LITHOLOGY AND WEATHERING OF SCAGLIA LIMESTONE

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SUMMARY

Laboratory corrosion experiments and analysis of naturally weathered material were performed in order to study the relationships between lithology and weathering in Scaglia limestone. The obtained results evidence that grain size and porosity are the main textural features influencing the durability of the limestone through their direct effect on the chemical reactivity and mechanical resistance of the material. In particular, the small grain and pore size greatly enhance the chemical reactivity of the limestone, but result in relatively lower extents of sulfation attained. In addition, the low amount of total porosity accounts for the observed low extent of chemical processes related to water circulation in the open porosity, such as iron mobilization in the femic accessory phases, dissolution and sulfation. Therefore the material shows a good resistance to ambient weathering and only gentle treatments are necessary to restore the original properties.

1. INTRODUCTION

Weathering of a material results from the combined action of environmental and lithological factors active during the centuries. In particular, the influence of atmospheric pollution has progressively grown in importance in the last decades, so that at present time dry deposition of pollutants has become a primary cause of stone decay (Haneef et al., 1993). The safeguard of historical buildings requires a quantitative evaluation of the durability factors of the materials in well defined environments. Scaglia limestone, whose name comes from the homonymous lithological formation, is a Cretaceous-Tertiary pelagic limestone widely outcropping in Central Italy. For its high diffusion and aesthetic value it was largely utilized in the past as building material, and many ancient monuments in Umbria are made of this limestone. The aim of this work was to study the lithological and weathering features of Scaglia limestone in order to establish and verify its response to weathering.

2. MATERIALS AND METHODS

Fresh samples of Scaglia limestone from different stratigraphic positions were taken in an ancient zone of quarries near Assisi. Sampling was carried out on the Santonian-Maastrichtian members of the formation because they are the only ones showing macroscopic similarities with the materials employed in monuments. They are represented by micritic limestones, white to pink in colour, forming layers 15 to 40 cm thick. The material was characterized from the textural and compositional point of view in order to test the extent and range of variability of its properties within the formation. The results of this preliminary study are the subject of a separate work (Moroni & Baldanza, 1996), and only the most significant results will be reported here.

A large block of fresh material representative of the general properties of the sampled portion of the formation was taken in quarry and accurately characterized, then selected samples cut from the block underwent laboratory experiments in order to study the mode and extent of chemical weathering of the material in polluted environments. Little slabs of Scaglia limestone were exposed to air containing SO2 and NO2 in different concentrations (1 to 15ppm SO2; 0.1 to 0.3ppm NO2) in a special apparatus simulating dry deposition of pollutants. The experiments were performed at constant temperature (25°C), relative humidity (100%) and dynamic flow conditions (300cc/min); duration of the experiments was at most forty days. Details on the employed apparatus may be found in Moroni (1995).

Finally, samples of weathered Scaglia limestone were taken from ancient monuments in Assisi, such as the Cathedral (XIIth century) and some of the town doors (XIVth to XVth century), in order to study the mode and extent of weathering of the material in the natural systems.
Different analytical techniques were employed in the different stages of the work. In particular, the development of the reaction products upon and within the material and the involvement of substratum in the chemical weathering were investigated on the naturally and artificially weathered samples by means of SEM-EDX S and Ca mapping, respectively. On the other hand, the mineralogical composition of deteriorated material was determined in the natural and artificial products of decay through X-ray diffractometry. In the natural products of decay, the relative abundance of the constituent phases in the crusts and deposits from monuments was obtained in the powdered samples by dividing the net intensity of the maximum intensity peak of each phase by the sum of the net intensities of the maximum intensity peaks of the other phases present; in the artificial products of decay, the quantitative mineralogical composition of the products of the laboratory simulations was obtained in the bulk solid samples using the Rietveld structure refinement method (Young, 1993).

3. RESULTS

3.1 Petrography of Scaglia limestone

Scaglia is a micritic limestone gray to brown in colour at microscopic scale due to a variable abundance of dispersed hematite pigments (fig. 1a). The other constituents are an optically unresolvable siliciclastic component and variable proportions of sparitic fossils and veins. The micritic carbonate fraction is composed by calcite grains smaller than 4mm, whereas the fossils and veins mainly consist of crystals larger than 10mm (fig. 1b). Micrite represents the original sedimentation of the deposit, whereas sparite is the result of post-sedimentary recrystallization of the fossil structures and infilling of the veins. Rare stylolites are also present in some cases; they are the product of diagenetic or tectonic pressure solution of the lithified material.

The mineralogical composition of the material is that of a slightly marly limestone as it is mainly composed by calcite (about 98%) and contains small quantities of quartz and traces of phyllosilicates (illite and/or illite-montmorillonite) and hematite. That is confirmed by the chemical composition which is characterized by the presence of high CaO values and low amounts of silica and other oxides typically related to the insoluble fraction such as TiO₂, Al₂O₃ and Fe₂O₃. The chemical composition is quite homogeneous within the sampled portion of the formation and well represented by the selected block. Moreover, it falls in the range of variability of homologous Scaglia samples from different zones in Central Appennine (Calderoni & Ferrini, 1984; Moroni & Poli, 1996a), so evidencing a large scale homogeneity of the formation due to its pelagic origin.

The physical properties of the selected block are reported in Table 1. Total porosity is about 5% and mainly represented by mesopores (Aveyard & Haydon, 1973) with a mean pore radius of about 0.01mm (fig. 2a). Most of the pores are interconnected, as evidenced by the high values of the saturation index, but a small extent of internal pores also exists, as evidenced by the relatively low values of specific weight. In addition, total porosity shows a negative correlation with saturation index, so higher values of porosity are due to the presence of greater extents of closed pores with no part in the water transport within the rock.

The imbibition curves (fig. 2b) show a typical exponential trend reaching a quasi steady-state after about four days from the beginning of the test. This behaviour is a consequence of the pore-size distribution, as mesopores may be rapidly filled with water by capillarity. The range of variability of the imbibition curves is quite narrow. In addition, the relationships between the type and extent of porosity on one hand, and the rate and extent of imbibition on the other hand, are ambiguous (tab. 2). In fact, no clear relationships between the relative abundance of the most representative porosimetric classes and the initial rate of imbibition may be observed, along with any relationship between the total porosity and the initial extent of imbibition attained. These particular occurrences are clearly due to the small variability of total porosity and pore size distribution within the material.

3.2 Interaction with polluted atmosphere

The laboratory simulations were performed in order to study the behaviour of the material during sulfation. Sulfation, which is the primary cause of carbonate stone decay in polluted environments, is the process of interaction between calcium carbonate from the rock and sulfur oxides from the atmosphere.
(SO$_2$ and SO$_3$) in the presence of water as atmospheric or condensed humidity. The whole results of the laboratory experiments are reported and discussed elsewhere (Moroni & Poli, 1996b), therefore only the most significant results illustrating the mode and extent of sulfation of the material will be reminded here.

In spite of the short duration of the experiments, the obtained results clearly evidence the progress of sulfation even at the lowest SO$_2$ concentrations. Chromatographic data show a typical ramp-flat trend and a subsequent resumption of sulfation at the lowest SO$_2$ and NO$_2$ concentrations. The initial rate and the total extent of sulfation attained are directly related to the SO$_2$ concentration in the reaction vessel, whereas contrasting effects can be observed after addition of NO$_2$. The products of sulfation are calcium sulfate hemihydrate and gypsum. The former is the main reaction product in the presence of SO$_2$ alone, whereas the latter is the main or the only product of sulfation in the presence of SO$_2$ and NO$_2$. The reaction products nucleate and grow at the external surface of the material whereas they are practically absent in the interior of the limestone. They develop in preference on the micritic matrix rather than on the sparitic fossils and veins and form aggregates progressively covering the surface itself.

3.3 Natural weathering

Scaglia limestone from monuments is characterized by the presence of black crusts as the main deterioration product (fig. 3). They are coherent and adherent to substratum and show a smooth to dendritic appearance and a massive to layered texture. Total thickness is very variable ranging from 20 mm in some massive smooth crusts to 600 mm in the thickest dendritic and layered crusts. The crusts often contain long-shaped cavities subparallel or perpendicular to the external surface. The formers are thin and discontinuous and show a crenulated appearance due to deposition of atmospheric particulate; the latters are little pipes 0.5 to 20 mm in diameter deriving from water circulation within pre-existent fractures. The limestone in contact with the crusts shows discontinuous cloudy zones with a leached appearance.

The main constituent of the crusts is a fine matrix containing large quartz and calcite fragments and variable amounts of opaque grains. The opaque grains may concentrate within or on the external surface of the crusts forming aggregates or compact thin films, respectively. The mineralogical composition is dominated by the presence of calcite with much smaller quantities of gypsum, calcium oxalate weddellite and silicate phases (fig. 4). The relative abundance of the mineral phases shows a different trend in the samples from the town doors with respect to those from the Cathedral. In particular, the gypsum and quartz amounts are much higher in the formers than in the latters, whereas the oxalate is slightly more enriched in the samples from the Cathedral. These features are clearly related to the different location of the monuments through the influence of different levels of air pollution by sulfur dioxide and atmospheric particulate. In fact the Cathedral stands in a small ventilated square reserved to pedestrians, whereas the town doors are affected by motor traffic.

The origin of gypsum and silicates is clearly from dry deposition of pollutants, as the former mainly derives from sulfation of substratum and the latters are from deposition of suspended atmospheric particulate. On the other hand, the origin of oxalate is still uncertain. In fact oxalic acid, which is the precursor to oxalate, may derive from biologic activity or from treatments applied in the past (Rossi Manaresi et al., 1989), or may be one of the products of automobile exhausts (Kawamura & Kaplan, 1987). In the case of interest, the biologic and treatment hypotheses are to be excluded for the town doors owing to the scarce degree of finishing of the constituent blocks and to the presence of intense motor traffic in the surrounding zones; therefore atmospheric pollution is the most reliable hypothesis in this case. On the contrary, biologic activity and treatment are the most reliable genetic hypotheses for the Cathedral owing to the lower extent of pollution in the outskirts of the building.

Other deterioration features involving Scaglia limestone from monuments are calcite incrustations, fracturing and chromatic change (fig. 3). Carbonate incrustations are present at the bottom or within the black crusts in zones of the monuments partially or indirectly exposed to rain washing. They consist of fibrous calcite layers 5 to 30mm thick that superimpose each other forming crenulated or festooned structures. Fracturing and chromatic change involve the outermost portion of substratum. The former is represented by little discontinuous fractures subparallel to the external surface, whereas the latter consists in the development of discontinuous orange patches.
Evaluation of the response to weathering of Scaglia limestone by SEM-EDX mapping revealed that gypsum (represented by S distribution), though present in variable amounts within the black crusts, is completely absent in the interior of the stone except in the fractures (fig. 3c); moreover, Fe is not enriched in the orange zones.

4. DISCUSSION

Scaglia limestone reveals a reactive behaviour to acid attack. That is evidenced by the results of the laboratory simulations in which appreciable amounts of the reaction products were found after only a few days from the beginning of the experiments even at the lowest SO₂ concentrations. This behaviour is similar to that of other lithotypes exposed to analogous experimental conditions (Gauri et al., 1973; Gauri et al., 1982/1983; Johansson et al., 1988; Kulshreshtha et al., 1989; Götürk et al., 1993). Therefore the general processes active during sulfation are the same in the range of temperature, relative humidity and concentration of pollutants characterizing the experiences, and the differences among the materials as for the rate and extent of sulfation are mainly due to their different chemical and/or textural features.

The chemical composition, which is dominated by the presence of the carbonate phase, is indeed an important factor enhancing the chemical reactivity of the material through its direct participation in the dissolution/reprecipitation and sulfation processes. In addition, the insoluble residue components may act as catalysts of sulfur dioxide oxidation on the surface of the material owing to their surface properties (clay minerals) or chemical composition (hematite pigments). The role of geochemistry, however, is secondary to that of texture. The textural parameters which control the reactivity of the material are grain size, type and extent of the open porosity and pore size distribution.

The small grain size of the micritic matrix has a great influence on the rate of the surface reactions as it greatly enhances the extent of the specific surface of the material. Therefore the different grain size between micritic and spartic calcite grains results in a different reactivity of the two portions of the material, as evidenced by the preferential development of sulfation products on the matrix rather than on the cement.

Porosity and pore structure control the reactivity of the limestone through their influence on the extent of adsorption and humidity condensation, and through their role in the penetration and movement of water within the pores. In fact porosity is represented by a great extent of interconnected, small size capillary pores which are favourable sites for the adsorption of atmospheric humidity and pollutants, for the condensation of adsorbed humidity and for the circulation of condensed water. On the other hand, the extent of total porosity is quite low, so the material is only moderately affected by water penetration and, consequently, by chemical weathering in the interior of its structure.

The pore structure plays an important role also in the development and completion of the processes of interaction. In particular, as evidenced by some authors (Borgwardt & Harvey, 1972; Bhatia & Perlmutter, 1981), the rate of sulfation is higher in the smaller than in the larger pores, but small pores more easily plug with the reaction products leading to a more rapid change in the rate-limiting mechanism from surface reaction to solid state diffusion. Therefore diffusion processes are likely to occur earlier in finely porous materials such as Scaglia limestone rather than in coarsely porous ones leading to a relatively lower extent of sulfation attained.

Most of the observed deterioration processes appear to be related to the presence of moisture upon or within the material. Water reaches the exposed surfaces during the rain events and penetrates within the material through the porous structure or the fractures of the overlying black crusts. In particular, the carbonate incrustations are the product of calcite precipitation from a supersaturated film of condensed water present on the stone surface, whereas the orange spots result from iron hydration of the hematite pigments by condensed water present within the pore structure. Fracturing, on turn, cannot be related to the presence of water within the material through the influence of salt crystallization and freeze/thaw cycles. In fact, no gypsum or other salts were found in the pore structure, and the pores are so small to adverse freezing of the water contained at the common winter temperatures of the zone (Stockhausen et al., 1979). Consequently, fracturing is the result of daily and/or seasonal thermal gradients.

In conclusion, Scaglia limestone reveals a reactive behaviour to chemical attack due to its small grain and pore size, but it is quite impervious to extensive water penetration within its structure due to the low
extent of total porosity. Therefore the effects of chemical weathering are quite moderate and the deterioration processes do not reduce significantly the durability of the stone at the ambient conditions. As a consequence, consolidation of the textural discontinuities and gentle water repellent treatments are sufficient to optimize the durability of this material.

ACKNOWLEDGEMENTS

We thank Dr. Angela Baldanza for the helpful contribution in the characterization of the stratigraphic samples through paleontologic dating, Mr. Andrea Scala for his generous assistance in the mercury porosimetric analyses, and the Soprintendenza per i Beni Ambientali Architettonici Artistici e Storici dell'Umbria for the necessary permits for sampling in the monuments.

REFERENCES


Table 1 - Specific weight (g/cm³), apparent specific weight (g/cm³), total porosity (%) and saturation index (%) of Scaglia limestone

<table>
<thead>
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<th>Specific weight</th>
<th>Apparent Specific weight</th>
<th>Total Porosity</th>
<th>Saturation Index</th>
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</table>

Data obtained through the analysis of 13 samples each formed by 5 specimens

Table 2 - Relative volume of the 0.004 - 0.008 µm pore radius range (\(R_{vo1}\)), initial rate of imbibition (\(v_i\)\(^A\)), total porosity (P) and initial water absorption coefficient (WAC)\(^B\) of representative Scaglia samples from the block

<table>
<thead>
<tr>
<th>samples</th>
<th>(R_{vo1}(%))</th>
<th>(v_i(g^*cm^{-1}*s^{-1})*10^{-3})</th>
<th>P (%)</th>
<th>WAC (%)</th>
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</tr>
<tr>
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<td>16.36</td>
<td>6.22</td>
<td>4.06</td>
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</tr>
<tr>
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<td>4.93</td>
<td>1.00</td>
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<tr>
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<td>1.15</td>
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</table>

\(^A\) rate calculated in the 10 - 100' interval

\(^B\) coefficient calculated at 10'

Figures

Fig. 1 - Petrographic features (a; optical microscopy, parallel nicols micrograph) and surface texture (b; SE scanning electron microscopy image) of Scaglia limestone. The different grain size of micritic and sparitic calcite is evidenced.

Fig. 2 - Pore size distribution of representative samples of Scaglia limestone (a) and corresponding imbibition curves in the range of variability of the selected block (b). The porosimetric data were obtained through mercury porosimetry assuming a cylinder-open pore model for the material and a pore-size measuring range of 0.004-7.5mm, whereas the water absorption tests were performed by total immersion of the samples in distilled water and subsequent measurement of the weight gain at fixed times (Raccomandazione NORMAL Doc. 7/81).

Fig. 3 - (a) Thin section photomicrograph of weathered Scaglia limestone with black crust (1), calcite incrustation (2), chromatic change (3) and fracturing (4). (b) Scanning electron microscopy BS view of a detail of the same sample and corresponding S map (c).

Fig. 4 - Relative abundance of the mineral phases in the black crusts from different monuments in Assisi. Mineral phases: Cc = calcite; Gy = gypsum; Wd = weddellite; Qz = quartz; Fd = feldspar; Ag = clay minerals.
Figure 1
Figure 2

(a) Graph showing relative volume (%) versus pore radius (µm).

(b) Graph showing water absorption coefficient (vol %) versus time (minutes).
Figure 3
Figure 4