2012 - Accepted, November 2012