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*

Mapping and characterization of stone materials and their alteration/deterioration products in the historical center of Palermo (Italy)

ROSARIO ALAIMO[1], ETTORE AZZARO[1], RENATO GIARRUSSO[2], PIETRO MARESCALCHI[3] and GIUSEPPE MONTANA[1]*

[1] Dipartimento di Chimica e Fisica della Terra ed Applicazioni alle Georisorse e ai Rischi Naturali (C.F.T.A.), Università di Palermo, Via Archirafi, 36, I-90123, Palermo, Italy
[2] CEPA s.r.l., Via Fonderia Oretea, 23 I-90139, Palermo, Italy
[3] Dipartimento di Rappresentazione, Università di Palermo, Viale delle Scienze, I-90100, Palermo, Italy

ABSTRACT. — In the last years, natural and man-made building materials from several important historical palaces and/or churches of Palermo (Italy) and their alteration/deterioration products started to be collected and analyzed.

In this paper are reported the relief and digital mapping of stone material's typology and conservation state of the Baroque palaces *Lungarini* (XVII century), *Alliata di Villafranca* (XVIII century), *Ugo delle Favare* (XVIII century) and the church of *Santa Maria dei Miracoli* (XVI century), all located in the historical center of the city. The results of mineralogical-petrographic analysis performed on the original building materials and their alteration/deterioration products are also discussed.

Graphic relief and materials mapping of the three Baroque palaces were realized starting from a classical graphic procedure which has been successively digitalized by means of standard commercial software. The main façade of the church of *Santa Maria dei Miracoli*, on the contrary, was relieved by the «total station» photogrammetric method, consisting of an electronic theodolite equipped with a laser-pointing diastimeter. Graphic restitution has been carried out via commercial software.

Mineralogical-petrographic analysis, XRD, thin section microscopy and SEM/EDS allowed to obtain the compositional and textural characterization of natural stones (Pleistocene biocalcarenite and Mesozoic well cemented limestone) and air lime plasters as well as their alteration/deterioration products. According to previous studies, the alteration/deterioration pathologies affecting both biocalcarenites and limestones are represented by brownish-blackish encrustations and sub-efflorescences of soluble salts (mainly gypsum and halite). Cyclic crystallization of soluble salts (mainly composed of magnesian sulphates such as epsomite, hexahydrite and kieserite) is the major cause of deterioration of air lime plasters. The predominance of magnesium sulphates is to be related to the widespread use of magnesian lime in the manufacture of Palermo's plasters from the XVII to the XIX century.

The acquisition of a thematic cartography relative to the most important natural or artificial building materials used in the monumental constructions of the historical center of Palermo supply a useful instrument for programming restoration interventions. The future realization of a database regarding compositions and mechanisms of degradation will concur to choose the best technologies and products.

RIASSUNTO. — Negli ultimi anni, i materiali lapidei naturali ed artificiali utilizzati nei più importanti edifici storici, civili e religiosi, di Palermo sono stati oggetto di una sistematica campagna di campionamento ed analisi.

Nella presente nota sono riportati i rilievi e le mappe digitali che riguardano la tipologia dei materiali lapidei ed il loro stato di conservazione, relativamente ai seguenti edifici: Palazzo *Lungarini* (XVII sec), *Alliata di Villafranca* (XVIII sec), *Ugo*

* Corresponding author, E-mail: gmontana@unipa.it

delle Favare (XVIII sec), chiesa di *Santa Maria dei Miracoli* (XVI sec). Vengono commentati i risultati delle indagini mineralogico-petrografiche effettuate sui materiali originali, finalizzate alla loro caratterizzazione ed alla identificazione dei prodotti di alterazione e degrado.

I rilievi e le mappature dei tre palazzi barocchi, sono stati realizzati a partire da una classica procedura grafica che è stata successivamente digitalizzata per mezzo di un software disponibile in commercio. Diversamente, per la rappresentazione del prospetto della chiesa di *Santa Maria dei Miracoli* è stato impiegato il metodo fotogrammetrico della "Stazione Totale" composta da un teodolite elettronico corredato di distanziometro a puntamento laser. La restituzione grafica anche in questo caso è stata ottenuta tramite l'utilizzo di un software commerciale.

Le analisi mineralogico–petrografiche, (XRD, microscopia ottica su sezione sottile, SEM/EDS) hanno consentito di caratterizzare, dal punto di vista composizionale e tessiturale, gli elementi lapidei, gli intonaci ed i loro prodotti d'alterazione. Conformemente a quanto ricavato da studi precedenti, le patologie degenerative che interessano sia le biocalcareniti che i calcari compatti si manifestano attraverso la formazione di incrostazioni bruno – nerastre e sub-efflorescenze di sali solubili (costituite principalmente da gesso e halite). La cristallizzazione ciclica di sali solubili (maggiormente rappresentati da solfati di magnesio quali epsomite, hexahydrite e kieserite) è la principale causa di degrado degli intonaci. In quest'ultimo caso, la presenza di solfati di magnesio è da porre in relazione al largo utilizzo di una calce magnesiaca per la realizzazione degli intonaci palermitani, soprattutto durante il periodo compreso tra il XVII e il XIX sec.

L'acquisizione di una cartografia tematica relativa ai più importanti materiali lapidei naturali ed artificiali impiegati negli edifici monumentali del centro storico di Palermo fornisce un utile strumento per la programmazione degli interventi di restauro. La futura realizzazione di una banca dati concernente composizioni e meccanismi di degrado concorrerà alla valutazione dei prodotti e tecnologie di restauro più idonei.

KEY WORDS: *Sicily; Palermo; building materials; alteration/deterioration; restoration; Archaeometry.*

INTRODUCTION

In the restoration of monumental buildings it is necessary to know in a comprehensive way the composition of the employed stone materials, their functionality in the architectonic structure as well as the state of conservation.

In the particular case of the recovery of the historical center of Palermo, the demand for a good scientific knowledge concerning natural and man-made building materials, traditionally used in the architectural practice of the past centuries, increased more and more. In fact, lacking of this kind of data in support of restoration projects has often induced to choose inadequate technological procedures, like as, for example, the use of integration materials or consolidating products scarcely compatible with the earliest stone substratum. It is well known that every kind of stone material has got a quite typical pattern of alteration/degradation (also depending on micro-environmental conditions) and it is therefore necessary to know in detail its nature to be aware of the mechanisms and provide for suitable restoration tests.

On the base of the above general considerations it has been made active, since a few years, an organic and systematic study of the building materials used in the historical architecture of Palermo, in order to obtain:

– mineralogical, petrographic, chemical and petro-physical characterization of numerous varieties of lower Pleistocene biocalcarenite cropping out in the Palermo's surroundings, whose utilization is documented in several buildings of great historical-artistic relief (Alaimo *et al.*, 1998);

– review of lime production techniques in the old city area during past centuries (Montana, 1997-a);

– mineralogical, petrographic and chemical characterization of mortars and plasters collected from monumental buildings of the historical center (Alaimo *et al.*, 2000-b);

– mineralogical, petrographic and chemical

characterization of decorative stucco-works in several Baroque oratories and churches (Montana, 1997-b; Montana and Ronca 2001).

The present contribution concerns with the compositional characterization of natural and man-made building materials as well as the products of alteration/degradation which have been identified in the main façades of three important Baroque palaces and a church, all located in the historical center of Palermo:

– *Ugo delle Favare* palace dates back to the first years of the XVII century. The main gate as well as the lateral ones with polygonal arch are decorated with mythological figures realized in manneristic style.

– *Lungarini* Palace was built up towards the half of XVII the century The wall surface is coated by two different layers of plaster. The most recent can be dated back to the XVIII century; it covers an older layer (XVII century) which is decorated with a painted «diamond» ashlar-work.

– In its current appearance the *Alliata di Villafranca* palace goes back to 1753, due to the transformations that became necessary after the 1751 earthquake, which produced notable damages to the original structure (La Duca, 1994; Chirco, 1996). Its wall structure is covered by two layers of plaster respectively manufactured in the XVII and XVIII century. Both the two gates are decorated with monolithic limestone columns and stucco medallions of valuable workmanship.

– The church of *Santa Maria dei Miracoli* was founded in 1547. Within a Renaissance outline the main façade (constituted of porous calcarenite) introduces several successive elements in Baroque style.

This study is also expected to acquire preliminary information on the frequency of employment of original lithotypes in the historical center of Palermo and it comprises a first attempt of realization of a thematic cartography concerning with the monumental buildings of the city.

METHODS, TECNIQUES AND SAMPLING

Mineralogical-petrographic analysis

Mineralogical and petrographic characterization of the collected materials and of their alteration/deterioration forms has been carried out according to Normal ICR/CNR 10/82, 12/83, 14/83, 16/84 and 23/86 recommendations. All the samples were initially studied by visible light microscopy. Plaster samples have been preventively impregnated with epoxy resin under vacuum, in order to realize polished cross sections and thin sections suitable for the study of stratigraphy. Abundance of aggregate components has been estimated by routine quantitative point counting procedures. X-ray powder analyses (XRD) were carried out with a Rigaku D/max IIIc diffractometer (CuKa 40 KV, 20 mA, graphite monochromator). SEM/EDS analysis has been performed on carbon-coated samples by a Leica Stereoscan 440 (Link Isis Oxford Instruments, Pentafet Si-Ge detector), using both secondary electron (SE) and back-scattered electron (BSE) imaging mode.

Relief of the façades

For the representation of the façade of the *Santa Maria dei Miracoli* church it has been employed the method of the photogrammetric relief, by an instrumentation composed of an electronic theodolite equipped with a laser-pointing diastimeter. The theodolite was also provided with a display that supplies data according to Cartesian coordinates. This «total station» methodology makes available the selection of points of the façade as well as the measurement of the angle between the line of view and the optical axis of the instrumentation. The sequence of measurement can be summarized as follow: 1) photogrammetric relief and reading of the data; 2) photographic survey of the prospect of the church by means of *Rollei metric* instrumentation (semi-metric, with calibrated lens and precision micro-grooving); 3) Roto-translation of the relieved points; 4) image

flattening (correction of the distortion); 5) C.A.D. plotting; 6) mapping of natural and man-made materials and alteration/degradation forms.

Graphic relief and materials mapping of the three Baroque palaces were realized starting from a classical graphic procedure which has been successively digitalized by means of standard commercial software.

Sampling

Up to 26 samples considered fully representative of the employed natural and man-made materials and of the most diffused alteration/degradation products have been collected from the main façades of the previously cited monumental buildings in order to be characterized by mineralogical-petrographic methods.

RESULTS AND DISCUSSION

Mapping of facades: employed materials and their conservation state

The three Baroque palaces resulted characterized by the employ of the similar building materials. Figures 1a and 1b show, as example, the digitalized relieves referred to *Lungarini* and *Alliata di Villafranca* palaces. The load-bearing walls are composed of squared blocks of the local porous Pleistocene biocalcarenite. They show only slight macroscopic differences, from place to place, which can be easily explained considering the use of the same lithotype although exploited in different quarries of Palermo's territory. The wall structure is constantly covered by one or two layers of plaster, whitish or light pinkish in color. The biocalcarenite is in full sight only in the balcony where constitutes brackets, members and various decorative sculptures. Monolithic columns decorating the main gate and their plinths are manufactured, in most of the cases, with a local hard gray limestone (breccias) of Mesozoic age, locally named *pietra di Billiemi*. More or less recent integrations made by bricks and cement also occur.

The forms of alteration/degradation affecting the studied monumental buildings have been mapped and described on the basis of the recommendation ICR/CNR Normal 1/88. The most important and diffuse are:

– *black crusts*: are mostly concentrated on the surfaces of the building repaired from the washing-action of rain waters (fig. 2a). They show variable thickness and morphologic characteristics according to the nature of the stone to which they adhere tenaciously. When spontaneously detached the substratum appears to be strongly disaggregated.

– *brownish-blackish films*: show small thickness and preferentially develop on compact materials (fig. 2b). They can be removed from the substratum which generally remains integral.

– *biological patinas*: are thin, soft and homogenous, adherent to the stone surface, with color from dark green to blackish.

– *differential degradation*: is in close relationship with the compositional or textural heterogeneity of the building material, resulting particularly evident in the calcarenite (fig. 2c).

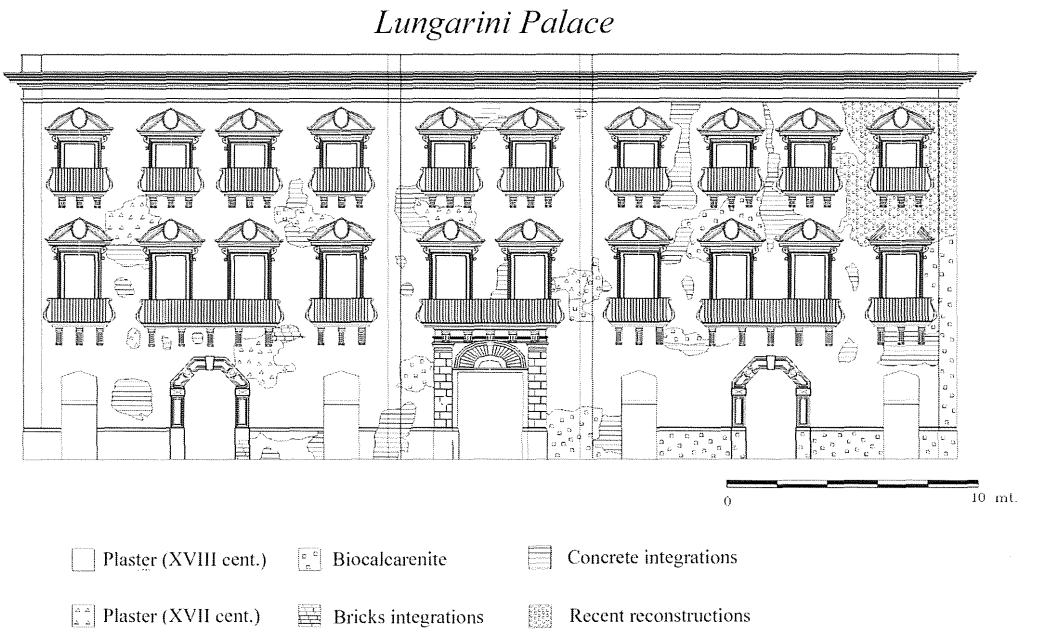
– *decohesion*: manifests itself by the separation of grains under minimal mechanical solicitations.

– *pulverization*: is represented by the spontaneous fall of powdered material or grains.

– *erosion*: mechanical removal of material from the surface due to various processes.

– *gaps*: are due to loss of parts of the surface plaster which brings to light the inner stone substratum (fig. 2d).

The main prospect of the church of *Santa Maria dei Miracoli* has been realized with a whitish Pleistocene biocalcarenite, very probably exploited in the north zone of Palermo. The whole façade is covered by an ocher film. The decorative elements are also made of calcarenite, with the exception for a coat of arms realized in marble (fig. 3). It has to be noticed that the upper part of the building has been realized in a successive age (XVIII



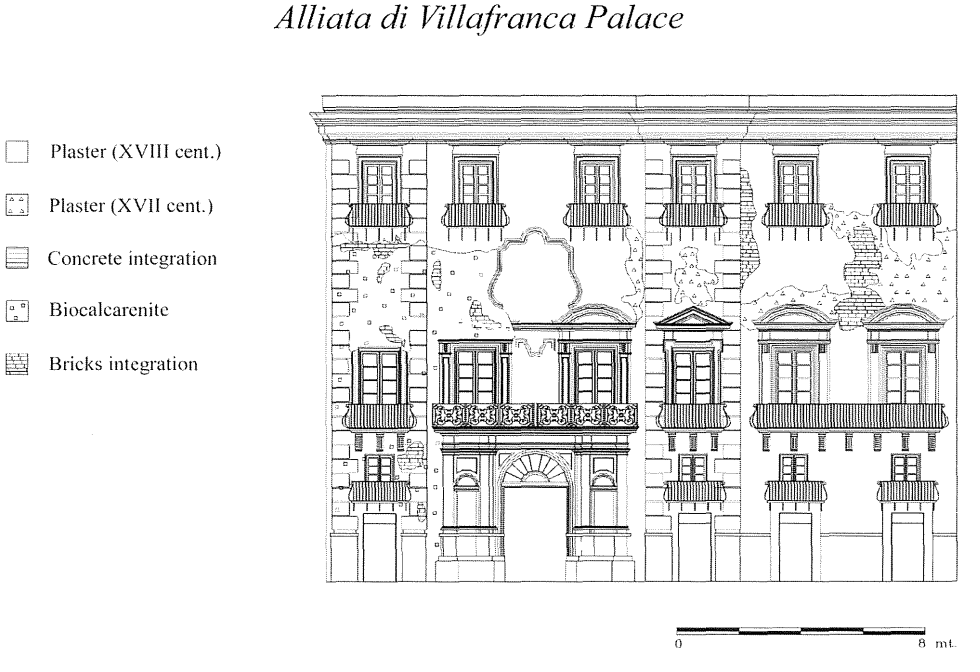


Fig. 1 – Mapping of natural and man-made building materials employed in the main façades of *Lungarini* and *Alliata di Villafranca* palaces.

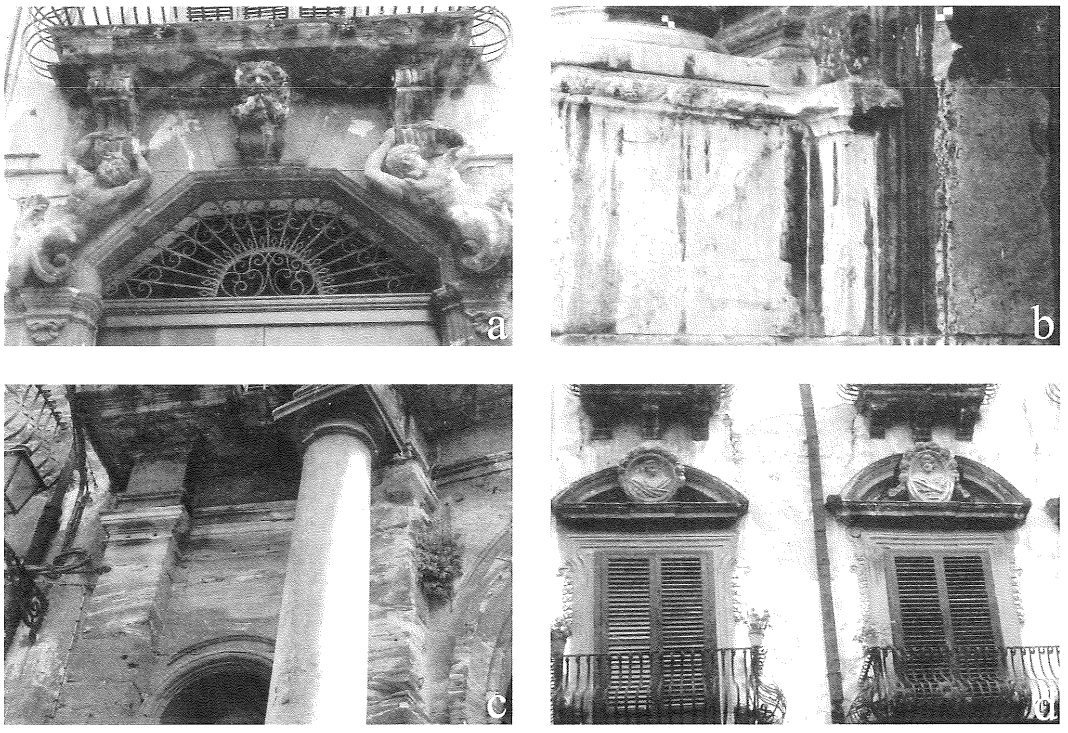


Fig. 2 – (a) *Ugo delle Favare* palace (XVII century): soluble salt efflorescences and black crusts; (b) *Alliata di Villafranca* palace (XVIII century) brownish-black films on *Billiemi* limestone; (c) *Alliata di Villafranca* palace (XVIII century) examples of black crusts and differential degradation in the biocalcarenite; (d) *Lungarini* Palace: detachment of the XVIII century plaster bringing to light the older one (XVII century) decorated with a painted «diamond» ashlar-work.

century) and probably the used calcarenite should be of different type from the one used in the lower order. Unfortunately this aspect, at present, cannot be supported by laboratory analysis due to difficulty of sampling.

In this building, from the examination of the state of the defects emerges a general picture in which the hardest degradations are related to humidity (capillary infiltrations) and therefore to the formation of soluble salts, as well as to environmental pollution and biological factors. Recognition of the defects by the photogrammetric relief has been processed in a graphical table according to the recommendation ICR/CNR Normal 1/88, allowing an immediate and synchronic reading (fig. 4). In general, most of the pathologies are very similar to those already described for the baroque palaces. Nevertheless, some others alteration/degradation forms have been noted:

– *patina*: all the wall surface of the main façade is covered by an ocher patina which alters the original color of the stone material. This is evident in the parts subjected to washing processes, in which it can be noted the original color of the stone;

– *loss of material*: it occurs in some parts of the façade, mainly in those jutting out of the cornices and moldings of the columns;

– *washing-effect*: Draining of rain water from the cornices and the protruding parts causes the washing away of the ocher coloring in the wall surface;

– *efflorescences*: this expression of degradation is caused by the evaporation of the water which permeates the squared blocks of

Fig. 3 – Image of the main façade of the church of *Santa Maria dei Miracoli* (XVI century) showing the different types of biocalcarenite (upper and lower orders) and the ocher film.

Fig. 4 – Graphic restitution of the photogrammetic relief of the church of *Santa Maria dei Miracoli* showing the state of defects.

biocalcarenite, with consequent crystallization of salts towards the external surface; it is found in some zones under the cornice of the architrave, over the two pilasters and in the frame of the left window.

Natural stones: notes on traditional use and compositional characteristics

The *Pleistocene biocalcarenite*, in antiquity named *Kiddan* by Arab conquerors (that is to say «golden stone»), is the most used building material in the monumental architecture of Palermo and of the whole western Sicily. This extensive employment strongly depended on the trouble-free quarrying and shaping of the lithotype as well as on the large distribution of its outcrops, generally located along the coastal areas. In the plain of Palermo these porous rocks, with a thickness of 20-30 m, cover by unconformity Mesozoic limestone and dolostones as well as tertiary flyschoid deposits (Caflisch, 1966; Ruggieri, 1973). Their peculiar depositional process is clearly responsible for the variability in color, grain size, degree of cementation, abundance of detrital accessory minerals and rock fragments. The heterogeneity of the textural, structural and, in some extent, compositional characteristics is sometimes found even in the same quarry, both laterally or vertically along the stratigraphic sequence. Different qualities of building stone were therefore exploited to be adapted to the various architectural employs. In the urban Palermo, at present days, are rarely visible the remains of ancient quarries which actually were dozens and dozens (Cipolla, 1929; La Duca, 1964; Todaro, 1988; Alaimo *et al.*, 1998; Montana and Scaduto, 1999). Since the first half of the XVI century started the exploitation of the areas located in the extra urban territory which continued unceasingly until the first decades of the XX century. The first phase of cultivation of a calcarenite quarry generally took place by means of underground galleries (or *mucate*, according to the Arabic denomination) in order to go after the productive rock-layers. Then, this system of exploitation was followed by cultivation under the open sky, which allowed lower costs and material waste (Todaro, 1988). The lands to be exploited were subdivided in smaller fields of rectangular shape, whose traces are still visible in the territory (fig. 5). Mining and the shaping of the blocks were carried out during summer in order to allow the porous stone to naturally dry. The squared blocks were usually left exposed two years to the atmospheric agents for being able to recognize and discard the most vulnerable ones (Cipolla, 1929).

As already seen in the previous paragraph, in the four studied monumental buildings, the local biocalcarenite constitutes by far the most representative lithotype, used both for the prospects and for ornamental elements. Nevertheless, the presence of diffuse black incrustations or films and patinas interfere with the appraisal of the macroscopic differences (color, degree of cohesion and prevailing grain size) between the stone's variety used in the walls and the one employed in the carved parts.

After the observation of thin sections under the polarizing microscope, the calcarenites used in *Lungarini* palace, *Ugo delle Favare* palace and in the church of *S. Maria dei Miracoli* are all classifiable as *grainstone* (Dunham, 1962). They showed quite comparable compositional and textural features, (fig. 6). The mean/prevalent grain size ranges between 0,4 mm (*Lungarini* palace) and 1,0 mm (*Ugo delle Favare*); maximum grain size is comprised between 1,0 mm (*S. Maria dei Miracoli*) and 3,0 mm (*Ugo delle Favare*). Concerning with the bioclasts, in these varieties, the fragments of calcareous algae resulted always prevailing, followed by relatively less quantities of foraminifera, lamellibranch, bryozoan and echinoderms; fragments of algae are often impregnated of iron oxides which are responsible of the slight yellowish color of the stone. Detrital minerals/lithoclasts resulted quite sporadic, represented by Mesozoic limestones, dolostones, with micritic or microsparitic structure and mono-crystalline quartz. Primary fine grained matrix (micrite mixed with clay minerals) is poorly represented (only scarce

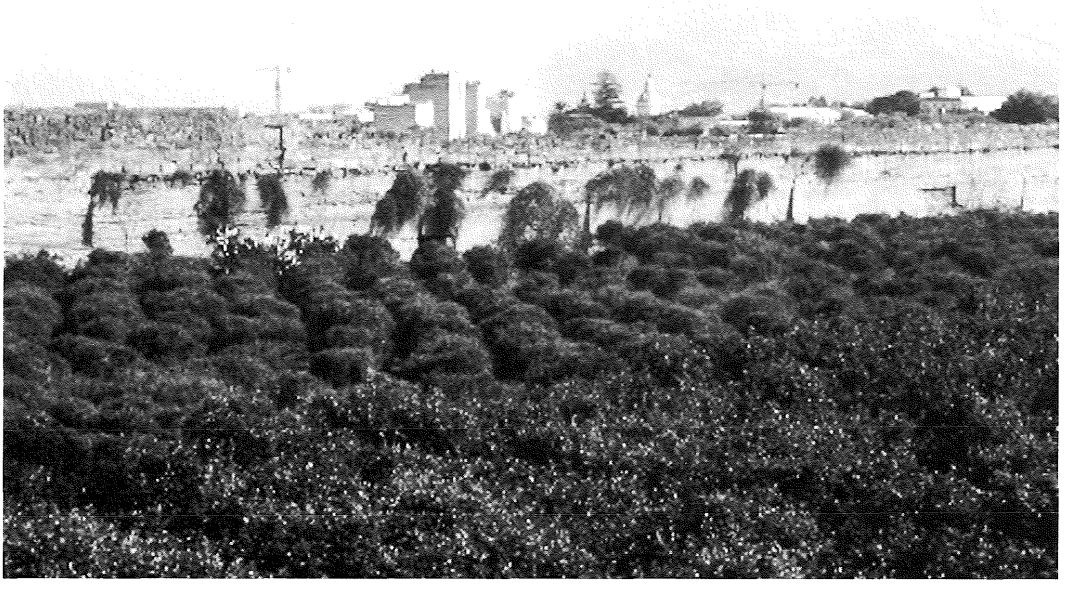


Fig. 5 – View of the remains an ancient quarry of biocalcarenite in the surroundings of Palermo (*Aspra*).

residues enclosing or filling the spaces between the larger particles). An interstitial cement made of sparry calcite is relatively more abundant even though it cannot be considered copious. It is also characterized by crystals showing the typical acute scalenohedral form and by small druse aggregate, filling the larger pore spaces. The total macroporosity has been valued to be around the 20%. Intergranular pores deriving from the selective dissolution of original bioclasts are prevalent. The walls of the pores often result covered by a thin layer of micrite.

This composition has been confirmed by the powder XRD patterns which showed the clear predominance of calcite with only small quantities or trace of dolomite, quartz and clay minerals.

The variety of biocalcarenite used in the main façade of *Alliata di Villafranca* palace resulted quite different. It can be classified as *packestone* (after Dunham, 1962). Therefore, the microcrystalline primary matrix is relatively more abundant with respect of the above described varieties (fig. 7). The prevalent grain size has been recognized around 0,2 mm (fine sand). Moreover, it is richer in detrital minerals/lithoclasts like limestone fragments, mono-crystalline quartz and chert grains, up to 10% (area).

Finally, some words should be spent about the well cemented and hard *Mesozoic limestone*, locally named *grigio di Billiemi*, which has been often used for plinths and columns. It belongs to the lower Lias - upper Trias and crops out in the mounts surrounding Palermo toward south. It is characterized by a rich fossil fauna and a dark gray color with plagues of fine black or yellowish material (fig. 8). Whitish calcite veins and concretions are also frequent. The more famous and appreciated variety, above all in baroque age,

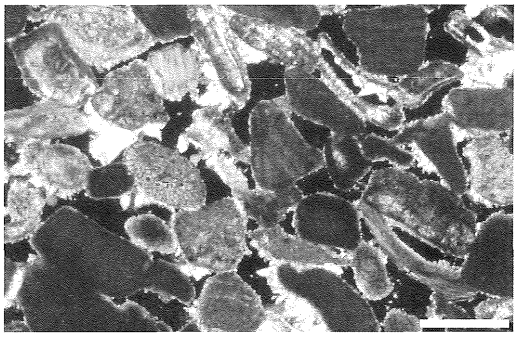


Fig. 6 – Polarizing microscope image of the biocalcarenite type used in the façade of *Lungarini* palace (crossed nicol; scale bar = 0,3 mm).

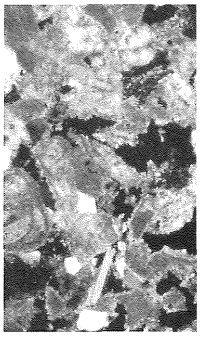


Fig. 7 – Polarizing mi type used in the façad (crossed nicol; scale b

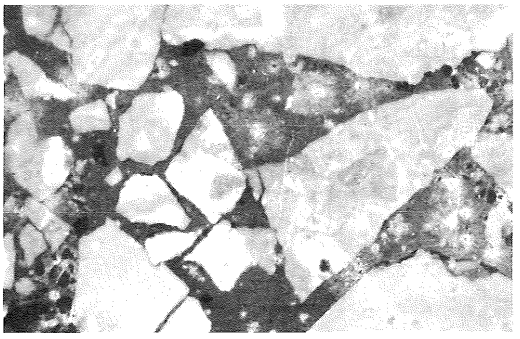


Fig. 8 – Macroscopic appearance of the brecciated variety of the *Billiemi* gray limestone.

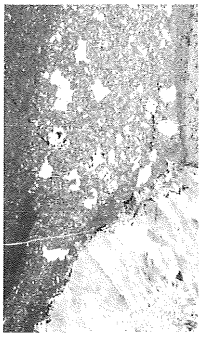


Fig. 9 – Transmitted variety of the *Billiemi*

shows a typical brecciated texture, constituted of elements with variable dimensions from a centimeter to various decimeters (fig. 9). The particular durableness and resistance to the atmospheric agents, if considered together with the nice appearance (in the several tonalities of gray) and, above all, the thickness of the strata which favored the exploitation of enormous monolithic blocks, have privileged the extraordinary diffusion of this lithotype in the building practice (specially as decorative stone) of Palermo in the past centuries (G. Montana & V. Gagliardo Briuccia, 1998).

Plasters: local tradition, raw materials and composition

X-ray diffraction, optical microscopy and SEM/EDS analyses allowed to define the nature of sand a studied plaster composition sati already determi buildings of Pale The same sequenc observed in the which resulted p more ancient la composed by an stone substratum around 10 mm, abundant and poo 60%); it follows a of thickness) con aggregate (40-60% sorted, with mediu mm); the sequenc

level (1-2 mm), containing a relatively smaller amount (< 5-20%) of fine aggregate grains (< 0.2 mm). Only few compositional differences have been established between plasters manufactured in the XVII and XVIII century. All the analyzed samples showed a similar composition of the sandy aggregate. In general, a slight predominance of siliceous materials (up to 50-65 % of total aggregate) has bee noted with respect to components of carbonate nature (45-50%). The siliceous constituents are: policrystalline and mono quartz (prevailing), chert, feldspar, quartzarenite and radiolarite grains (fig. 10b and fig. 10c). Sporadically fragments of powdered pottery have also been noted. The carbonate components are lithoclasts deriving from the Pleistocene biocalcarenite as well as Mesozoic limestones and dolostones. Even as regards composition of the binder matrix strong analogies between plaster manufactured in different ages can be pointed out. By X-ray patterns and SEM/EDS imaging is evident that a magnesium-rich lime has been used (fig. 10d). It has been clearly manufactured from the calcination of magnesian carbonate rocks (both dolomites and dolomitic limestones), is characterized by the presence, together with calcite, of magnesite and, secondarily, hydromagnesite. Brucite-composed white clots have been frequently observed (up to several millimeters in size), which are consistent with a bad carbonation. In fact a magnesium rich carbonate rocks if heated at about 900 °C, will produce CaO together with MgO, the most part of which is sintered. In this case, the hydration reaction (in the course of lime slaking) takes place with lower efficiency in comparison with pure CaO.

The comparison of the mineralogical-petrographic data with the lithology of the rocks cropping out in the surroundings of Palermo and the consultation of ancient manuscripts, books and notarial acts, let to deduce the exploitation areas of raw materials. The composition of the aggregate essentially reflects the contribute of the *Numidian Flysch* formation (Upper Oligocene-Lower Miocene) as regards siliceous fragments, while the calcareous component derives from Mesozoic relieves and Pleistocene biocalcarenites. Sand aggregate compositional sorting put forward a fluvial sand, therefore the supplying sites should be chosen between the watercourses of the Palermo surroundings whose drainage basins draw on the above mentioned geological formations. In a notarial act dated back to the 1654 is evidently requested that the sand for making up the plaster must come from the *Sperone*, a locality along the shoreline which three centuries ago was only about 3 kilometers far from the city walls. However, the final stretch of the *Oreto*, another stream nearby the old walls of Palermo, should be considered as sand supplying site.

As regard the binder, its composition is consistent with the Mesozoic dolostones (*Fanusi* formation) widely cropping out in the relieves which surround the western side of the city. Moreover, chemical analysis of this rock (Montana, 1997-a) demonstrate a very low concentration of SiO_2 and Al_2O_3 (both around 0.2 wt%) and, consequently, an hydraulic index (weight % $SiO_2+Al_2O_3+Fe_2O_3/CaO + MgO$) even lower than 0.1, therefore appropriate for an air lime binder. In these lands, which in time past belonged to the Benedictine abbey of *S. Martino*, it developed a widespread craft production of lime. Ruins of several ancient lime kilns are still visible and dozens of original documents, notarial acts of the 17th and 18th centuries expressly require the *«Santo Martino»* lime for the manufacture of plasters, mortars and stucco works (Montana, 1997-a).

Alteration/degradation products

Precipitation affects stone primarily in two ways: dissolution and alteration. In exposed areas of the buildings roughened surfaces can bee observed, due to removal of material and loss of carved details. The alteration/deterioration pathology affecting both the described biocalcarenite and limestones consists of brownish-blackish encrustations and films. Both showed a similar mineralogical composition: calcite and gypsum

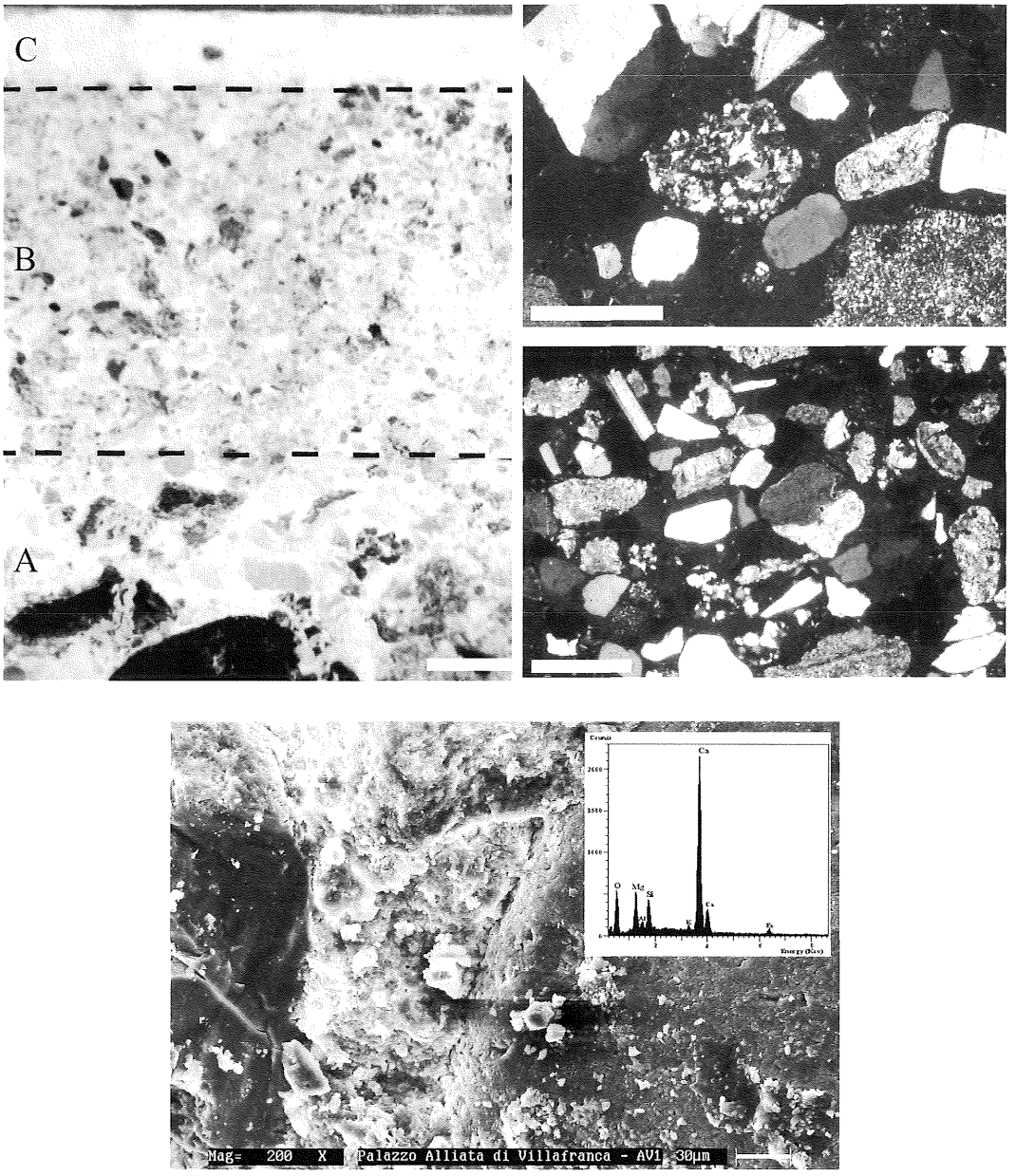


Fig. 10 – (a) Reflected light micrograph of the XVIII century plaster from Lungarini palace showing a typical stratigraphy sequence composed of three layers: (A) inner and coarser level; (B) intermediate level; (C) thinner finishing level (scale bar = 2.0 mm); (b) polarizing microscope image of the inner layer of the XVIII century plaster (crossed nicol; scale bar = 0.6 mm); (c) polarizing microscope image of the intermediate layer of the XVIII century plaster (crossed nicol; scale bar = 0.5 mm); (d) SEM micrograph of the XVIII century plaster from Alliata di Villafranca palace showing the adherence of the binder to the aggregate grains; qualitative chemical composition carried out by EDS point analysis (upper right) is referred to the binder matrix.

turned out to be the most representative phases by XRD and SEM/EDS analyses. This black crust, although it can form anywhere on exposed carbonate stone surfaces; nevertheless, it only remains on protected surfaces which are not directly washed out by rain-water. Gypsum crystals form networks that trap particles of dirt and pollutants, so the crust looks black. Sooner or later the black crusts swell up and the crumbled stone become exposed. SEM investigations revealed some ultra-structural differences between the outer and the inner parts of the crusts. In the latter single grains are coalescing and porosity is reduced, while in the external part, where particulate matter deposits prevails, the aggregate is always more porous and, specially in the thickest black crusts, it is heterogranular. Soluble salt, such as gypsum and halite (the latter deriving from marine aerosols) are mainly present in sub-efflorescences (fig. 11). Their cyclic growth, carried by humidity and water migration in pores space produce a strong disaggregating effect. They preferentially form under the cornices which are subjected to stagnation and evaporation of water infiltrating from the upper part. Sometimes alkaline soluble salts may form due to the use of incompatible recent integration materials (*Portland* cement based mortars).

Intergranular decohesion due to the crystallization of soluble salts inside pores is the main deterioration effect in the studied plasters. In some cases the effects of degradation are particularly heavy and interest the entire stratigraphic sequence, above all in the lower parts of the masonry (capillary action). The water imprisoned in the porous stone substratum migrates more slowly towards the outside due to the smaller permeability of the plaster, favoring soluble salt crystallization and, consequently, deterioration phenomena (detachments). XRD and SEM/EDS analyses established what has been already seen on other

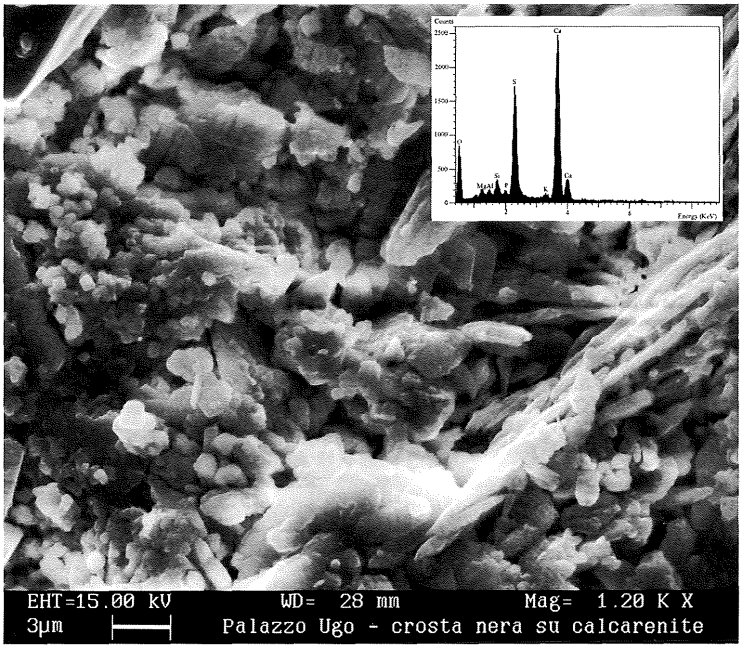


Fig. 11 – SEM micrograph of the black crust developed on the biocalcarenite from *Ugo delle Favare* palace; EDS area analysis is also showed (upper right).

external plaster samples collected from others historical buildings of Palermo (Alaimo *et al.*, 2000-b). Magnesium sulphates (epsomite, hexahydrite and kieserite), calcium sulfate (gypsum) and sodium chloride (halite) are the predominant mineralogical phases (fig. 12). Gypsum seems to slightly prevail in respect with magnesium sulphates in the sub-efflorescences. The process which originate such a deterioration effect starts from the deposition of atmospheric particulate matter and sea spray on the external wall surface covered of plaster. As well known, either acid pollutants or salts become chemically reactive when in contact with precipitation and/or condensation waters. The main effect are dissolution and sulphation of the calcareous binder matrix as well as formation of soluble salts efflorescence and subefflorescence. It should be emphasized that, in the specific case of Palermo, the source of sulphate ions seems to be only to a lesser extent of anthropogenic origin (e.g. emission of SO_2) but has to be related to the great influence of sea spray and to windborne gypsum particles carried by the southern winds (Alaimo *et al.*, 1989). The predominance of magnesium sulphates is to be related to the widespread use of magnesian lime in the manufacture of Palermo's plasters from the XVII to the XIX century, as already underlined. In fact, $[SO_4]^{2-}$ enriched percolation water reacting with magnesium carbonate in the binder matrix are liable to precipitate calcite and soluble magnesium sulphates (solubility of epsomite = 720 g/l at 20°C). In fact calcite is by far less soluble than magnesite, respectively 0,014 g/l (20°C) and 0,11 g/l.

CONCLUSIVE REMARKS

Acquisition of data on the natural or artificial building materials used in the monumental constructions of the historical center of

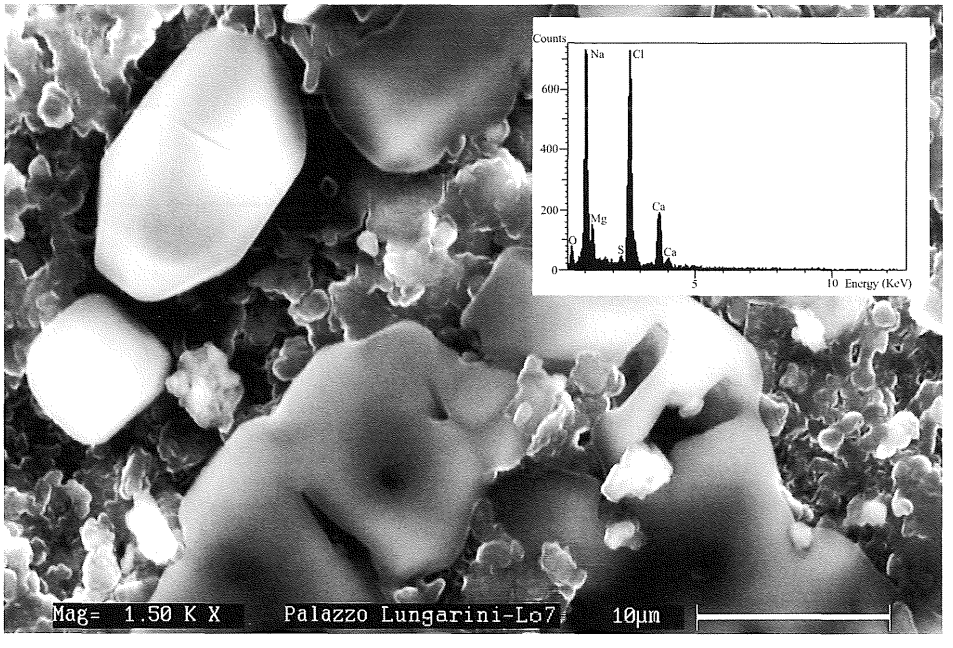


Fig. 12 - SEM micrograph showing deliquescent crystals of NaCl (halite) growth in the binder matrix (composed of magnesite and calcite) of the XVIII century plaster collected from the façade of *Lungarini* palace; EDS area analysis is showed in the upper right part of the image.

Palermo with the relief of the state of conservation and a thematic cartography relative to the most important prospects, is expected to supply a useful instrument for programming restorations. The realization of a database regarding the compositional characteristics and types of degradation of used building materials in the architecture practice of the ancient city would concur to the planning of restoration interventions, with technologies and products custom-made for the specific requirements. At the same time, the study of the mechanisms of alteration/ degradation, for every single case study, has the scope to adjust the research towards specific procedures and materials to be used for substitutions, integrations or reconstructions.

Like already pointed out in the introduction, one of the more arduous problems to solve in the course of the planning of an architectonic restoration consists in the quantitative definition of the «compatibility» between the original materials and those to be used in the integrations. In some cases, the choice of products technologically considered in the forefront, which are not, however (in the specific case), the most suitable ones, might seriously compromise the restoration intervention (especially in terms of duration) and also cause worsening. In the cases studied, concerning with the historical center of Palermo, it has been shown that the stone substratum on which the most ancient layers of plaster adhere, it is constituted of the local biocalcarenite. This rock type generally possesses a very elevated open-porosity, ranging from the 25% to beyond 40% (Alaimo *et al.*, 2000-c). Being Palermo a coastal city with a temperate humid climate and characterized by an intense vehicular traffic, problems associated with soluble salts deposition and migration (essentially alkaline/earth-alkaline sulfates and sodium chloride), should be checked, specially in presence of such a porous lithic substratum.

Therefore, the possibility to determine the petrographic and physical characteristics of natural and man-made building materials as well as to replicate the receipts of to ancient plaster and, if it is the case, improve them in the light of current knowledge, it seems to assume a great importance in the safeguard of cultural heritage.

ACKNOWLEDGMENTS

This research has been financially supported by 1999 MURST-Cofin grant.

REFERENCES

ALAIMO R., DEGANELLO S., DI FRANCO L. and MONTANA G. (1989) — *Caratteristiche composizionali del particolato solido atmosferico e chimismo delle acque di precipitazione nell'area urbana di Palermo.* In «proceedings of the 1st International Symposium *The Conservation of Monuments in the Mediterranean basin*», Bari 7-10 Giugno 1989, F. Zezza ed., 369-377.

ALAIMO R., MONTANA G. and POLIZZI G. (1998) — *Caratteristiche mineralogico-petrografiche delle calcareniti in opera nei complessi monumentali della Sicilia Occidentale.* Mineralogica et Petrographica Acta, **41**, 243-266.

ALAIMO R., GIARRUSSO R. and MONTANA G. (2000a) — *La diagnosi del degrado come strumento indispensabile per il restauro dei manufatti lapidei: il caso del chiostro del Duomo di Monreale.* Boll. Acc. Gioenia Sci. Nat., **33**, 43-60.

ALAIMO R., GIARRUSSO R., MONTANA G. and POLIZZI G. (2000b) — *Le malte da intonaco del centro storico di Palermo: materie prime, composizione e meccanismi di degrado.* Atti del 1° Congresso Nazionale della Societa' Italiana di Archeometria - AIAr (Verona 2-3 Dicembre 1999). M. Martini and C. D'Amico eds., Pàtron Editore, Bologna, 271-282.

ALAIMO R., GIARRUSSO R., MONTANA G. and POLIZZI G. (2000c) — *Meccanismi di trasporto dell'acqua nelle calcareniti in opera su edifici monumentali della Sicilia occidentale.* Boll. Acc. Gioenia Sci. Nat., **33**, 31-42.

CAFLISH L. (1966) — *La geologia dei monti di Palermo.* Riv. Ital. Paleont. Stratig., Memoria **12**, 108 pp.

CHIRCO A. (1996) — *Palermo, la città ritrovata.* D. Flaccovio Editore, Palermo, 295 pp.

CIPOLLA F. (1929) — *Cave di tufi calcarei della Sicilia (età dei giacimenti e metodi di coltivazione).* Boll. Ass. Miner. Sicil., **5**, 8-20.

DUNHAM, R.J. (1962) — *Classification of carbonate rocks according to depositional texture.* In: Ham

ed. *Classification of carbonate rocks*. Memoir 1, Amer. Ass. Petrol. Geol., 108-121.

LA DUCA R. (1964) — *Cave di tufo del palermitano*. Boll. Ord. Ing. Palermo, **3-4**, 7-20.

LA DUCA R. (1994) — *Repertorio bibliografico degli edifici pubblici e privati di Palermo*. D. Flaccovio Editore, Palermo, 127 pp. 292.

MONTANA G. (1997a) — *Materiali e tecnologia di produzione della calce a Palermo nei secoli passati: implicazioni nel restauro dell'architettura monumentale barocca e neoclassica*. Mineralogica et Petrographica Acta, **XL**, 373-383.

MONTANA G. (1997b) — *La materia degli stucchi di Giacomo Serpotta (1656-1732): nuove conoscenze dedotte dai risultati di analisi mineralogico-petrografiche*. TEMA-Tempo Materia Architettura. Dipartimento di Conservazione e Storia dell'Architettura, Politecnico di Milano, **2/3**, 59-73.

MONTANA G. and GAGLIARDO BRIUCCIA V. (1998) — *I marmi ed i diaspri del barocco siciliano*. S.F. Flaccovio Editore, Palermo, 129 pp.

MONTANA G. and SCADUTO R. (1999) — *La pietra d'Aspra: storia ed utilizzo*. S.F. Flaccovio Editore, Palermo, 83 pp.

MONTANA G. AND RONCA F. (2001) — *Composizione e meccanismi di degrado delle sculture in stucco di Giacomo Serpotta a Palermo*. In «proceedings Scienza e Beni Culturali XVII. 2001 *Lo stucco, cultura, tecnologia, conoscenza*» (Biscontin G. and Driussi G. ed's), Edizioni Arcadia Ricerche, Venezia, 189-206.

RUGGERI, G. (1973) — *Ostracofauna delle calcareniti bianche quaternarie delle falde a Palermo*. Riv. Min. Sicil., **142**, 160-170.

TODARO P., (1988) — *Il sottosuolo di Palermo*. D. Flaccovio Editore, Palermo, 127 pp.