

SEM-XRD investigation of deterioration morphologies and consolidation prior to restoration: the case of Porta Nuova in Ravenna (Italy)

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ABSTRACT - Porta Nuova in Ravenna (Northern Italy), built in the XVI century, has been the object of an interdisciplinary study, comprising an architectural survey of the Gate, mapping ashlar stones and drawing thematic maps. The following ornamental stones have been identified: Pietra d'Istria, Rosso Ammonitico Veronese, *Marmor Proconnesium*, *Marmor Troadense*, Pietra di Prun and Trachite dei Colli Euganei. Among these, *Marmor Proconnesium* and *Marmor Troadense* could be ancient materials recovered from monuments of Roman age.

In order to carry out conservative restoration, it is of primary importance to know not only the nature and provenance of ornamental stones and building materials for possible replacement and/or integration, but also to define accurately their deterioration morphologies. The *in situ* analysis, implemented by mineralogical-petrographic analysis, SEM-EDS and XRD investigations, allowed drawing a map of the main types of deterioration morphologies, i.e. differential deterioration, black crusts, oxalate films, rust spots, fracture systems, biological patina and presence of vegetation (NORMA UNI 11182 - 2006). Moreover, the enhanced deterioration of the

architectonic structure of the Gate has required specific investigation by microseismicity, endoscopic tests and georadar analyses. These results allowed to make a preliminary intervention with consolidation of fractured and detached stone elements, and to secure the building elements prior to the restoration intervention.

RIASSUNTO - Porta Nuova in Ravenna (Nord Italia), costruita nel XVI secolo, è stata oggetto di un lavoro interdisciplinare che ha realizzato il rilievo architettonico e la mappatura della natura litologica degli elementi lapidei naturali ed artificiali messi in opera. Sono state riconosciute: Pietra d'Istria, Rosso Ammonitico Veronese, *Marmor Proconnesium*, *Marmor Troadense*, Pietra di Prun e trachite dei Colli Euganei. Fra queste, *Marmor Proconnesium* e *Marmor Troadense* si suppone possano essere materiali di reimpiego da più antichi monumenti di età romana.

Nella prospettiva di realizzare un intervento di restauro conservativo, oltre alla natura ed alla provenienza degli elementi costruttivi, utile per definire il luogo d'approvvigionamento per eventuali sostituzioni o integrazioni, risulta di primaria importanza anche la conoscenza delle tipologie di degrado che

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essi hanno subito. L'analisi *in situ*, integrata con lo studio mineralogico-petrografico, l'analisi SEM-EDS e XRD, hanno permesso di realizzare la mappatura completa delle morfologie di degrado dei materiali lapidei che comprende: degrado differenziale, croste nere, patine ad ossalato, macchie di ruggine, fratturazioni e fessurazioni, patina biologica e presenza di vegetazione. (NORMA UNI 11182 - 2006). La situazione di degrado della struttura architettonica ha inoltre richiesto l'esecuzione di indagini microsismiche, prove endoscopiche ed indagini georadar che hanno consentito di effettuare il consolidamento ed il fissaggio dei materiali lapidei fratturati e distaccati del monumento, una prima messa in sicurezza, preliminare all'intervento di restauro conservativo.

KEY WORDS: *Deterioration, SEM-EDS and XRD, consolidation and securing, Porta Nuova.*

INTRODUCTION AND PREVIOUS WORK

Porta Nuova in Ravenna (Northern Italy), built in the XVI century, has been the object of an interdisciplinary study concerning an architectural survey of the gate, mapping ashlar stones and drawing thematic maps. This has been accomplished by mesoscopic analysis of the materials, implemented by petrographic, diffractometric and electron microscopy studies, which brought to a classification of both natural and artificial stone materials.

Results of a recent work (Marocchi *et al.*, 2009) indicate the presence of different ornamental stones. The widespread material is the Pietra d'Istria Orsera. Also important was the use of the "marble" Rosso Ammonitico Veronese. Valuable architectural components such as the composite capitals and the columns drums are carved in *Marmor Proconnesium* (Island of Marmara-Turkey) and *Marmor Troadense* (Çiğri Dâğ, NW Turkey) respectively. Peculiar is also the use of the Pietra di Prun (Verona), Trachite dei Colli Euganei (Padua) and limestones of Istrian or Venetian provenance ("vacuolar", "nodular" and "facies liburnica") (Fig. 1).

The hanging wall façade is built with recovery

bricks of different size and chromatic shades.

Original lime bedding mortars and finishing plaster mortars with fine sand framework have been distinguished in the hanging wall. A micro-conglomeratic finishing plaster mortar has also been detected, likely ascribed to a later restoration intervention.

As demonstrated by recent studies (e.g. Lazzarini *et al.*, 2007), information obtained on provenance, mineralogical and petrographic composition, textural characteristics and the degradation of natural and artificial stone materials of monuments are of primary importance in restoration and conservation.

In this paper we have analyzed and accurately mapped the main types of stone deterioration morphologies, i.e. differential deterioration, black crusts, coloured patinas, rust spots, fracture systems, biological patina and presence of vegetation. These results have been achieved by mesoscopic *in situ* analysis of the materials, implemented by diffractometric and electron microscopy studies, which allowed to clarify the causes and to recognize the mineralogical composition of the deterioration products. Microseismic, endoscopic and georadar investigation have also been carried out to assess the conservation status of the monument and to plan an intervention of consolidation and securing of the stone materials. We stress that such information are regarded of primary importance for cultural heritage and should be taken into account prior to any conservative restoration.

MATERIALS AND METHODS

The mesoscopic analysis and mapping carried out *in situ* were crucial for the study of the morphologies and of the products of deterioration of stone materials. Fragments of black crusts were removed from the Gate and coloured patinas fragments were gently scraped (cf. Fig 2 for sample location within the Gate).

Mineralogical data of the materials were

obtained by X-Ray Diffraction (XRD). Analyses were performed by using a computer-controlled Philips PW 1710 diffractometer with the following operative conditions: $\text{CuK}\alpha$ radiation, 40kV and 30mA, 0.02° (2θ) step size, counting time of 1 s/step. All powder samples were prepared by side loading of an aluminium holder to obtain a quasi-random orientation. The mineralogical identification was based on comparison with JCPDS data.

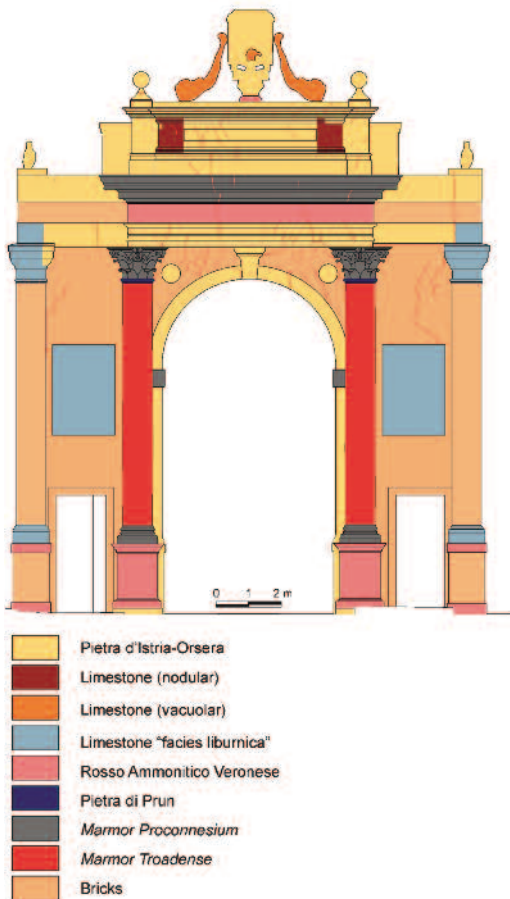


Fig. 1 - Schematic sketch of Porta Nuova front with the classification of the ornamental stones (modified after Marocchi *et al.*, 2009).

SEM-EDX observations were carried out using a Scanning Electron Microscope (SEM) Philips 515B fitted with an EDAX DX4 microanalytical device.

Microseismic investigations were employed to assess the degree of compactness of ornamental stones, to detect the presence of voids and to obtain information on the mortars. The instrument used was a TICO PROCEQ equipped with geophones and transducers with emission of sonic pulses at 54kHz. Further investigations into the cavities and the cracks of the ornamental stone slabs and of the architectural elements have been performed with direct observations using a fibre optic endoscope. Profiles on the status of the first 3 meters underground and for the entire thickness of the walls was obtained through measurement of georadar sections with a GPR (Ground Probing Radar) GSSI SIR SYSTEM 2 equipped with a 400 MHz monostatic antenna.

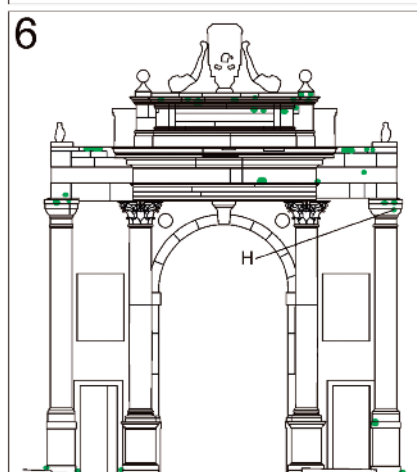
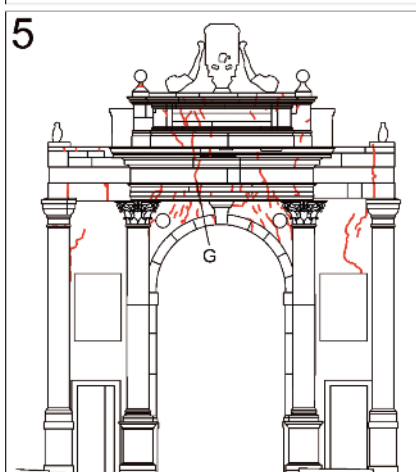
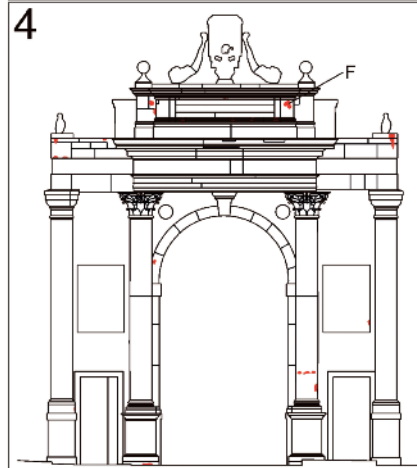
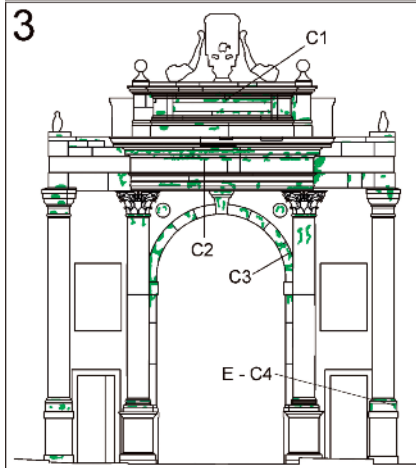
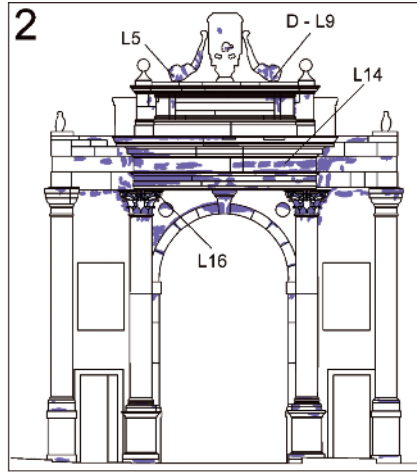
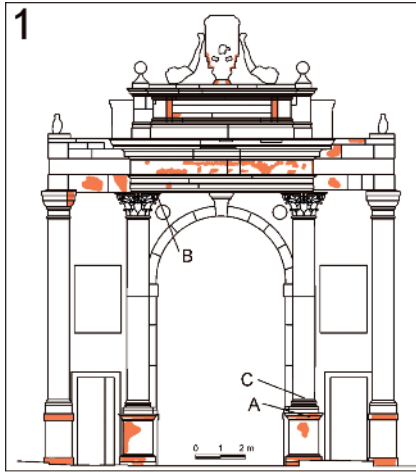
RESULTS

Deterioration morphologies

Differential deterioration

One of the peculiar characters of stone ashlars and other architectural elements used for the construction of Porta Nuova is that all surfaces are generally bush hammered, with the exception of the Marmor Troadense polished columns (cf. Attanasio, 2003). Despite this extensive care for the superficial finishing of stones, differential deterioration morphologies are widespread with a strict relation of cause and effect between textural and compositional characters of stone materials and connected deterioration.

One of the materials that suffered major deterioration is the Rosso Ammonitico Veronese limestone, which shows diffuse detachment of nodular portions. This kind of deterioration is less evident on vertical surfaces, whereas it is particularly enhanced on the projecting and finely finished elements (Fig. 2-1-A and Fig. 3-



A). The nodular structure represents an intrinsic property of this limestone and the presence of matrix between the nodules has favoured the detachment as a consequence of stress caused by cycles of freezing and thawing of interstitial water and sudden temperature changes. The nodular and inter-nodular portions present a different degree of compactness and cementation. Therefore humidity and chemical and biological agents while favouring the detachment of the first, easily crumble the latter. Differential deterioration is particularly enhanced also on Marmor Proconnesium above all on ashlar corners and on capitals, where the surficial decohesion with detachment of calcite crystals is associated to fractures penetrating the marble. The surface decay and erosion can also be appreciated on limestone “vacuolar” (Fig. 2-2-D and Fig. 3-D) where we assist to consumption of the cornucopias fruits.

Exfoliation is particularly enhanced on the Marmor Troadense columns (Fig. 2-1-C and Fig. 3-C), with formation of surface sub-parallel flakes, often followed by detachment of the exterior part and consequent reduction of the column diameter. The single fragments (flakes) show a series of inter- and intra-granular fractures. This kind of deterioration can be ascribed to different causes, among which thermal shocks (particularly in the sun exposed zones) and the rock processing (all the ornamental stones were carved perpendicularly to the surface, which favours the following detachment of flakes, cf. Lazzarini, 1987). Contour scaling can be also observed at the base of the Marmor Troadense columns. Here, maximum humidity and static load occur where the columns lean on the stylobate.

Black crusts

Another major deterioration morphology reported for Porta Nuova is the formation of cm-thick black crusts that cover the material surfaces and are mostly developed on the undercut surfaces protected by washing away rain (Fig. 3-B and Fig. 3-D).

XRD investigation has been carried out on black crusts detached by the cornucopias fruits carved in limestone “vacuolar” (Fig. 2-2-L9) and from the Rosso Ammonitico Veronese slab (Fig. 2-2-L14). The analysis of XRD spectra (Fig. 5) has revealed the presence for sample L9 of abundant gypsum associated to minor calcite and quartz and for sample L14 of abundant gypsum associated to calcite, quartz and traces of weddellite (bihydrated calcium oxalate).

Black crusts have also been investigated by SEM-EDS. Figure 4 reports BSE images of black crusts from the surface of the limestone “vacuolar” L5, Rosso Ammonitico Veronese L14 and Marmor Proconnesium L16. They are formed by an association of lamellar gypsum crystals perpendicular to the supporting surface. In the interstices between crystals are entrapped carbon particles, quartz-feldspar grains and pollen. Spherical empty particles of silica-alumina composition also occur (Fig. 4-L16), these being related to combustion processes in industrial plants (Del Monte & Sabbioni, 1983). The compositional spectrum of the black crust L14 shows that main components of gypsum (S and Ca) plus minor Si.

Coloured patinas

Yellow-greenish coloured, discontinuous films of patinas occur on the calcareous stones (Figs. 2-3) with higher frequency on Pietra d’Istria-

Fig. 2 (front page) - Schematic sketch of Porta Nuova front with the distribution of the main deterioration morphologies. 1- Differential deterioration. 2- Black crusts. 3- Oxalate films. 4- Rust spots. 5- Fracture systems. 6- Biological patina and vegetation. A, B, C, D, E, F, G, H location of the macrophotographs of figure 3. C1, C2, C3, C4 location of the specimens of Ca oxalates analyzed by XRD, figure 6. L9, L14 location of the specimens of black crusts analyzed in XRD, figure 5. L5, L14, L16 location of the specimens of black crusts analyzed by SEM-EDS microscopy, figure 4.

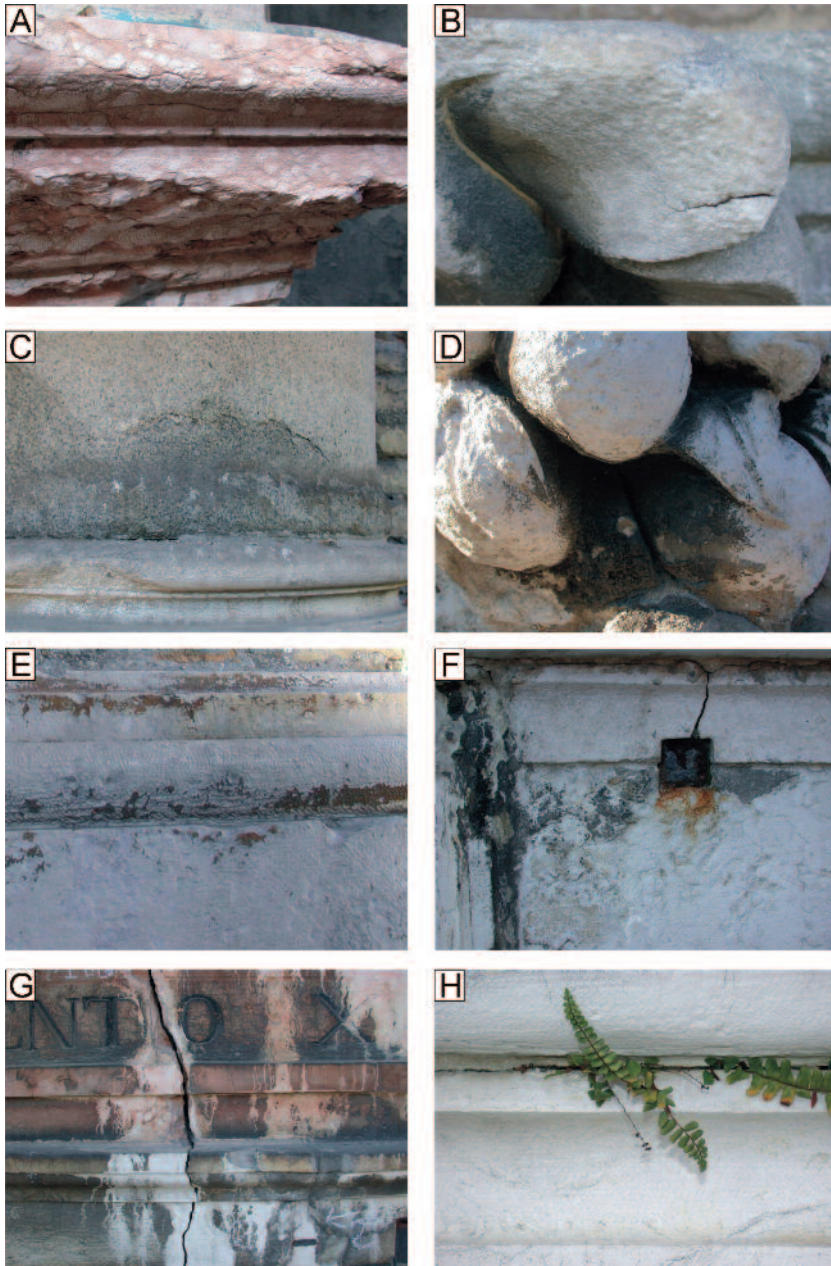


Fig. 3 - Macrophotographs of the main deterioration morphologies. Differential deterioration of Rosso Ammonitico Veronese (A), *Marmor Proconnesium* (B), *Marmor Troadense* (C), limestone "vacuolar" (D). Black crusts *Marmor Proconnesium* (B), limestone "vacuolar" (D). Oxalate films, limestone "facies liburnica" (E). Rust spots between Pietra d'Istria-Orsera and limestone "nodular" (F). Fracture systems along the Rosso Ammonitico Veronese and the Pietra d'Istria-Orsera (G). Vegetation (fern *Asplenium trichomanes*) between two elements of the limestone "facies liburnica" (H).

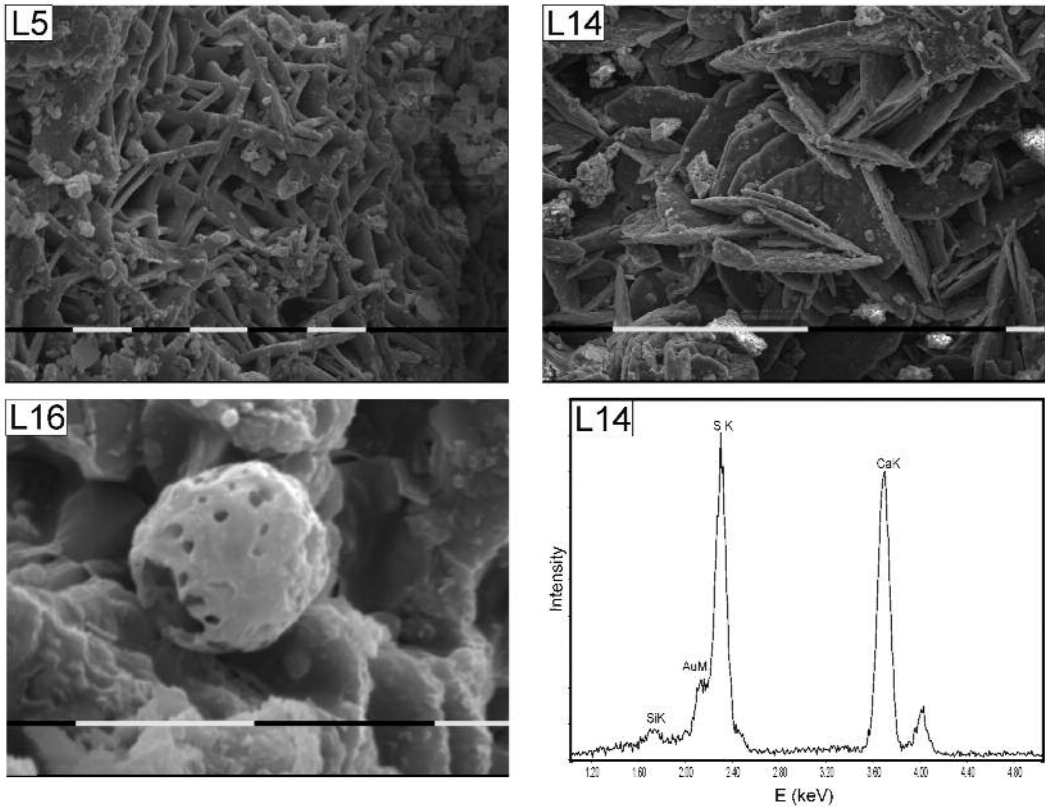


Fig. 4 - SEM-EDS images of black crusts developed on the surface of the limestone “vacuolar” L5, Rosso Ammonitico Veronese L14 and *Marmor Proconnesium* L16. Length of bar is 0.1 mm for the images L5 and L14 and 10 μm for the image L16. Compositional spectrum of the black crust L14. Au peak derives from sample coating.

Orsera and limestone “facies liburnica” (E). Some patina also occur in the higher part of the granite columns below the marble capitals. We noticed that black crusts cover most of the patinas. In order to assess the composition of the patinas, we performed XRD analyses reported in Figure 6. The patinas have been gently scraped from the stone surface trying to avoid the detachment of the black crusts and of the host material. Samples C1 and C3 come from the surface of the Pietra d’Istria-Orsera, sample C2 from the surface of the Rosso Ammonitico Veronese and sample C4 from the surface of limestone “facies liburnica”. We observe that in

all the investigated samples both whewellite (monohydrated calcium oxalate) and weddellite (bihydrated calcium oxalate) occur. Calcite occurs on some portions of the calcareous substratum, gypsum on the black crusts and quartz from solid particles.

Rust spots

Most of the slabs and architectonic elements of Porta Nuova are represented by recovered materials. (cf. Marocchi *et al.*, 2009), which during the centuries underwent several interventions of replacement, restoration and consolidation. During these interventions,

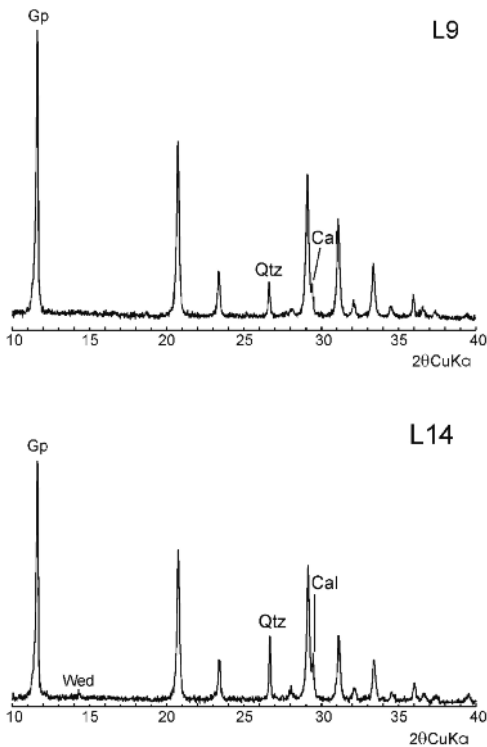


Fig. 5 - XRD patterns of the black crusts developed on the surface of limestone “vacuolar” L9 and of the Rosso Ammonitico Veronese L14. The main peaks corresponding to the identified minerals were labelled as follows. Gp: Gypsum; Cal: Calcite; Qtz: Quartz; Wed: Weddellite. Mineral abbreviations are after Kretz (1983) except Weddellite.

cramps, clamps and iron nails fixed by molten lead have often been employed. The oxidation of these elements has brought to the formation of iron oxides with consequent volume increase. Main consequences are stone fractures around swelled metallic elements and disfiguring rust spots often percolating below the rusty iron (Fig. 2-4 and Fig. 3-F).

Fracture systems

Porta Nuova was an access gate to Ravenna across the city walls. The railway “tramvai” was circulating under the Gate from the end of the

XIX century. The walls demolition, in the first half of the XX century, caused a loss of lateral supports. Vibrations and shocks produced by the movement of heavy goods vehicles, brought to fracturation of the main supporting elements of the Gate. The fracture system (Fig. 2-5 e Fig. 3-G) in turn led to a progressive subsidence and bending of both the arch and the architrave, yet overloaded by the overlying attic.

Biological patina and vegetation

On Porta Nuova stones has not been reported the occurrence of lyophilic lichens. Their disappearance has likely to be related to the air quality that in the historic centre of Ravenna is particularly polluted. The mapped weeds are represented almost exclusively by *Parietaria officinalis* L., whose roots grow within the joints of ashlar stones. The presence of the fern *Asplenium trichomanes* (Fig. 2-6 and Fig. 3-H) has also been detected. Green algae and moss have been observed in humid areas.

Structural investigations

The investigation carried out on Porta Nuova has not only documented the main deterioration morphologies of ornamental stones, but has also evidenced a severe condition of deterioration of the architectonic structure of the Gate. In particular, the decorative elements at the top of the Gate (court of arms and cornucopias) resulted to be extremely precarious and lacked supporting elements, whereas the lower entablature was severely fissured and bent in the centre.

A structural diagnosis of the monument has been therefore carried out. Ultrasound microseismicity and endoscopic tests have been employed for the Gate, whereas the georadar technique has been used to investigate the foundations.

The results outlined a situation of complex deterioration that affects not only the single materials but also the whole structure of the

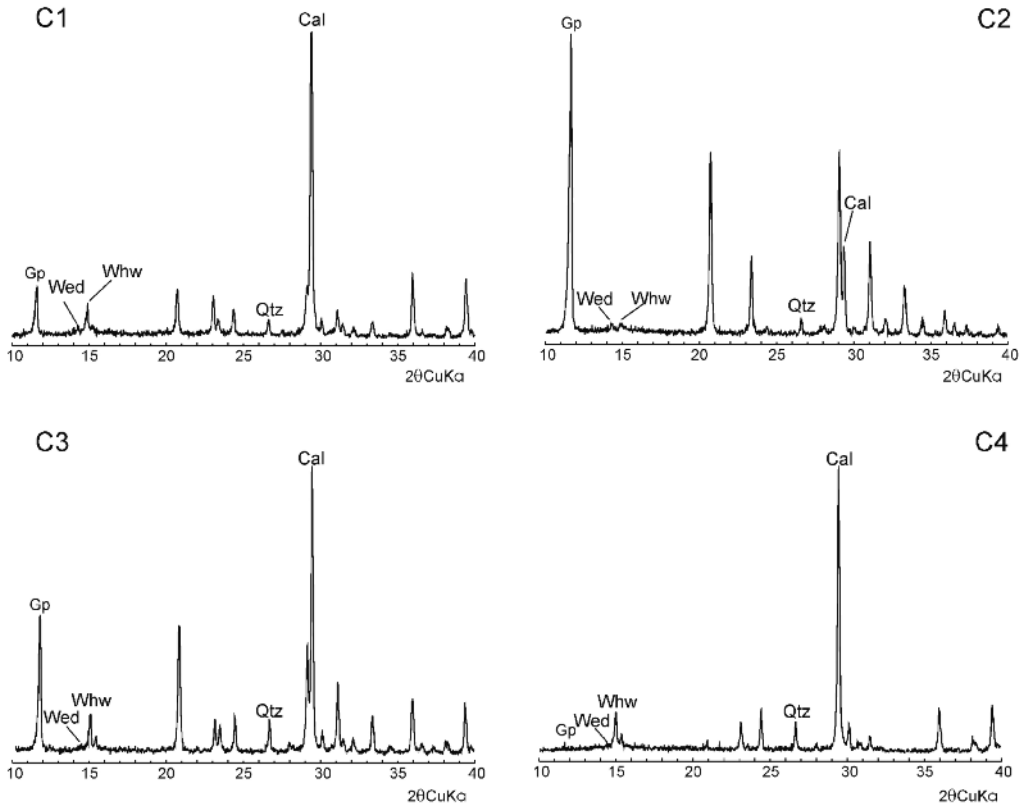


Fig. 6 - XRD patterns of the Ca-oxalates patinas developed on the surface of the Pietra d'Istria-Orsera C1, C3, of the Rosso Ammonitico Veronese C2 and of the limestone "facies liburnica" C4. The main peaks corresponding to the identified minerals were labelled as follows. Gp: Gypsum; Cal: Calcite; Qtz: Quartz; Wed: Weddellite; Whw: Whewellite. Mineral abbreviations are after Kretz (1983) except Weddellite and Whewellite.

Gate. In places, apparently without any direct connection, ashlar stones or pieces of walls show deep deterioration with discontinuities and fissurations. In other places, the walls look disconnected (Fig. 7).

The georadar profiles of the first 3-metre underground have shown in detail the good conditions of the foundations and their continuation at both sides of the Gate (Fig. 8).

DISCUSSION

The mineralogical-petrographic investigation allowed to characterise all the ornamental stones

employed in the Gate, to define their provenance (Marocchi *et al.*, 2009) and also to analyse the main deterioration morphologies. Such a combined approach represents a preliminary investigation prior to a proper restoration intervention and allows to better define the provenance of stone materials in case of stone elements substitution or integrations (Grillini *et al.*, 2010).

Moreover, the diagnostic approach has improved the knowledge of causes and mechanisms of deterioration, knowledge that can be extended to other similar case studies. Our results stress the importance of a diagnostic

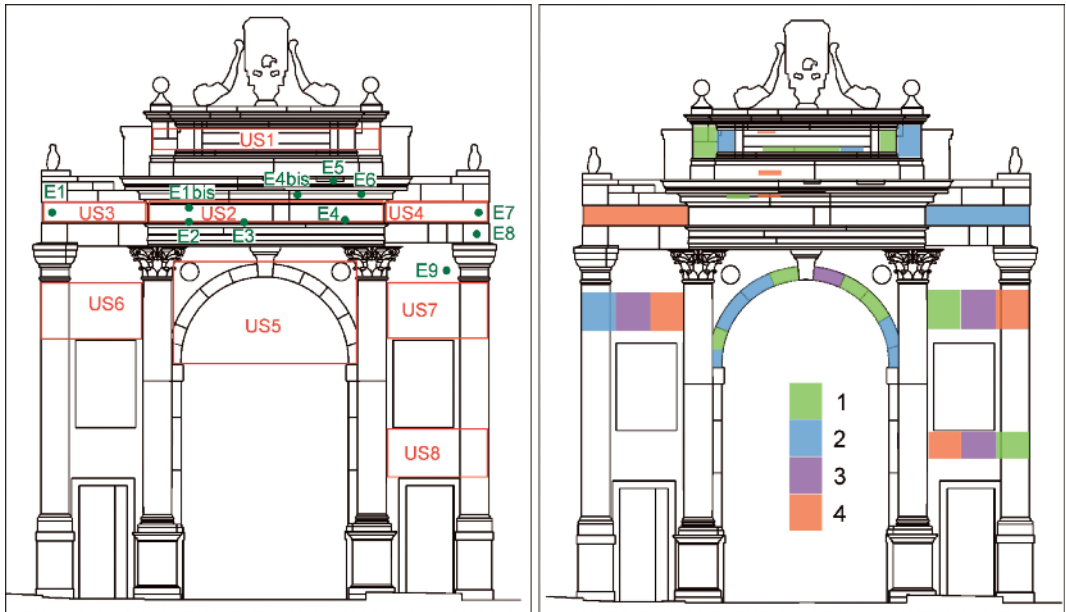


Fig. 7 - (A) Location of ashlar stones, dimension stones and hanging walls investigated with ultrasound microseismicity (US1-US8) and point of endoscopic inspections (E1-E9). (B) Results of ultrasound microseismicity: 1 good preservation state; 2 surficial deterioration; 3 surficial to deep deterioration; 4 deep deterioration.

study, which evidenced the necessity of a consolidation of detached stones and conservation treatments prior to the beginning of restoration works.

On the basis of the results presented above, different hypotheses concerning the nature of oxalate patinas have been formulated (cf. also Apollonia *et al.*, 1996; Rossi Manaresi *et al.*, 1989a, b; Lazzarini *et al.*, 2007) and will be discussed: i) chemical reaction with organic compounds which were commonly employed in the past centuries on the stones for aesthetic and/or conservative purposes (Amadori *et al.*, 1989; Rossi Manaresi *et al.*, 1989a, b); ii) atmospheric particles; iii) polishing of the marbles with compounds derived by plants containing oxalic acid; iv) biological activity by lithophytic lichens (Rossi Manaresi *et al.*, 1989a, b). Taking into account that the stone surfaces

are usually bush-hammered and rough, we can exclude hypothesis (iii). Since the oxalate patinas usually occur underneath the black crust, their origin by atmospheric particles (ii) is also unlikely. The most likely hypothesis seems to be the one related to a conservation treatment of the stone with organic matter (i), a common practice in the last centuries up to the beginning of the XX century (Rossi Manaresi *et al.*, 1989a, b). Such organic matter may have then undergone mineralization processes through the action of micro-organisms (cf. Lazzarini and Salvadori, 1989). The presence of the oxalate patinas may also be related to the action of micro-organisms such as lichens that are not present now but that may have disappeared due to air pollution. In the case of the Bab Agnaou gate in Marrakech, a comparable investigation of decay morphologies has been carried out (Lazzarini *et al.*, 2007). The

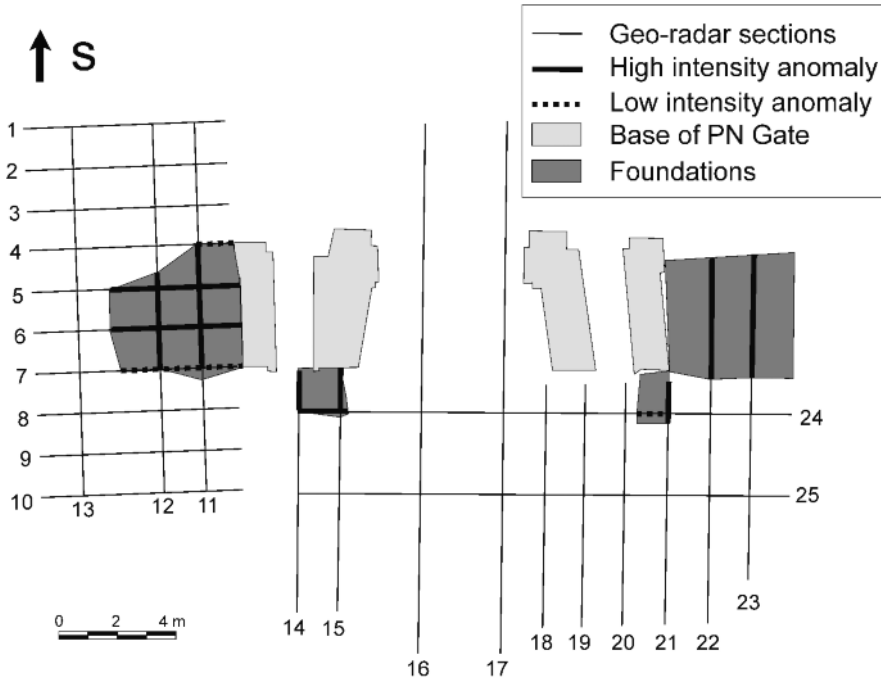


Fig. 8 - Location of georadar sections of the Porta Nuova area.

authors relate the origin of similar Ca-oxalate patinas to conservation treatments of the stone with organic matter. This hypothesis was strongly supported by the homogeneity of the distribution and aspect of the patina, and by the residual presence of animal glue.

Our results present a proposition of conservation treatments that are in agreement with recent works (Lazzarini *et al.*, 2007) and can be extended to other case studies. First of all, conservation treatments need preliminary laboratory analyses to find out the best materials for the type of stones used in the monuments. Then deteriorated stones should be in principle structurally consolidated with ethyl silicate, which can glue the loose particles and thin sheets of powdering and flaking stones. Where heavy flaking occurs, epoxy resins should be used to bridge together two parts of a flake. All these

treatments should be carried out prior to any further restoration in order to decrease the speed and intensity of deterioration phenomena affecting ornamental stones.

PRELIMINARY INTERVENTION

The preliminary intervention presented in this work has been limited to the consolidation and securing of fractured and detached stone elements that not only represent a damage of an historic monument, but may also be dangerous. The intervention is summarized as follows:

- i. Removal of weeding and treatment with biocides (benzalconioclorure at 3% and/or neoDesogen and Algophase) to inhibit the growing of vegetation and microflora (algae, moss, etc.);
- ii. Removal of old detached fillers, which have

been substituted by proper mortars made by Lafarge lime, powder of the same lithotype and a solution of acrylic resins (Primal AC 33);

- iii. Maintenance of the still efficient iron clamps by treatment with rust converter followed by iron-micaceous paint. The small cracks due to dilatation around clamps have also been filled with mortars made by lime, marble powder and a solution of acrylic resins. Moreover, the damaged clamps have been replaced by new ones in stainless steel or titanium, which bring as major advantages the minimum thermal dilatation compared to the marble, lightness and minor rigidity compared to iron;
- iv. Micro-injections within stones damage and fractures by epoxy resins (Araldite, Epoinj) to re-consolidate the latent stone material;
- v. Insertion of fibreglass pivots within fracture points of single elements and connection of detached elements to the walls by pivots and clamps and injection of low salinity hydraulic mortars;
- vi. The cracks of the walls were rejoined by employing mortars made by lime and fine to coarse-grained sand;
- vii. Consolidation of stone surfaces presenting decohesion and powdering of the material, by ethyl-silicate (Estel1000 Cts) applied with brush up to saturation.

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