Periodico di Mineralogia (2012), 81, 1, 1-17 DOI: 10.2451/2012PM0001

PERIODICO di MINERALOGIA
established in 1930

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

Historical building stones of the western Tuscany (Italy): the Acquabona Limestones from Mts. Livornesi

Angela Baldanza[1], Anna Gioncada[2] and Marco Lezzerini[2,*]

[1]Dip. di Scienze della Terra, Università degli Studi di Perugia, Piazza Università 1, 06123 - Perugia, Italy
[2]Dipartimento di Scienze della Terra, Università di Pisa, Via S. Maria 53, 56126 - Pisa, Italy
* Corresponding author: *lezzerini@dst.unipi.it*

Abstract

Within the framework of a wide-ranging research on the historical stones used as building materials in the western Tuscany, the chemical, mineralogical, petrographic, physical and mechanical characteristics of the Acquabona Limestones (member of the Rosignano Limestone Formation, Late Miocene) were investigated.

From the Middle Age up to the 20th century, the Acquabona Limestones were widely used as an inexpensive, rather high-grade building material and as an essential raw material for soda production. For a construction purpose, these rocks were employed in the local buildings at Rosignano Marittimo and Livorno, the areas where they were quarried. Minor amounts of Acquabona Limestones were also employed in historical buildings of Pisa.

The paper presents the results of a study on forty-seven un-weathered samples collected from the historical Acquabona quarries near Rosignano Marittimo, a small town 35 km south from Pisa, and from two small outcrops located on the southern outskirts of Livorno, in the localities of Ardenza and Antignano. Unfortunately, the intensive extraction has almost completely exploited the existing stone material in the latter area, and now only two small outcrops remain.

The analysed rocks show comparable macroscopic and textural features, and a rather narrow range of chemical and mineralogical characteristics and of physical and mechanical properties, except for those depending on the calcite/dolomite ratio. The samples collected from the historical Acquabona quarries are characterised by calcite as main mineralogical phase, whereas those from the Ardenza and Antignano outcrops show a variably high content in dolomite that could be in part related to the peculiar biofacies identified in these samples, dominated by large bivalve shells.

Key words: Limestone; building material; XRF; XRPD; physical and mechanical properties; Tuscany.

Introduction

The historical and monumental buildings of the towns in the western Tuscany were built using a great variety of rocks (Franzini, 1993; Franzini and Lezzerini, 1998; 2003; Franzini et al., 2001; 2002; 2007). The organogenic *Calcari dell'Acquabona* (Acquabona Limestones), belonging to the Messinian reef complex (as described by Bossio et al., 1978; 1981 and Bartoletti et al., 1986), have been extensively used from the Middle Age to the mid-20th century as an inexpensive, rather high-quality building material for both masonry constructions and architectural purposes. They are the most widely used building stone in the civil and religious architecture of Rosignano Marittimo, a small town 20 km SE from Livorno. The castle and its defensive walls (XII-XVI century) as well as almost all the other medieval buildings of the town have been constructed by using the Acquabona Limestones as an exclusive building material (Figure 1A and 1B). In the seaside town of Livorno, the Acquabona Limestones have

Figure 1. Photographs of some uses of the Acquabona Limestones in the Rosignano Marittimo and Pisa architecture. A) The small tower of the southern defensive walls at Rosignano Marittimo; B) Detailed view of the ashlars used for building the small tower; C) Detail of the parapets along the Arno River at Pisa; D) The Statua dell'Abbondanza (Statue of Abundance) in Piazza del Mercato at Pisa.

been used to build the parapets of the canals running through the old town. These rocks have been also employed for building the curved breakwater protecting the mercantile port of Livorno, begun in 1853, as well as for decorative purpose of some historic buildings in the Ardenza and Antignano area, where the stone quarrying was historically carried out (Lazzarotto et al., 1990). Also the parapets between one bridge and the next one along the Arno River in the historic centre of Pisa build in the late 19th century with brick walls have been embellished with several hundred of large ashlars of Acquabona Limestones (Figure 1C), some of which, damaged in World War II have been replaced with granite, travertine and local limestones belonging to the Tuscan sedimentary sequence. No other example of the use of the Acquabona Limestones has been observed in Pisa, except for an interesting work of sculpture, the *Statua dell'Abbondanza* (Figure 1D). As stated in the Giorgio Vasari's Lives of the Artists, Pierino da Vinci (the nephew of the famous Leonardo) obtained by Cosimo I de' Medici in 1550 AD the commission for that statue representing Abundance and he carved it "with much softness and facility, although the stone is rough and difficult to work".

Despite the historical importance of this building stone, only incomplete information is available in the literature, except for its geological, sedimentological (De Stefani, 1911; Giannini and Tongiorgi, 1959; Giannini, 1955; 1962; Barsotti et al., 1974; Bartoletti et al., 1983; 1986; Boccaletti et al., 1985; 1992; Giannelli et al., 1982; Lazzarotto et al., 1990) and paleontological features (Fuchs, 1874; Manzoni, 1874; Stefanini, 1956; Ruggieri, 1956; Chevalier, 1961; Bartolini et al., 1975; Bossio et al., 1978; 1981; 1986; 1993; 1996; 1997; 1999; Esteban, 1978; 1979; 1996).

For this reason, we carried out a study on the mineralogical, petrographic and geochemical characteristics, as well as on the main physical and mechanical properties of the Acquabona Limestones, by analysing rock samples from old quarries. In situ observations revealed that the Ardenza quarrying area is disappeared without almost trace due to extensive exploitation. Nowadays, only two small outcrops of Acquabona Limestones about ten square metres wide can be found near Livorno, at Ardenza and Antignano localities, and much of what remains of this stone is useless. Therefore, the sampling was carried out by collecting samples in the Acquabona quarrying area near Rosignano Marittimo and some samples were taken in the two outcrops near Livorno for the sole purpose of doing a comparison. Our purpose is to contribute to the knowledge on the main properties of the stone, which may be useful both for cleaning the stone and its restoration.

Geological setting

The *Calcari dell'Acquabona* is one of the four informal members of the *Calcare di Rosignano* Formation (Late Miocene) outcropping in limited areas near Rosignano Marittimo and Livorno. The *Calcare di Rosignano* Fm includes a variety of heterogeneous lithologies: mainly detrital limestones (produced by the erosion of nearby bioclastic and organic carbonatic boundstones), sand and clay levels, conglomerates, breccias, marls and biogenic limestones. The outcrops of Rosignano Marittimo were referred by Giannini (1962) to the eastern side front of a marginal reef, in which the *Calcari dell'Acquabona* corresponded to shallow water reef - upper scarp paleoenvironments. The aforesaid member was subdivided by Bartoletti et al. (1986) into two lithofacies referable to a reef - forereef complex and related scarp facies; the first facies was characterized by bioclastic calcarenites, while the second one, visible in the Acquabona quarries according to Bartoletti et al. (1986), was constituted by interdigitated bodies of bioconstructions (reef complex with *Porites* coral colonies). The basal portion of the member is composed of well stratified and poorly cemented bioclastic calcarenites of sands and pebbles, and of clayey bioclastic calcarenites deeply affected by bioturbation; the middle portion was dominated by coral *Porites* vertical bioconstructions, subordinated disc-shaped laminated coral colonies, frequent red algae, ostreids, bryozoans, serpulids and molluscs. The upper portion was characterized by thick clynostratified banks of bioclastic breccias, more competent in the proximity of the reef complex; a gradual transition from breccias to bioclastic calcarenites is visible in a more distal position (Bartoletti et al., 1986).

Sampling and analytical methods

A total of forty-seven samples of the Acquabona Limestones have been collected (Table 1). Thirty-four samples (Group 1) come from the Acquabona quarries (less than 1 km north of Rosignano Marittimo), where stone quarrying was historically carried out (Figures 2a and 3). In order to have a complete sampling of the known extraction sites, we have collected thirteen samples in the Livorno area (Figure 2b), also. Three of these samples come from the quarry, now almost exhausted, that we have pinpointed at 1 km to the southeast from Livorno, in the place formerly known as Mt. Tignoso (near the Ardenza railway station) (Group 2a), whereas the others come from a small outcrop by the sea at Antignano (near the former Villa Carolina) (Group 2b). Fifteen of the forty-seven samples that we have analysed in the present study are those sampled and preliminary studied by Langella (2001).

Mineralogical and petrographic investigations of the samples were performed by optical microscopy (OM) observations on thin sections using a Zeiss-Axioplane polarising microscope. The same equipment was used to study the main textural features and the bioclastic components of the rocks.

Chemical analyses were performed through X-ray fluorescence (XRF), according to the procedure suggested by Franzini et al. (1975). Within the range of measured concentrations, the analytical accuracy varies from 15% (MgO and MnO) to 1% (CaO), with a mean value of 5% for major elements. Loss on ignition (L.O.I) was determined at 950 °C on 400 mg of powder dried at 105 ± 5 °C for twenty-four hours in a drying oven with forced ventilation. CO_2 was determined separately via the calcimeter method (Leone et al., 1988) on 600 mg of the same powder, and the difference between the L.O.I. and the CO_2 content was entirely ascribed to H_2O^+.

Insoluble residues of selected samples were obtained by dissolving about 100 g of sample fragments in a 0.1N HCl solution. Qualitative mineralogical compositions of whole rock and residue were obtained via X-ray powder-diffraction (XRPD) using a Bragg-Brentano geometry and Ni-filtered CuKa radiation obtained at 40 kV and 20 mA.

The normative mineralogical compositions of the rock samples were obtained by combining the chemical analyses with qualitative mineralogical compositions, as suggested by Leoni et al. (2008). Stoichiometric chemical compositions were used for calcite and dolomite.

Real densities (ρ_r) were computed from the normative compositions and, afterwards, the collected data were compared with those measured by means of an automatic He-pycnometer (Ultrapycnometer 1000, Quantachrome Corporation). The measurements were performed on 10 g of very-fine-grained powders, dried at 105 ± 5 °C for twenty-four hours in a drying oven with forced ventilation, under the following experimental conditions: ultrahigh purity compressed Helium with outlet pressure of 140 kPa; target pressure, 100 kPa; equilibrium time, automatic; purge mode, 3 minutes of continuous flow; maximum number of runs, 6; number of averaged runs, the last three.

Measurements of both apparent density (ρ_b) and water absorption by total immersion (A_b) at atmospheric pressure were performed for each sample on a cube-shaped specimen (50 ± 5 mm), according to EN 1936 and EN 13755 guidelines, respectively. In particular, apparent density was computed as the ratio between the mass of the dry sample and its volume, measured by means of a hydrostatic balance on waterproofed samples. For seventeen selected samples, the water absorptions by total immersion were measured by repeating the measurement at 2, 5, 10, 15, 30, 45 minutes, 1, 2, 3, 4, 5, 6, 7, 8, 24, 48, 72, 96, 168, 240, 336 and 432 hours.

Total porosity (P) and saturation index (SI) were respectively computed as follows:

$P (\%) = 100 \cdot (1-\rho_b/\rho_r)$

$SI (\%) = 100 \cdot A_b \cdot (\rho_b/\rho_{H_2O})/P$

Uniaxial compressive strengths (σ_c) were measured for each sample on a cube-shaped specimen (50 ± 5 mm) with normal orientation of the load axis with respect to the existing planes of anisotropy, according to EN 1926 guidelines.

All the original chemical data of the studied samples can be found online at the website: http://www.dst.unipi.it/min.

Results

Petrographic features and biofacies characterization

The Acquabona Limestone samples from the Acquabona quarries and from the Ardenza and Antignano sites were studied by both macroscopic observations on polished slabs and thin section analyses, using a polarizing optical microscope, to recognize the different lithologies and their constituents; the main macroscopic and microscopic features (colour, main mineralogical phases, texture, and bioclastic components) are reported in Table 1.

The analysed samples show a rock colour ranging from white to pale yellow and a dominant carbonatic bioclastic component represented by poorly sorted sub-angular to rounded clasts with grain size variable from medium to very coarse sands. The calcarenites are more frequent in respect to the calcirudites. Variable amounts of micritic matrix and of sparitic calcite cement are present. An appreciable silicoclastic fraction composed of quartz and micas was recognized only in samples 6, 26, 41 and 47.

The examined samples are porous rocks characterised by both fabric-selective and non-fabric-selective porosity, according to the classification proposed by Choquette and Pray (1970). Since the primary pore-space among the grains is partially unfilled, the rocks show a high fabric-selective interparticle porosity. A minor amount of primary fabric-selective porosity is intraparticle porosity due to the chambers and other spaces of some bioclasts that are empty or only partially filled with cement. In some samples a secondary mouldic porosity and a non-fabric-selective porosity due to cavities and channels were also observed. These types of porosity combine to give a highly variable total porosity, ranging from 9% (samples 30 and 31) to 43 % by volume (sample 18).

The samples from the Acquabona quarries refer to three main biofacies types, identified on the basis of the presence and relative abundance of the main biogenic components: 1) Porifera biofacies, 2) Biocalcarenites and 3) Tuberolithic-spicolithic facies.

The Porifera biofacies (Table 1 and Figure 4A and 4D) is characterised by biosparites (samples 1-5, 8-15, 17, 19-21, 24, 25, 27, 29-34) and rare lithoclastic calcirudites (samples 22 and 23); the textures, following Dunham (1962), are packstone - grainstone with common Demosponges, Calcisponges, Coralline algae, bivalves, boring sponge *Aka*, bryozoans, echinoid fragments, oysters, miliolids, rare micropelletoidal micrite,

Table 1. Sampling, main petrographic features and biofacies types identified in the Acquabona Limestone samples.

<table>
<tr><th>Sampling sites</th><th>Samples</th><th>Lat.</th><th>Long.</th><th>Rock colours [1]</th><th>Cc</th><th>Do</th></tr>
<tr><td rowspan="34">Acquabona quarries</td><td>1</td><td>43°24'52"N</td><td>10°28'35"E</td><td rowspan="3">5Y 8/1 white</td><td rowspan="34">abundant</td><td rowspan="34">trace</td></tr>
<tr><td>2</td><td>43°24'48"N</td><td>10°28'34"E</td></tr>
<tr><td>3</td><td>43°24'49"N</td><td>10°28'34"E</td></tr>
<tr><td>4</td><td>43°24'47"N</td><td>10°28'33"E</td><td>5Y 7/3 pale yellow</td></tr>
<tr><td>5</td><td>43°24'48"N</td><td>10°28'33"E</td><td rowspan="2">5Y 8/1 white</td></tr>
<tr><td>8</td><td>43°24'50"N</td><td>10°28'33"E</td></tr>
<tr><td>9</td><td>43°24'51"N</td><td>10°28'33"E</td><td>5Y 7/3 pale yellow</td></tr>
<tr><td>10</td><td>43°24'51"N</td><td>10°28'32"E</td><td rowspan="14">5Y 8/1 white</td></tr>
<tr><td>11</td><td>43°24'56"N</td><td>10°28'31"E</td></tr>
<tr><td>12</td><td>43°24'54"N</td><td>10°28'30"E</td></tr>
<tr><td>13</td><td>43°24'51"N</td><td>10°28'29"E</td></tr>
<tr><td>14</td><td>43°24'56"N</td><td>10°28'27"E</td></tr>
<tr><td>15</td><td>43°24'57"N</td><td>10°28'25"E</td></tr>
<tr><td>17</td><td>43°25'04"N</td><td>10°28'25"E</td></tr>
<tr><td>19</td><td>43°24'59"N</td><td>10°28'23"E</td></tr>
<tr><td>20</td><td>43°25'04"N</td><td>10°28'23"E</td></tr>
<tr><td>21</td><td>43°25'08"N</td><td>10°28'23"E</td></tr>
<tr><td>24</td><td>43°24'54"N</td><td>10°28'21"E</td></tr>
<tr><td>25</td><td>43°24'53"N</td><td>10°28'20"E</td></tr>
<tr><td>27</td><td>43°25'01"N</td><td>10°28'20"E</td></tr>
<tr><td>29</td><td>43°24'51"N</td><td>10°28'18"E</td></tr>
<tr><td>30</td><td>43°24'41"N</td><td>10°28'17"E</td><td>5Y 7/1 light gray</td></tr>
<tr><td>31</td><td>43°24'44"N</td><td>10°28'17"E</td><td rowspan="5">5Y 8/1 white</td></tr>
<tr><td>32</td><td>43°24'57"N</td><td>10°28'17"E</td></tr>
<tr><td>33</td><td>43°24'54"N</td><td>10°28'16"E</td></tr>
<tr><td>34</td><td>43°24'44"N</td><td>10°28'14"E</td></tr>
<tr><td>22</td><td>43°25'09"N</td><td>10°28'23"E</td></tr>
<tr><td>23</td><td>43°25'09"N</td><td>10°28'23"E</td><td>5Y 7/1 light gray</td></tr>
<tr><td>7</td><td>43°24'50"N</td><td>10°28'33"E</td><td rowspan="3">5Y 8/1 white</td></tr>
<tr><td>16</td><td>43°25'04"N</td><td>10°28'25"E</td></tr>
<tr><td>18</td><td>43°24'51"N</td><td>10°28'23"E</td></tr>
<tr><td>26</td><td>43°24'55"N</td><td>10°28'20"E</td><td>5Y 7/3 pale yellow</td></tr>
<tr><td>28</td><td>43°24'53"N</td><td>10°28'19"E</td><td rowspan="3">5Y 8/3 pale yellow</td></tr>
<tr><td>6</td><td>43°24'49"N</td><td>10°28'33"E</td></tr>
<tr><td rowspan="3">Ardenza (ex-M. Tignoso)</td><td>35</td><td rowspan="3">43°30'56"N</td><td rowspan="3">10°19'48"E</td><td rowspan="4">present</td><td rowspan="4">abundant</td></tr>
<tr><td>36</td><td>5Y 7/3 pale yellow</td></tr>
<tr><td>37</td><td rowspan="2">5Y 8/3 pale yellow</td></tr>
<tr><td rowspan="10">Antignano</td><td>38</td><td rowspan="10">43°30'25"N</td><td rowspan="10">10°19'09"E</td></tr>
<tr><td>39</td><td>5Y 8/4 pale yellow</td><td>abundant</td><td>present</td></tr>
<tr><td>41</td><td rowspan="5">5Y 8/3 pale yellow</td><td>abundant</td><td>trace</td></tr>
<tr><td>43</td><td>abundant</td><td>abundant</td></tr>
<tr><td>44</td><td>present</td><td>abundant</td></tr>
<tr><td>45</td><td>abundant</td><td>present</td></tr>
<tr><td>46</td><td>abundant</td><td>trace</td></tr>
<tr><td>40</td><td rowspan="2">5Y 8/2 pale yellow</td><td>abundant</td><td>abundant</td></tr>
<tr><td>42</td><td>present</td><td>abundant</td></tr>
<tr><td>47</td><td>5Y 8/4 pale yellow</td><td>abundant</td><td>present</td></tr>
</table>

Lat., latitude Long., longitude Cc, calcite Do, dolomite (detected by XRPD). 1= Determination of rock colour was obtained by comparison with Munsell colour charts 2= Classification of porosity according to Choquette and Pray (1970) 3= Total porosity was measured for each sample on a cube-shaped specimen (50 ± 5 mm) and computed as follows P (%) = 100 · (1-ρ_b/ρ_r) 4= Classification of limestones according to Dunham (1962).

Table 1. Continued...

Porosity types[2]	Porosity[3] (% by vol.)	Petrographic classification[4]	Bioclastic components	Biofacies types
inter- and intra-particles, vugs, channels	25.7	packstone/ grainstone	Common Demosponges, Calcisponges, Corallinae algae, bivalves, boring sponge Aka, bryozoans, echinoid fragments, oysters, miliolids, rare micropellettoidal micrite calcite cement (micro and pseudospar).	Porifera biofacies
inter- and intra-particles, moulds	17.3			
inter- and intra-particles, vugs	15.9			
	26.2			
interparticles	18.8			
inter- and intra-particles	16.6			
interparticles, vugs	10.3			
	13.6			
inter- and intra-particles, vugs	37.3			
	20.6			
inter- and intra-particles, moulds	26.8			
inter- and intra-particles, vugs	25.4			
inter- and intra-particles, moulds, vugs	26.2			
inter- and intra-particles	22.1			
inter- and intra-particles, vugs	19.2			
	19.9			
	10.7			
	29.6			
inter- and intra-particles, moulds, vugs	39.3			
interparticles, vugs	28.6			
inter- and intra-particles, vugs	13.3			
interparticles, moulds	8.8			
interparticles, vugs	9.2			
inter- and intra-particles, vugs	27.2			
	29.4			
	22.1			
inter- and intra-particles, moulds	23.3	grainstone	Sharp edged clasts of porifera bearing lithotypes, oysters, gastropods, benthic foraminifers and rare tuberoids.	
inter- and intra-particles, vugs	12.9			
	30.3	packstone	Benthic foraminifers (Ammonia sp., Elphidium sp.), miliolids, Corallinae algae fragments, bivalve shells and echinoid spines.	Biocalcarenite facies
	21.0			
inter- and intra-particles, moulds, vugs	43.2			
inter- and intra-particles	14.0			
	29.4			
	13.3		Micritic tuberoid structures, bioclasts, boring demosponge, gastropods, echinoid fragment and bivalve shells.	Tuberolithic-spicolithic facies
	16.3		Demosponges, ostracods, bivalve shells, micropelletoidal micrite, rare tuberoids.	Porifera biofacies
	19.3			
inter- and intra-particles, vugs	27.6		Common Pycnodonta shells, echinoid fragments,rare micropelletoidal micrite, tuberoids, Corallinae algae fragments.	Pycnodonta calcarenite
interparticles, vugs	29.3			
inter- and intra-particles	16.1			
	16.6			
inter- and intra-particles, vugs	10.8			
	32.0			
inter- and intra-particles, moulds, vugs	19.9			
interparticles, vugs	11.8			
inter- and intra-particles	13.6			
	11.0			
	23.4		Micritic tuberoids, boring sponges, algal laminites and calcite cements.	Tuberolithic-spicolithic facies

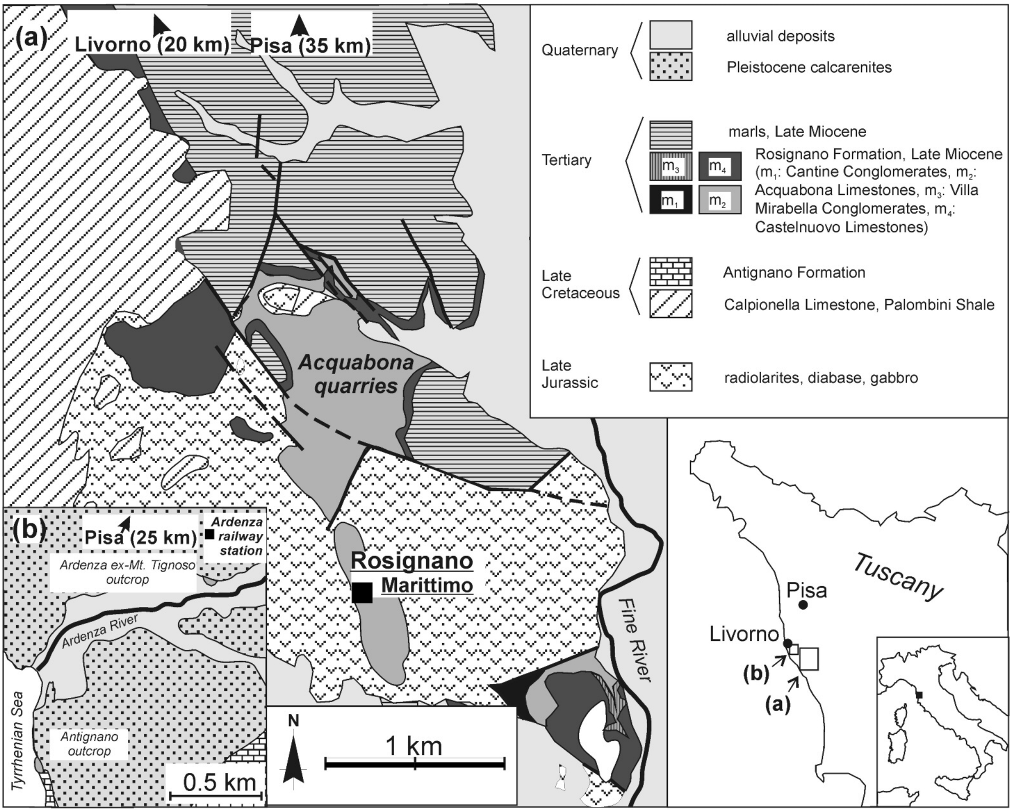

Figure 2. Simplified geological sketch map of the Rosignano Marittimo (a) and Livorno (b) areas, showing the main outcrops of the Acquabona Limestones and sampling-site locations.

few micritic tuberoid structures and calcite cement (as micro and pseudospar). The coral *Porites*, reported by Bartoletti et al. (1986) was not found in our samples. Biocalcarenites (mainly biomicrites) were identified in five samples (7, 16, 18, 26 and 28) coming from the Acquabona quarries and they are characterized by packstone with benthic foraminifers, fragments of Coralline algae, bivalve shells and echinoid spines (Figure 4B and 4C). Tuberolithic-spicolithic facies, a particular lithotype firstly identified by Flugel and Steiger (1981) in the German Upper Jurassic Porifera bioconstructions and reported also by Vantaggi and Baldanza (2006) in the Umbria-Marche Apennine Lower Jurassic sponge levels, was identified in sample 6; this biomicrite shows a packstone texture with micritic tuberoid structures, bioclasts, boring demosponge (referable to the *Aka* genus), gastropods, echinoid fragments and bivalve shells (Figure 4E). The Acquabona quarry samples could be referred to the basal portion of the Acquabona Limestones, and in particular the Porifera facies represented a stage of sea-floor colonization with a probable meadow shape organization developed on a biodetritic softground substrate. The variability of lithotypes is coherent with the aforesaid characters of this member.

Figure 3. A partial view of the Acquabona quarries at Rosignano Marittimo (m_2: Acquabona Limestones).

Ten samples from the Livorno outcrops are bioclastic packstone (biosparites) characterised by common to abundant large bivalve shells, referable to *Pycnodonta* sp. (Figure 4F). The remaining samples are representative of the porifera (samples 35 and 36) and tuberolithic-spicolithic (sample 47) facies, with the same bioclastic components formerly described about the samples from the Acquabona quarries. The accumulation of the large *Pycnodonta* shells into the biocalcarenites can be due to a local sea-current resedimentation event. In fact, Bartoletti et al. (1986) identified the Argille a *Pycnodonta* formation as a heteropic facies to the Acquabona Limestones.

Interestingly, these large bivalves own multilayered shells, composed by aragonite and calcite layers; the chemical composition of the bivalve shells varies depending on the environmental ecology conditions. As reported by Aal et al. (1987), substantial variations occur in fossil bivalve shells with the increasing of Sr, Mn and Mg contents when the sea water temperature increases and the salinity decreases; on the contrary, the Al, Si and Fe contents in the shells increase with increasing salinity and decreasing temperature. This is very important because the chemical composition of the fossil shells, diversifying in response to paleoenvironmental variations, may deeply influence the chemical composition of the resulting bioclastic rock.

Chemical and mineralogical characteristics

The average chemical and mineralogical data are reported in Table 2. Calcium oxide and CO_2 are the most abundant chemical components of

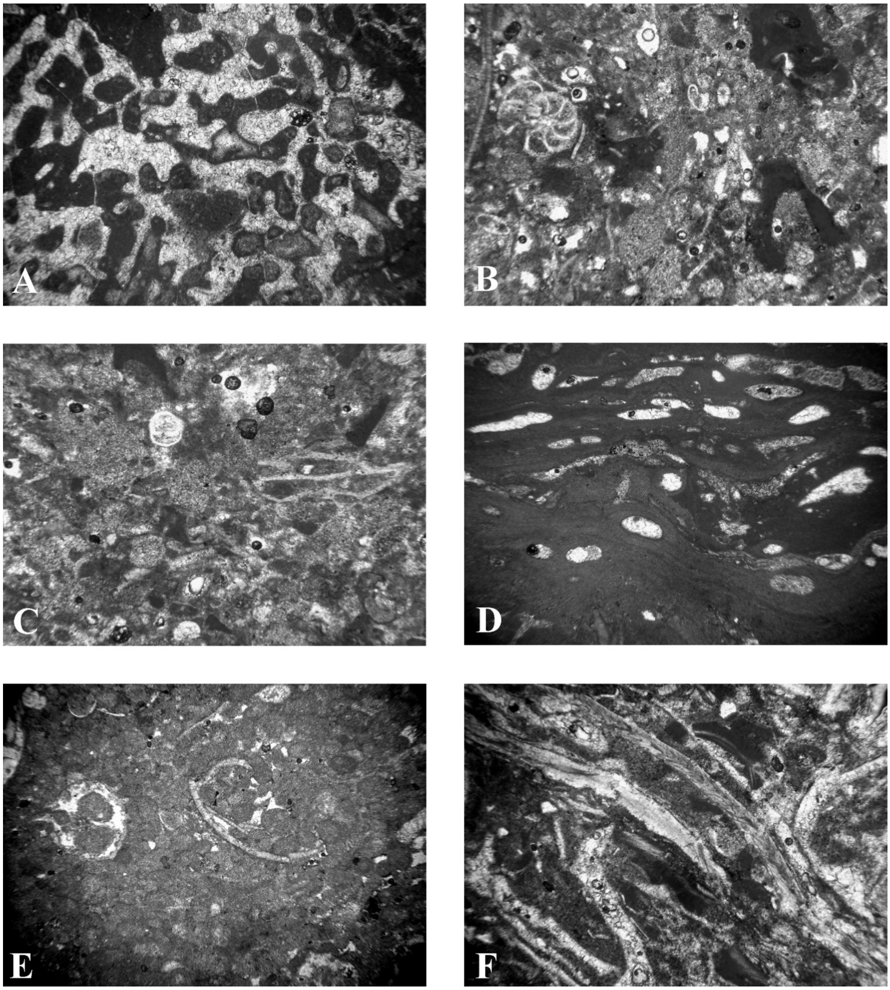

Figure 4. Microphotos of the main microbiofacies recognized in the Acquabona Limestones samples. A) Porifera biofacies: Demosponge "mummies"; B and C) Bioclastic calcarenites; D) Coralline algae; E) Tuberolithic-spicolithic facies; F) Large bivalve shells of Pycnodonta sp. All microphotos are at a magnification of 20X.

samples 1-34 (Group 1, samples from the Acquabona quarries), followed by silica, magnesia and alumina, whereas samples 35-47 (Group 2, samples from Livorno outcrops) are made up mainly of calcium oxide, CO_2 and magnesia, followed by silica and alumina.

Hence, the samples are composed mainly of Ca- and Mg-carbonates and can be described as mixtures of (CaO + MgO), CO_2 and a "residue". This last is mainly composed of silica and alumina, with minor amounts of iron and alkali oxides.

The ternary diagrams of Figure 5 show the main relationships among the major chemical components of the rocks. Group 1 samples are characterised by higher CaO contents than most of Group 2, and all samples show constant K_2O/Fe_2O_3 and SiO_2/Al_2O_3 ratios.

Table 2. Chemical and normative compositions of the Acquabona Limestones samples (% by weight).

	Acquabona quarries (samples 1-34)				Antignano and Ardenza outcrops (samples 35-47)			
	Average	Dev. St.	Min.	Max.	Average	Dev. St.	Min.	Max.
H_2O^+	0.14	0.11	0.05	0.47	0.21	0.18	0.02	0.7
CO_2	43.11	0.67	40.96	43.70	43.64	2.30	37.08	45.64
Na_2O	0.02	0.02	<0.01	0.08	0.21	0.11	0.02	0.35
MgO	0.67	0.17	0.48	1.11	9.22	6.40	0.61	16.21
Al_2O_3	0.34	0.23	0.10	1.16	0.67	0.39	0.09	1.55
SiO_2	1.13	0.83	0.37	3.82	2.49	2.61	0.47	10.79
P_2O_5	0.02	0.03	<0.01	0.10	0.03	0.03	<0.01	0.09
K_2O	0.07	0.05	0.03	0.26	0.12	0.09	0.01	0.35
CaO	54.25	0.84	51.71	55.01	43.11	7.09	35.09	54.71
TiO_2	0.01	0.01	<0.01	0.05	0.03	0.02	<0.01	0.07
MnO	0.07	0.09	0.01	0.51	0.02	0.01	0.01	0.06
Fe_2O_3	0.17	0.15	0.05	0.62	0.25	0.23	0.03	0.87
Total	100.00				100.00			
Dolomite	3.04	0.76	2.20	5.07	42.19	29.29	2.79	74.19
Calcite	95.13	1.90	89.83	96.91	53.99	28.30	22.92	95.90
Others	1.83	1.26	0.71	5.92	3.82	3.31	0.90	13.99
Total	100.00				100.00			

Fe_2O_3* = total iron expressed as Fe_2O_3.

The last four rows in Table 2 report the average normative compositions and their variability ranges computed separately for Group 1 and Group 2 samples. The entire CaO and MgO contents have been converted to calcite and dolomite percentages, and the difference with respect to 100% of the sum of these two components has been ascribed entirely to a non-carbonate "residue".

Chemical data and normative compositions show that all the analysed samples are essentially made up of calcite and dolomite. The two

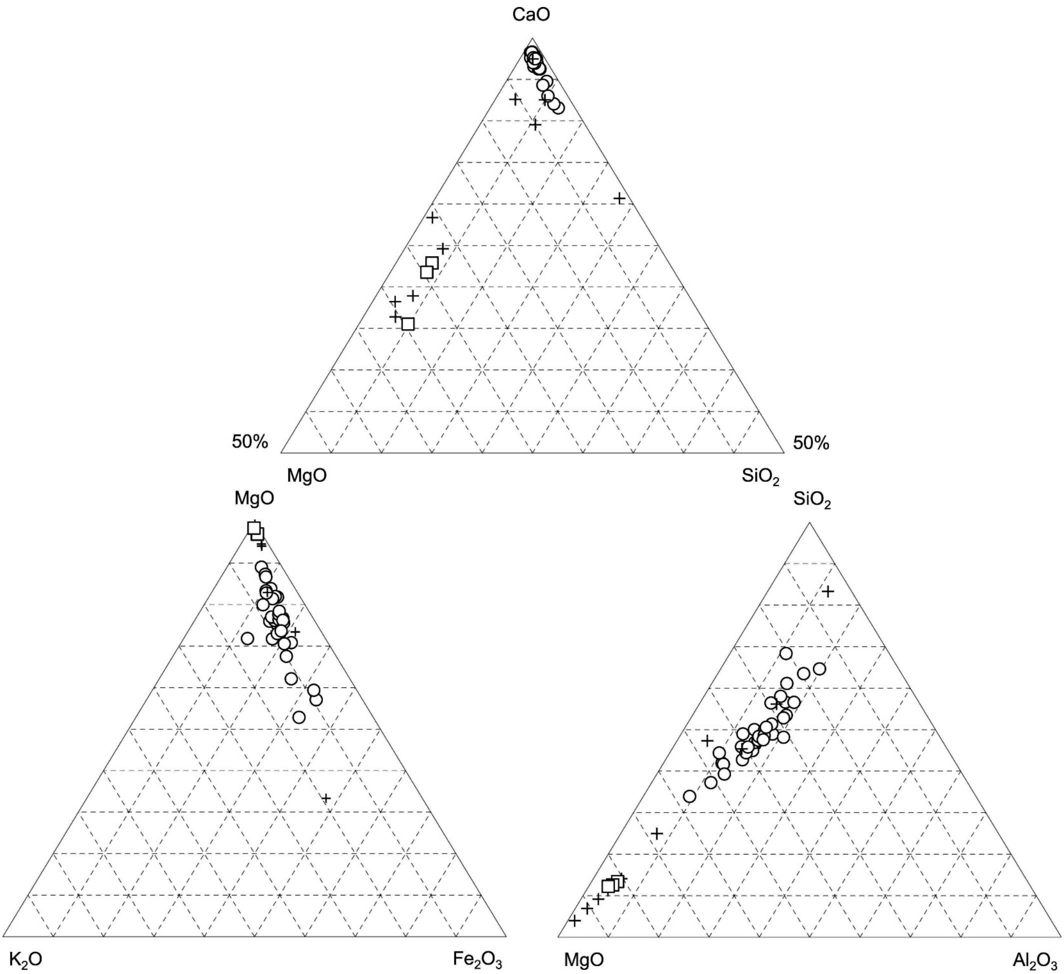

Figure 5. Ternary diagrams showing the main relationships among the major chemical components (wt%) of the Acquabona Limestone samples. Circles: samples from the Acquabona quarries; Square: samples from the Ardenza ex-Mt. Tignoso outcrop; Cross: samples from the Antignano outcrop.

minerals account for 98 and 96 % by weight on average, respectively, in the samples of Group1 and Group 2, and their amount is over than 86 % in all analysed samples. Considering samples of Group 1, calcite and dolomite contents range respectively from 90 to 99 % and from 2 to 5 %. As regard to Group 2 samples, these mineralogical phases range respectively from 23 to 96 % and from 3 to 74 %.

The XRPD analyses carried out by Langella (2001) on the insoluble residues of sixteen samples and performed in this work on those of six samples (two for each sampling area: samples 20 and 34 from the Acquabona quarrying area, samples 26, 6 and 36, 41 respectively from Ardenza and Antignano

Table 3. Physical and mechanical properties of the Acquabona Limestone samples.

	Acquabona quarries (samples 1-34)				Antignano and Ardenza outcrops (samples 35-47)			
	Average	Dev. St.	Min.	Max.	Average	Dev. St.	Min.	Max.
ρ_r (g/cm^3)	2.71	0.01	2.70	2.73	2.77	0.04	2.71	2.82
ρ_b (g/cm^3)	2.12	0.23	1.54	2.48	2.24	0.19	1.91	2.51
A_b (wt.%)	8.0	4.4	1.1	19.4	6.0	3.5	2.3	13.4
σ_c (MPa)	18.6	10.9	3.9	46.0	25.4	15.8	5.2	53.8
P (vol.%)	22.0	8.6	8.8	43.2	19.1	7.1	10.8	32.0
S.I. (%)	71	14	29	91	65	10	47	80

ρ_s = real density; ρ_b = apparent density; A_b = water absorption by total immersion at atmospheric pressure; σ_c = uniaxial compressive strengths; P = total porosity; S.I. = saturation index.

outcrops) revealed that the composition of the non-carbonate fraction can be described as a mixture of quartz ± plagioclases ± K-feldspar ± clay minerals ± Fe-oxides and hydroxides ± heavy minerals. Mica-like minerals and subordinately expandable minerals are the main clay minerals as identified by XRPD on Mg^{2+}-saturated oriented-mounts processed both in the air-dried (AD) and in glycolated (EG) states.

Physical and mechanical properties

Table 3 reports the measured values of the real (ρ_r) and apparent (ρ_b) densities, the water absorption by total immersion at atmospheric pressure (A_b), and the uniaxial compressive strengths (σ_c) of the analysed samples. The derived quantities, total porosity (P) and saturation index (S.I.) have also been reported.

The real density is almost constantly around 2.71 g/cm^3 in Group 1 samples, but it is higher and more variable in Group 2 samples. The real density is strongly correlated with the dolomite content (r = 0.983). The computed linear best fit is $\rho_r = 0.0015 \cdot$ (dolomite %) + 2.7096, which is quite near the theoretical formula for dolomite and calcite mixtures.

On the other hand, the apparent density and the water absorption at atmospheric pressure, as well as the compressive strength, show wide ranges of variation, roughly similar in Groups 1 and 2 (Table 3). The water absorption at atmospheric pressure is strongly related to the apparent density (r = -0.972). The computed linear best fit is A_b (weight %) = 46.4202 - 18.1155 ρ_b. Using this equation, the A_b values can be computed from the ρ_b values within an average error of 15%. The compressive strength value is well correlated to the apparent density, and hence to the total porosity value (r = 0.835) and their relationships may be expressed as $\sigma_c = 0.2829 \cdot \rho_b^{5.686}$ and $\sigma_c = 858.1016 \cdot P^{-1.3173}$, respectively.

Discussion and conclusions

The Acquabona Limestones, belonging to the formation known as *Calcari di Rosignano*, have been used as a building material in Rosignano Marittimo, Livorno and Pisa from the Middle Age to the late 20th centuries. Historically, these stones were exploited near Rosignano Marittimo in the Acquabona quarrying areas and near Livorno.

Table 4. Regression equations describing the main correlation existing between mineralogical, physical and mechanical data.

Equation	n	r	e
$\rho_r = 0.0015 \cdot (\text{dolomite\%}) + 2.7096$	47	0.983	1.3‰
$A_b\ (\text{wt.\%}) = 46.4202 - 18.1155 \cdot r_b$	47	-0.972	15%
$\sigma_c = 0.41014 \cdot r_r^{4.9274}$	47	0.858	29%
$\sigma_c = 858.1016 \cdot P^{-1.3173}$	47	-0.835	31%

ρ_r = real density (g/cm3); A_b = water absorption by total immersion at atmospheric pressure (wt%); ρ_b = apparent density (g/cm3); σ_c = uniaxial compressive strength (MPa); n = number of samples; r = correlation coefficient; e = average of relative error on recalculated values.

The present research contributes to the knowledge on the chemistry, mineralogy and petrography of the Aquabona Limestones.

From the macroscopic point of view, the rock samples from the Acquabona quarries are white in colour and subordinately pale yellow or light gray, while those from Ardenza and Antignano are characterised by a pale yellow colour; the total porosity is highly variable in the examined samples, ranging from 9% to 43% by volume; thus, porosity cannot be useful to discriminate the samples from the different quarrying sites.

The chemical and mineralogical analyses reveal that the rocks collected from the Acquabona quarries are quite pure limestones with a dolomite content < 5%, whereas those from the Livorno outcrops are prevalently dolostone samples. The terrigenous fraction of the analysed samples can be described as a mixture of quartz ± plagioclases ± K-feldspar ± clay minerals ± Fe-oxides and hydroxides ± heavy minerals, and results on average more abundant in the Livorno samples (2 wt%) in respect to those from the Acquabona area (4 wt%).

The rocks coming from the Acquabona quarries are mostly represented by lithotypes referable to the Porifera biofacies, with subordinate biocalcarenites. On the contrary, in the Livorno area a peculiar lithotype at this time named *Pycnodonta* calcarenite dominates, while the Porifera biofacies is very scarce. The examined samples do not reveal evidences of bioconstructions with *Porites* coral colonies as instead reported by Bartoletti et al. (1986) in the Acquabona quarries; this fact could be ascribed to the quarrying and antropic activities (developed after the 1986) that removed the upper and middle portion of the *Calcari dell'Acquabona* member where the *Porites* bioconstructions were frequent. The lithotypes analyzed in this paper, if not representative of all the different lithofacies recognized in the past literature, are comparable to those commonly employed in Rosignano Marittimo, Livorno, Pisa and surrounding area.

The highest content of dolomite in the samples from the Livorno outcrops could be related to the large amount of fossil bivalve *Pycnodonta* shells here found and to a possible increasing of Mg percentage in the original aragonite-calcite multilayered shell. Further analyses of these shells would be required to corroborate these suggestions according to the data reported by Aal et al. (1987) for the Cretaceous *Pycnodonta* shells.

The physical properties of the Acquabona Limestones are poorly correlated with the chemical and mineralogical properties of the stone, with the notable exception of real density that correlates with dolomite content.

The uniaxial compressive strength values of the Acquabona Limestones, depending on rock porosity and subordinately on its dolomite content, indicate that these stones are from moderately weak to moderately strong rocks, according to the classification suggested by Smith (1999), and they are lower than those measured on other building stones used in the western Tuscany (e.g. Maiolica and Nummulitico limestones, Macigno sandstone, Apuan and Mt. Pisano marbles).

The collected data highlighted the main differences useful to discriminate the Acquabona Limestones coming from the three sampling areas. The rocks coming from the Acquabona quarries differ from those of the Antignano area on the basis of macroscopic features and bioclastic content and from those of the Ardenza ex-Mt. Tignoso on the basis of the dolomite content. The appreciable technical properties of the Acquabona Limestones prompted their widespread use from the Middle Age to the recent times, as building and ornamental stones. Furthermore, the chemical and mineralogical characteristics of the rocks from the Acquabona quarries favoured the use of the quite pure limestone as a natural raw material for the chemical industry.

Acknowledgements

The authors are grateful to two anonymous reviewers for their helpful suggestions, which improved the paper significantly.

References

Aal A.A., Mohammed R.M. and Rezk A.T. (1987) - Chemical composition of some Senonian bivalvian shells and its significance in palaeoecological studies, in the area of Abu Roash, Egypt. *Journal of African Earth Sciences*, 6 (2), 127-132.

Barsotti G., Federici P.R., Giannelli L., Mazzanti R. and Salvatorini G. (1974) - Studio del Quaternario livornese, con particolare riferimento alla stratigrafia ed alle faune delle formazioni del Bacino di carenaggio della Torre del fanale. *Memorie Società Geologica Italiana*, 13, 425-495.

Bartoletti E., Bossio A., Esteban M., Giannelli L., Mazzanti R., Mazzei R., Salvatorini G., Sanesi G. and Squarci P. (1983) - Carta geologica del Comune di Rosignano Marittimo. S.EL.CA., Firenze.

Bartoletti E., Bossio A., Esteban M., Mazzanti R., Mazzei R., Salvatorini G., Sanesi G. and Squarci P. (1986) - Studio geologico del territorio comunale di Rosignano Marittimo in relazione alla carta geologica alla scala 1:25000. In: La Scienza della Terra, nuovo strumento per la lettura e pianificazione del territorio di Rosignano Marittimo. *Quaderni Museo Storia Naturale di Livorno*, 6 (1), 33-128.

Bartolini C., Berlato S. and Bortolotti V. (1975) - Upper Miocene shallow-water turbidites from western Tuscany. *Sedimentary Geology*, 14, 77-122.

Boccaletti M., Coli M., Eva C., Ferrari G., Giglia G., Lazzarotto A., Merlanti F., Nicolich R., Papani G. and Postpischl D. (1985) - Considerations on the seismotectonics of the Northern Apennines. *Tectonophysics*, 117, 7-38.

Boccaletti M., Cerrina Feroni A., Martinelli P., Moratti G., Plesi G. and Sani F. (1992) - Late Miocene-Quaternary compressive events in the Tyrrhenian side of the Northern Apennines. *Annales Tectonicae*, 6, 214-230.

Bossio A., Esteban M., Giannelli L., Longinelli A., Mazzanti R., Mazzei R., Ricci Lucchi F. and Salvatorini G. (1978) - Some aspects of the Upper Miocene in Tuscany. 4th Messinian Seminar, Rome, Field Trip Guidebook, 1-88.

Bossio A., Bradley F., Esteban M., Giannelli L., Landini W., Mazzanti R., Mazzei R. and Salvatorini G. (1981) - Alcuni aspetti del Miocene superiore del Fine. *IX* Convegno della Società Paleontologica Italiana, 21-63.

Bossio A., Mazzanti R., Mazzei R. and Salvatorini G. (1986) - Analisi micropaleontologiche delle formazioni mioceniche, plioceniche e pleistoceniche dell'area del Comune di Rosignano M.mo. *Quaderni Museo Storia Naturale di Livorno*, 6 (1), 129-170.

Bossio A., Costantini A., Lazzarotto A., Liotta D., Mazzanti R., Mazzei R., Salvatorini G. and

Sandrelli F. (1993) - Rassegna delle conoscenze sulla stratigrafia del neaoautoctono toscano. *Memorie Società Geologica Italiana*, 49, 17-98.

Bossio A., Esteban M., Mazzanti R., Mazzei R. and Salvatorini G. (1996) - Rosignano reef complex (Messinian) Livornesi Mountains, Tuscany, Central Italy. In: Franseen E.K., Esteban M., Ward W.C., Rouchy J.M. (Eds), Models for Carbonate Stratigraphy from Miocene Reef Complexes of Mediterranean Regions. SEPM Society for Sedimentary Geology, 277-294.

Bossio A., Foresi L.M., Mazzanti R., Mazzei R. and Salvatorini P. (1997) - Note micropaleontologiche sulla succesisone miocenica del torrente Morra e su quella pliocenica del bacino dei fiumi Tora e Fine (Provincie di Livorno e Pisa). *Atti Società Toscana Scienze Naturali*, Memorie A, 104, 85-134.

Bossio A., Foresi L.M., Liotta D., Mazzanti R., Mazzei R., Salvatorini G. and Squarci P. (1999) - Riordino delle conoscenze sul bacino neogenico del Tora-Fine (Toscana, Italia). *Atti Società Toscana Scienze Naturali*, Memorie A, 106, 1-16.

Chevalier J.P. (1961) - Recherches sur les Madréporaires et les formations récifales miocènes de la Méditerannée occidentale. *Mémoires de la Société Géologique de France*, Nouvelle Série, 40 (93), 1-252.

Choquette P.W. and Pray L.C. (1970) - Geologic nomenclature and classification of porosity in sedimentary carbonates. *Bulletin of the American Association of Petroleum Geologists*, 54, 207-250.

De Stefani C. (1911) - Sunto geologico dei Monti Livornesi, Pliocene e post-Pliocene. *Atti Società Toscana Scienze Naturali*, Memorie A, 27, 15-48.

Dunham R.J. (1962) - Classification of carbonate rocks according to depositional texture. In: Ham W.E. (Ed.) Classification of carbonate rocks. American Association of Petroleum Geologists, Memoir 1, 108-121.

EN 1926, 1999. Natural stone test methods - Determination of compressive strength.

EN 1936, 1999. Natural stone test methods - Determination of real density and apparent density, and of total and open porosity.

EN 13755, 2001. Natural stone test methods - Determination of water absorption at atmospheric pressure.

Esteban M. (1978) - Significance of the Upper Miocene reefs in the Eastern Mediterranean. 4th Messinian Seminar, Rome, Field Trip Guidebook, 1-88.

Esteban M. (1979) - Significance of the Upper Miocene coral reefs of the Western Mediterranean. *Palaeogeography, Palaeoclimatology, Palaeoecology*, 29, 169-188.

Esteban M. (1996) - An overview of Miocene reefs from Mediterranean areas: general trends and facies models. In: Franseen E.K., Esteban M., Ward W.C. and Rouchy J.M. (Eds), Models for Carbonate Stratigraphy from Miocene Reef Complexes of Mediterranean Regions. SEPM Society for Sedimentary Geology, 3-54.

Flugel E. and Steiger T. (1981) - An upper Jurassic sponge-algal buildup from the Northern Frankenalb, West Germany. In: Toomey D.F. (Ed.), European Fossil Reef Models. SEPM Special Publication, 30, 371-397.

Franzini M. (1993) - Le pietre toscane nell'edilizia medioevale della città di Pisa. *Memorie Società Geologica Italiana*, 49, 233-244.

Franzini M., Leoni L. and Saitta M. (1975) - Revisione di una metodologia analitica per fluorescenza-X, basata sulla correzione completa degli effetti di matrice. *Rendiconti della Società Italiana di Mineralogia e Petrologia*, 31(2), 365-378.

Franzini M. and Lezzerini M. (1998) - Le pietre dell'edilizia medievale pisana e lucchese (Toscana occidentale). 2. I calcari selciferi del Monte Pisano. *Atti Società Toscana Scienze Naturali*, Memorie A, 105, 1-8.

Franzini M. and Lezzerini M. (2003) - The stones of medieval buildings in Pisa and Lucca provinces (western Tuscany, Italy). 1 - The Monte Pisano marble. *European Journal of Mineralogy*, 15, 217-224.

Franzini M., Lezzerini M. and Mannella L. (2001) - The stones of medieval buildings in Pisa and Lucca (western Tuscany, Italy). 3 - Green and white-pink quartzites from Mt. Pisano. *European Journal of Mineralogy*, 13, 187-195.

Franzini M., Lezzerini M. and Marandola F. (2002) - The stones of medieval buildings in Pisa and Lucca provinces (western Tuscany). 4 - "Agnano" breccias from Mt. Pisano. *European Journal of Mineralogy*, 14, 447-451.

Franzini M., Gioncada A. and Lezzerini M. (2007) - Le pietre dell'edilizia medievale pisana e lucchese (Toscana occidentale). 5 - La Maiolica ed il

Nummulitico della bassa valle del fiume Serchio. *Atti Società Toscana Scienze Naturali*, Memorie A, 112, 43-50.

Fuchs, T. (1874) - Relazione di un viaggio geologico in Italia. *Bollettino del Regio Comitato Geologico Italiano*, 5.

Giannelli L., Mazzanti R., Mazzei R., Salvatorini G. and Sanesi G. (1982) - Nuove osservazioni sul Quaternario di Livorno. Centro Livornese di Studi Archeologici, 30-61.

Giannini E. (1955) - Osservazioni sulla geologia del bacino della Fine e delle colline fra Rosignano Marittimo e la valle della Cecina. *Bollettino della Società Geologica Italiana*, 74, 297-316.

Giannini E. (1962) - Geologia del bacino della Fine (Provincie di Pisa e di Livorno). *Bollettino della Società Geologica Italiana*, 81, 99-224.

Giannini E. and Tongiorgi M. (1959) - Osservazioni sulla tettonica neogenica della Toscana Marittima. *Bollettino della Società Geologica Italiana*, 77, 147-170.

Langella R. (2001) - Caratteristiche chimiche, mineralogiche, fisiche ed impieghi del Calcare dell'Acquabona (membro della formazione del Calcare di Rosignano). Unpublished MD Thesis, Univ. of Pisa, 212 pp.

Lazzarotto A., Mazzanti R. and Nencini C. (1990) - Geologia e morfologia dei Comuni di Livorno e Collesalvetti. *Quaderni Museo Storia Naturale di Livorno*, 11 (2), 1-85.

Leone G., Leoni L. and Sartori F. (1988) - Revisione di un metodo gasometrico per la determinazione di calcite e dolomite. *Atti Società Toscana Scienze Naturali*, Memorie A, 95, 7-20.

Leoni L., Lezzerini M. and Saitta M. (2008) - Calcolo computerizzato dell'analisi mineralogica quantitativa di rocce e sedimenti argillosi basato sulla combinazione dei dati chimici e diffrattometrici. *Atti Società Toscana Scienze Naturali*, Memorie A, 113, 63-69.

Manzoni A. (1874) - Aggiunta di notizie e considerazioni a: Fuchs, T., Relazione di un viaggio geologico in Italia. *Bollettino del Regio Comitato Geologico Italiano*, 5.

Ruggieri G. (1956) - I lembi miocenici del Livornese nel quadro della tettonica dell'Appennino. *Atti Accademia delle Scienze dell'Istituto di Bologna*, Serie 11, 3.

Smith (1999) - Stone: Building stone, rock fill and armourstone in contruction. Geological Society London, Engineering Geology Special Publications, 16.

Stefanini G. (1956) - Calcare di Rosignano. In: Lexique Stratigraphique International, 1 - Europe, (11), Italia.

Vantaggi M. and Baldanza A. (2006) - The rich sponge levels in the Lower Pliensbachian of the Umbria-marche Apennines: birth and death. Palaeoecological evidences of a bacterial attack. In: Coccioni R. and Marsili A. (Eds) - Proceedings of the second and third italian Meetings on Environmental Micropaleontology. Grzybowski Foundation Special Publication, 11, 91-101.

Submitted, June 2011 - Accepted, September 2011