Chapter 5.4

NATURAL AND ACCELERATED WEATHERING OF TWO COLOURED SICILIAN BUILDING STONES

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Abstract: Among many coloured stones employed as "marbles" in the rich baroque architecture in Sicily, the dark grey *Breccia di Billiemi* and the *Rosso di Piana* degli Albanesi are of widespread use. Nowadays they are also exported in Northern Europe and in Arabian countries. Both stones were employed outdoor and indoor as slabs and for structural elements, such as columns, but when exposed outdoor, they undergo significant alteration processes, affecting not only their chromatic aspect but also the state of aggregation. Aim of this experimental work is to investigate some alteration processes induced by weathering in order to understand the mechanism of their evolution. The effects of accelerated weathering in laboratory are compared with natural ageing in the urban environment. The study of such stones includes the description of lithofacies, the characterisation by means of petrographic and physical-chemical techniques - optical and electronic microscopy, XRD - and finally accelerated weathering experiments on both lithotypes - UV radiation plus dew, thermal treatments, washout, exposition to both oxidative and acid environment.

Key words: carbonatic stones; artificial weathering; natural weathering.

1. GEOLOGICAL SETTING AND USE OF THE LITHOTYPES

Billiemi grey stone, known since XI century, has been widely quarried starting from the XVI century to nowadays from the southwestern mountains surrounding Palermo. This lithotype was employed, mainly in the Baroque architecture, as monolithic high columns (up to 10.50 m high) and for monu-

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mental basins because of its good physical and mechanical properties (apparent density 2.71 g/cm^3, compressive strength (dry) 115-158 MPa). The rock formed in Upper Trias-Early Lias (Jurassic) during the tectonic deformation of a platform margin, and could be considered as a resedimented limestone because of its multigenerational composition: in fact the breccia allochems of all shapes and sizes are in their turn made of breccia clasts of polimictic composition (intraclasts).

The quarries of coloured “marbles" of Piana degli Albanesi, located on the northern cliff and on the eastern walls of Kumeta mountain, were exploited since XVII sec., providing significant varieties of sedimentary stones with very different textural and chromatic characteristics, i.e. nodular and brecciated, red white and green coloured, the widespread used one being the Ammonitic red, apparent density 2.72 g/cm^3, compressive strength (dry) 126-132 MPa. The *Ammonitic red* of Kumeta mountain, ascribed to Toarcian - Callovian age (Late Lias-Dogger), sedimented in a seamounts environment[1], identified as a zone of the Trapanese pelagic platform[2], that was tectonically deformed during the Tortonian age.

The red stones had a significant use in baroque architecture for grand staircases and columns, often associated with *Breccia di Billiemi* in order to create bichromatic effects, e.g. in the amazing courtyard of Palazzo Ganci with a staircase of *Breccia di Billiemi* and columns of *Rosso di Piana*, and in Palazzo Comitini and Palazzo Cutò, where the staircase is made of *Rosso di Piana* and the dark grey columns of *Breccia di Billiemi*[3]. Such stones were used also in some important historic palaces elsewhere in Italy, like Palazzo Montecitorio in Rome, the Italian Chamber of Deputies, so that the most uniform, deep red, variety of *Rosso di Piana degli Albanesi* is often named *Rosso Montecitorio*.

2. EXPERIMENTAL

2.1 Mineralogical analysis

Thin sections were studied by optical microscopy in polarised transmitted light with the aim of characterizing the microtexture.

The mineralogical characterisation was carried out by X-ray diffraction (XRD) using a Philips PW 1130/1050 equipment with CuKa radiation, tube conditions 40 kV and 30 mA. The identification of the clay content was carried out by XRD pattern after separation treatment in order to obtain oriented aggregates. Samples of orientated aggregates were also analysed after a treatment with ethylene-glycol or after heating at 550 °C [4]. EDS microanalysis was carried out on fragments of different parts of the rocks, i.e. both veins and grains.

2.2 Artificial weathering

Experimental tests were performed using at least two slabs of each lithotypes, 2 cm thick. The exposed surfaces, 2.5x10 cm, were polished in order to evidence the degradation effects. The light induced fading was simulated in a QUV apparatus, produced by the Q-Panel Company. Weathering was induced by the combined effects of both UV radiation and water condensation on the sample surface. Treatment cycles were settled consisting of 8 hours dry UV irradiation at 70°C followed by 4 hours water condensation at 50°C. The maximum duration of such tests was 5.6×10^3 hours.

The effect of thermal ageing was investigated using two different procedures. Some samples were heated up to high temperature, with the purpose of inducing both degradation of organic matter and microcracking as effect of thermal stresses. Samples were heated in an oven from room temperature up to 150 °C, then up to 600 °C in steps of 50 °C; samples were kept at each temperature for 24 hours. Other samples underwent thermal cycles performed to induce stresses at temperature close to the environmental one. The thermal cycles were performed in a sealed dry box with silica gel, moved alternatively between an oven at 70 °C and a freezer at -13 °C.

The effect of acid chemical agents, present in any urban environment, was simulated by exposure of samples to moisture and HCl vapours at room temperature. Samples were kept in a sealed glass box in presence of HCl 12M for ten days.

The effect of rain washout was simulated by means of an ad-hoc apparatus consisting of two tanks (Figure 1). CO_2 was bubbled in water in order to enhance the rock dissolution. A film of water, with a flow rate of about 3.5 lt/min, flowed continuously on the surface of the rock samples for a maximum time of 10^3 hours.

Figure 1. Details of the washout equipment.

3. PETROGRAPHICAL AND MINERALOGICAL CHARACTERISATION OF THE LITHOTYPES

3.1 Microtexture

The texture and the composition of *Breccia di Billiemi* at both macroscopic and microscopic scale were thoroughly described in previous works[5,6]. It is worth reminding that the rock shows elements of light grey coloured limestone (allochems) of all shapes and size, from a few millimetres to one meter, in an aphanitic darker matrix and cement, generally dark grey or black, somewhere ochre or red (Figure 2a). In thin section the elements of breccia, in their turn, show a clastic texture - calcarenitic to fine calciruditic - made of carbonatic intraclasts. The composition of intraclasts is both micritic (calcite) and sparry, the cement is microsparitic calcite and/or dolomite; the dolomite somewhere forms a drusy texture (sparry dolomite surrounded by rims of sparry magnesian calcite). The cement between allochems of the breccia is an argillaceous-micritic-apatitic mud, containing a dense intergrowth of dolomite crystals, somewhere cutted by sedimentary microdikes and sparry veins. The contact between allochems and the ground mass is somewhere stylolitic and exhibits a residual concentration of pyrite and organic matter (Figure 2c).

As for *Rosso di Piana*, the study concerns two varieties of a lithotype - referred as “pink" and “red" - with a bulk appearance very similar to other Jurassic “Ammonitic reds", e.g. the better known *Rosso di Verona* and *Rosso di Castellammare*, another widespread sicilian red stone. All of these Jurassic red limestones appear very similar to each other, even if some are characterized by a nodular structure and others by a flaser macrotexture.

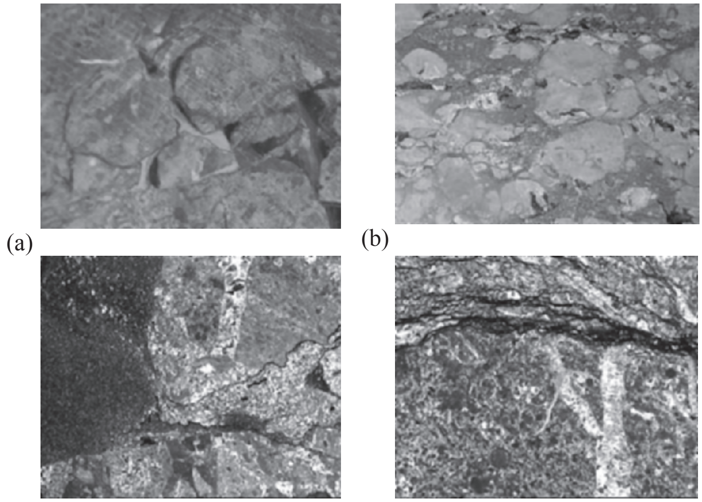

Figure 2. Slabs and thin sections of Breccia di Billiemi (a and c) and Rosso di Piana (b and d).

The pink variety of *Rosso di Piana* at a macroscopic scale looks like an aggregate of calcareous roughly rounded lithoclasts, cream white coloured, wrapped in thin red-violet patinas; in the red variety the lithoclasts are pale brick red and the patinas are dark-ochre and dark-red, the latter darker material forming also thicker veins and zones (Figure 2b). Optical microscopy shows that both kinds of *Rosso di Piana* are made of centimetric elements of two different textural grainstones, welded by grain to grain pressure-solution contacts that originated stylolithic interfaces with residual concentration of clays and oxides. Somewhere the veins are forked, with calcite crystals in-between. In particular for both varieties of *Rosso di Piana* two different grainstones were observed: a) Grainstone with 70% bioclasts, (esoscheletal fragments of echinoderms, mollusca, brachiopods) and 30% of micritic botroids and peloids, with a grain size varying between 30 and 450 µm. b) Grainstone characterised by elements between 30 and 350 µm, made of micritic botroids and peloids, more than 80%, and about 20% of bioclasts, mainly lamellibrancs fragments, streaked by very thin sparitic veins.

The grainstone of type (b) is more abundant in the "pink", whereas the "red" is richer of sparitic zones. The thickness of patinas wrapping the nodular elements ranges from 25 to 150 µm in the "red" and from 10 to 150 µm in the "pink". The areas appearing as dark red zones in fact are made by smaller grainstone lithoclasts wrapped by patinas, which are so close each other that appear like cement zones. These textural characteristics play a major role in the evolutive mechanism of decay phenomena.

3.2 Mineralogical composition

3.2.1 Breccia di Billiemi

Because of the heterogeneity of Billiemi stone, each textural component was individually analysed: i) allochems; ii) black matrix plus cement; iii) red matrix plus cement; iv) ochre matrix plus cement. In Table 1 the crystalline components, as individuated by XRD analysis, are compared with results[7].

Table 1. Crystalline components of *Breccia di Billiemi*

Crystalline phases (°enriched samples)	Rizzo, Ercoli[5,6]				Bellanca[7]
	Allochem	Black matrix	Red matrix	Ochre matrix	(Tout venant)
Calcite	***	***	***	**	***
Dolomite	*	**	***	***	*
Apatite-Fluorapatite °	-	*	-	-	tr
Kaolinite °	-	-	tr	*	-
Smectite °	-	*	*	*	-
Illite °	-	*	*	*	-
Quartz °	-	-	-	-	tr
Pyrite °	-	*	-	-	-

Table 2. EDS results for *Breccia di Billiemi*, atomic percentages

	O	Ca	Mg	Si	Al	P	F	Na	K
Grain	63.80	32.73		0.63		2.84			
Vein	46.21	27.64	1.01	4.44	1.87	11.88	4.55	1.25	0.58

The results of EDS analysis in Table 2, performed on both grain and black matrix plus cement scanning an area of about 150x200 µm, are in agreement with the XRD results. The absence of iron and sulphur is due to the fact that there was no pyrite crystal within the analysed spot. As reported by Rizzo and Ercoli[5], EDS analysis performed on the residual ground powder (<180 µm), attacked by HCl, confirms the presence of Si and Al as main components, followed by S and Fe, P, K and Mg; all these elements are compatible with the XRD evidence of apatite, phyllosilicates and pyrite, the latter two not resulting from Bellanca XRD analysis, but compatible with his chemical analysis[7]. As reported[8], the colour of the black matrix plus cement is due to the presence of aliphatic hydrocarbons with both linear and branched chain, whereas the available analytical apparatus was not right for evidencing heavy aromatic components.

3.2.2 Rosso di Piana

The same analytical procedure was performed on samples of *Rosso di Piana*, after separating the different macrotextural areas (light coloured "nodules" and darker red veins). The XRD results show the presence of predominant calcite in the bulk sample; a further analysis after a weak acid attack reveals the presence of traces of quartz, feldspar and clay minerals, identified as illite and swelling chlorite[4] in the XRD patterns of oriented aggregates.

Table 3. Mineralogical composition of some Jurassic Ammonitic Reds

Crystalline species	*Rosso di Piana*		*Rosso di Castellammare*	*Ammonitic red, Tuscany*	*Rosso di Verona*
	Present work	Bellanca[7]	Bellanca[7]	Fazzuoli et alii[9]	Spadea & Perusini[10]
Calcite	(1) ****	96.19	93.21	>95	95.8-84.5
Quartz	(2) *	(3)	0.82	0-5	(3)
Kaolinite		(3)	traces	traces	traces
Illite	(2) ***	(3)	1.50	2-7(4)	(3)
Vermiculite		-	-		
Chlorite	(2) *** (swelling)	-	-	-	(3)
Apatite and Phospates		(3)	3.62	-	-
Fe minerals	(2) traces	traces	traces	-	(3)
Feldspar	(2) traces	-	-	(5)	-
Magnesium carbonate		2.05	-	-	-

(1) tout-venant; (2) enriched sample; (3) not quantified, identified by XRD; (4) plus accessories minerals; (5) lower than instrumental detectability

In Table 3, the composition of other Italian Jurassic Ammonitic Reds is compared with *Rosso di Piana*. Fazzuoli et al.[9] describe the Ammonitic Red employed in the monumental complex of S. Maria del Fiore in Florence, as made of bioclastic wackstones and micritic nodules with stylolitic joints and thin spatic veins. The *Rosso di Verona* studied by Spadea and Perusini[10] is a rosy nodular biomicrite in a brick-red matrix, formed of hematite and clay minerals bearing biomicrite. EDS analysis was performed on both nodular elements and stylolitic veins, scanning an area of about 150x200 μm. The compositions, summarized in Table 4, are in agreement with the XRD results.

The above results show that grains are made of calcite, whereas the veins contain also clay minerals, quartz, hematite and feldspar. Even if the XRD patterns do not provide evidence for the existence of apatite the presence of phosphorous, as revealed by EDS, confirms the results of Bellanca[7]. The main differences are the absence of kaolinite and the presence of swelling chlorite.

Table 4. EDS results for the two varieties of *Rosso di Piana*, atomic percentages

		O	Ca	Mg	Si	Al	Fe	P	K	Others
Red	Grain	63.05	36.95							
	Vein	54.22	6.99	2.49	21.32	8.25	2.67	0.65	3.05	0.36
Pink	Grain	59.13	40.87							
	Vein	52.14	25.03	2.00	9.91	3.68	2.19	0.37	1.51	3.18

4. EFFECTS OF ACCELERATED WEATHERING

4.1 UV radiation and water condensation on the sample surface

After weathering in the QUV apparatus, the *Breccia di Billiemi* samples show opacifying of surfaces and a noticeable chromatic inversion, i.e. the allochems preserve their grey original colour, whereas the black matrix plus cement becomes whitish, due to UV degradation of organic matter. As for *Rosso di Piana,* no detectable colour variation due to UV radiation occurs; the only remarkable effect is a slow dissolution of the boundary between lithoclasts and stylolitic joints, produced by dew in a relatively few cycles, even in the absence of any aggressive polluting agent.

4.2 Thermal ageing

Samples of each lithotype, after heated from room temperature up to 600 °C, show considerable modification in colour and texture. Starting from 250 °C, the bioclastic texture of elements (both allochems and nodules) becomes sharper, as well as the interfaces between lithoclasts and surrounding elements, probably due to thermal stresses. Furthermore, in *Breccia di Billiemi*, the opaque spots around the pyrite crystals become more circumscribed since they lose the halo, which is compatible with the degradation of organic matter, whereas *Rosso di Piana* keeps its red colour, thus indicating that the red pigmentation is not related to the presence of organic matter. At 600°C thermal decomposition of carbonates starts for *Breccia di Billiemi*, due to the presence of dolomite.

The thermal cycles were performed in isostatic conditions, i.e. without rigid bonds, between +70 °C and – 13 °C. They don't produce any significant effect even after 50 cycles, as no new cracks seem to grow or propagate.

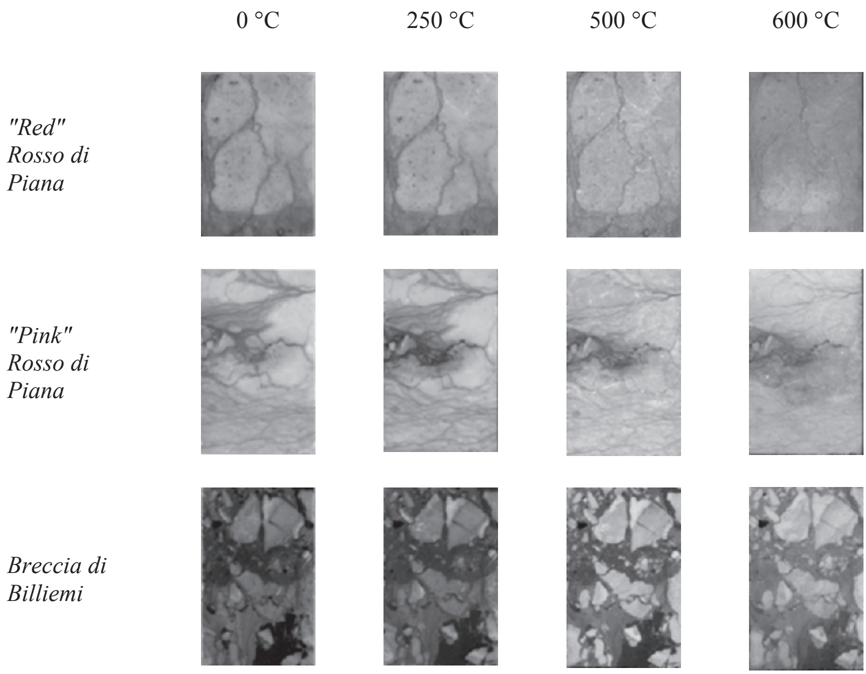

Figure 3. Effects of step by step heating on *Breccia di Billiemi* and *Rosso di Piana* slabs.

4.3 Acid chemical agents

The acid attack produces similar degradation effects on both lithotypes, *Breccia di Billiemi*[6] and *Rosso di Piana.* After ten days exposure to vapours of hydrochloric acid and moisture an highly deliquescent brine drops out from the veins on both the varieties of *Rosso di Piana*, Figure 4, and the grain surface appears to be dull due to a mild corrosion. The samples were photographed after rinsing with fresh water, showing that red veins were corroded.

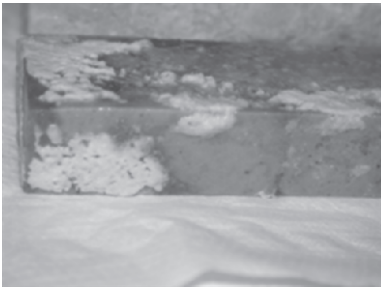

Figure 4. Deliquescent brina due to the acid attack on red *Rosso di Piana* slabs.

In both kinds of *Rosso di Piana* and in *Breccia di Billiemi* a severe aggression of the cement occurs, so that veins withdraw with respect to the elements in the more decayed zones, as illustrated in Figure 5 for "pink". The red variety underwent a particular decay: the red inclusions within the whitish grain were dissolved leaving holes and cracks, whereas the surface of grains is in a quite good condition, Figure 6.

(a)

(b)

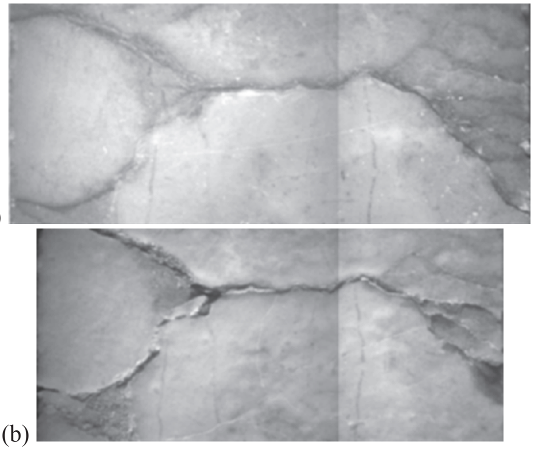

Figure 5. The pink *Rosso di Piana*: (a) before and (b) after acid attack. The dissolution of vein between clasts is evident.

(a) (b)

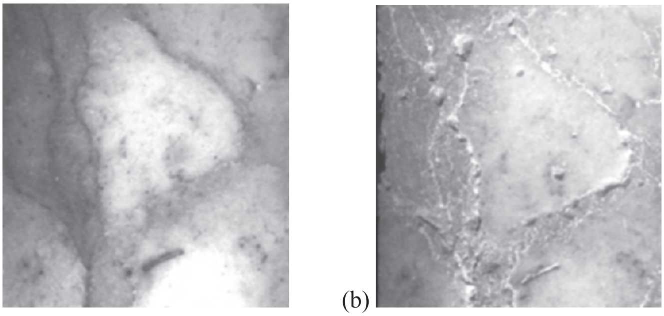

Figure 6. The red *Rosso di Piana*: (a) before and (b) after acid attack. Dissolution of vein between clasts can be observed and some holes replace the red inclusions in the clast.

4.4 Accelerated washout

As a result of the washout process all of the tested materials show significant differential dissolution phenomena of lithoclasts with respect to welding contacts. This process goes on differently for each lithotype and, in some cases, growing of microcracks can be observed.

As for *Breccia di Billiemi*, the surface is strongly faded, with an evident strong inversion of the grey scale, after 51 days of treatment[5,6].

Both kinds of *Rosso di Piana* underwent a quite different decay as effect of accelerated washout. As a first step, dissolution is more severe in the grain, which withdraws with respect to the stylolitic joints, so that the red veins appear in relief, showing new microporosity due to the dissolution of calcite microcrystals within the red matter, Figure 7. As a second step the red veins collapse resulting in withdrawing of stylolitic joints with respect to the grains. This second step of decay occurs when the first step has gone ahead enough to allow mechanical removal of the clay minerals present in the veins as a result of washing water and the vein becomes a furrow. As a consequence of these steps, for the red veins it appears to be equally possible either relief or withdrawn (Figures 8 and 9).

The dissolution of the lithoclasts proceeds uniformly but at different rate for the two kinds of grainstone as shown in Figure 9.

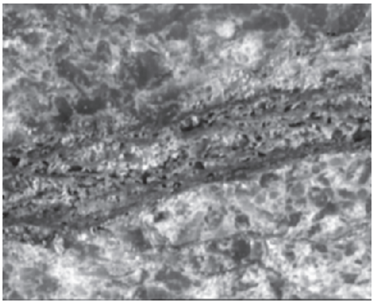

Figure 7. Dissolution of calcite microcrystals within the red veins on *Rosso di Piana* due to accelerated washout.

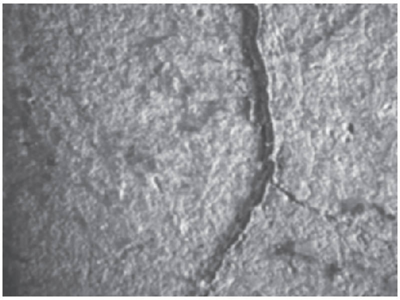

Figure 8. Accelerated washout of *Rosso di Piana*. First step of decay: the vein appears in relief.

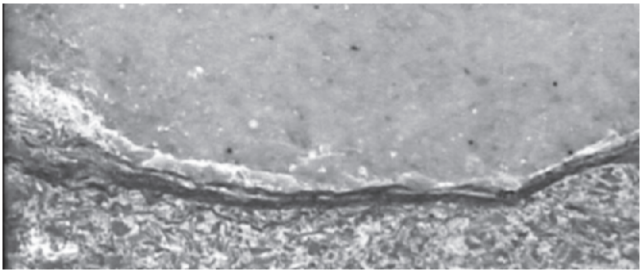

Figure 9. Accelerated washout of *Rosso di Piana.* Second step of decay: the vein withdraws with respect to the grain. Note the different behaviour of the two grainstones above and below the vein.

5. TYPOLOGIES OF NATURAL WEATHERING

As for *Breccia di Billiemi* several typologies of decay can be observed on monuments exposed outdoor and indoor[5,6]: i) the fading of exposed outdoor surfaces, due to synergy of two degradation processes that have been simulated in laboratory, i.e. UV photodegradation of organic matter and development of neater rims between the allochems and the background, probably due to microcracking; ii) the differential withdrawing of allochems and matrix plus cement due to both acid attack and rain washout, Figure 9a.

As for *Rosso di Piana* the main typology of decay is deepening of the red veins, that results in a rough surface. No evident fading or colour change is observed, the veins keep their red colour even when exposed to very aggressive environment - i.e. marine spray and heavy traffic pollutants (Figure 9b). A similar behaviour is also described[10] for *Rosso di Verona*, a stone appearing very similar to *Rosso di Piana*: the nodules are reported to become prominent with respect to the internodular areas as a result of loss of material by scaling, exfoliation and pulverisation, with swelling when covered by black crusts. The authors relate such swelling to an increase of volume due to formation of both gypsum and mixed layers of illite-smectite, the latter originated from the illite present in the unweathered rock.

(a)  (b) 

Figure 9. (a) *Breccia di Billiemi* slab in S. Matteo church, Palermo; (b) ammonitic red column in Palazzo Jung, Palermo.

6. CONCLUDING REMARKS

The main features of natural weathering of *Breccia di Billiemi* and *Rosso di Piana* were documented by observation of monuments in the area of Palermo. The major environmental factors assumed as possible decay agents were thermal excursion, water washout, UV irradiation, acid attack by polluted atmosphere. Some of these aggressive agents were reproduced in the laboratory performing accelerated ageing tests on stone slabs. The expected effects on the stone were modification of surface microtexture, microroughness and/or formation of new species as effects of chemical attack, degradation of organic matter.

The accelerated washout treatment showed for *Breccia di Billiemi* a differential dissolution rate between lithoclasts and cementation contacts. The higher solubility of calcite grains with respect to dolomite, pyrite and organic matter of matrix plus cement produces withdrawing of grain. For *Rosso di Piana* a more complex dissolution process was evidenced: the red veins are less soluble than grain, but they can appear alternatively withdrawn or in relief depending on the progress of the washout. In fact the withdrawal of the "nodules" is the first step, followed by opening of stylolitic contacts, due to mechanical removal after dissolution of limy particles.

The acid attack produced in both lithotypes a preferential dissolution of veins, as observed for natural weathering. The conditions of acid attack are closer to the natural ones than for washout test. In the washout test a steady state dissolution condition is simulated, so that the major factor in producing decay is the solubility of the different parts of the rocks. In the acid attack the pollutant is a gas and the dissolution reaction can take place only when both gaseous hydrochloric acid and moisture dew on the surface of the rocks; in both lithotypes grains have lower porosity than the elements so that, even if they consist of more soluble minerals, they can resist to the aggressive environment. The soluble salts formed during the acid attack are then removed by rain washout, without any steady state conditions.

The different effects of UV radiation, fading of *Breccia di Billiemi* versus no significant change in colour of *Rosso di Piana*, suggest a different role of organic matter in the pigmentation of the two stones. Similar indication comes from thermal treatments. Such a detailed analysis of the role played by each component of the rocks in producing decay could direct further research towards both products and techniques which are the most suitable for a durable conservation process.

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