

Article

Pietra Alberese: Building Material and Stone for Lime in the Florentine Territory (Tuscany, Italy)

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Abstract: The *Pietra Alberese* is a marly limestone belonging to the Ligurian series (Monte Morello Formation of Eocene age). It is a material rarely mentioned in the historical Florentine architecture because the *Pietraforte*, the stone of the Medieval Florence and the *Pietra Serena*, the stone of the Renaissance, were the main lithotypes commonly used in those periods. Nevertheless, the *Pietra Alberese* has been widely utilized to build the town, because it is the only limestone cropping out in this part of Tuscany allowing the production of lime. In Prato and Pistoia, the *Pietra Alberese* was also used as stone (e.g., ashlar) in the structures and façades of many public and religious buildings. In this work, the geological setting and a mineralogical, petrographic and physical characterization of *Pietra Alberese* used as building stone are proposed together with a discussion about its durability. Moreover, the different compositional and macroscopic characteristics of two lithotypes (namely the *sasso alberese* and *sasso porcino*) utilized to produce the two types of lime used in the local traditional architecture (*calcina dolce* and *calcina forte*) are highlighted.

Keywords: *Pietra Alberese*; Tuscany; marly limestone; lime; vernacular building material; conservation

1. Introduction

1.1. General Information

In the northern Apennines and in Tuscany, traditionally the term *Alberese* has been used to mean all the marly limestones belonging to different successions of the Ligurian tectonic units (see Section 1.2). Therefore, the term *Alberese* stone was generally used in the lithological sense, without having a clear stratigraphic significance. These ambiguities have been resolved in the last decades with the attribution of the *Alberese* stone ss. to the Monte Morello Formation (Eocene age) belonging to the Morello tectonic Unit. The name “Monte Morello Formation” comes from the locality close to Florence where this marly formation shows the typical outcrop.

The Tuscan naturalist Targioni Tozzetti [1] in his *Relazioni d’alcuni viaggi fatti in diverse parti della Toscana* (Report on some excursion carried out in different parts of Tuscany) described the *Alberese* as a more or less fine-grained stone, grey to hazelnut in color in the fresh cut, that becomes lighter due to alteration, with conchoidal fracture and including frequent calcite veins (Figure 1a). He explains that the name *Alberese* derives from the presence of “small tree figures” (‘tree’ is *albero* in Italian) due to concentrations of iron oxides and manganese in the form of dendrites (Figure 1b).

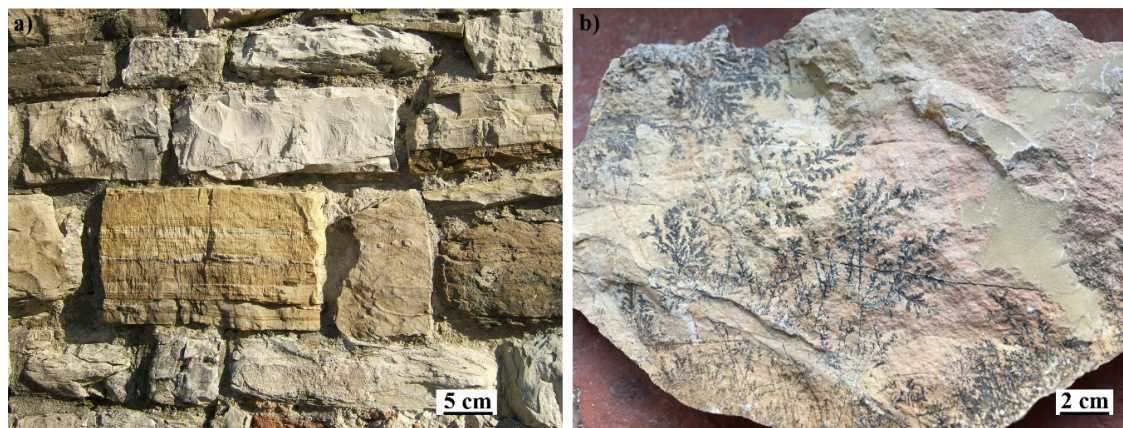


Figure 1. (a) Certosa of Florence: masonry in *Pietra Alberese* with conchoidal fractures and frequent calcite veins; (b) *Pietra Alberese* with the presence of “small tree figures.”

Together with the *Pietra Serena* and *Pietraforte* sandstones, this is the third important and well known lithotype which crops around the basin Florence-Prato-Pistoia. It can be found in Mt. Morello (northwest of Florence), in the Calvana ridge (north of Prato) and in the hills around Pistoia. Small outcrops are located south of Florence, near Grassina and Galluzzo and in the west (Soffiano, Scandicci, Lastra a Signa) (Figure 2) [2]. In Tuscany, important outcrops are also present in the Chianti Mountains, in Casentino, in Val Tiberina and outside Tuscany in Val Marecchia (Montefeltro-Marche) and in the Tolfa Mts. (Northern Latium) [2].

The *Pietra Alberese* is a material rarely mentioned in the historical Florentine architecture because the *Pietra Serena* (the stone of the Renaissance) and the *Pietraforte* (the stone of medieval Florence), were the main building stone materials used in those periods. However, it is necessary to underline that the building of the town would not have been possible without the *Pietra Alberese*, because it is the only limestone in this territory making possible the production of lime. Instead, in Prato and Pistoia, the *Pietra Alberese* was used both for the production of lime and as stone material in the structures and façades (e.g., as ashlar) of many public and religious buildings.

The purpose of this work is to illustrate the traditional use of this stone as a building material, as a raw material to produce lime and as a material in the artistic production. Furthermore, the compositional and physical characteristics of the two varieties used in the production of lime (one of which is also the variety used as a building material) are investigated.

1.2. Geological Setting of *Pietra Alberese*

The typical *Pietra Alberese* belongs to the Eocene Mt. Morello Formation of the Calvana Supergroup [3] or Morello Tectonic Unit [4,5]. It sedimented in the Liguria-Piedmont Ocean opened between the European (Sardinia–Corsica block) and the Adriatic margin during Early–Middle Jurassic times. The Morello tectonic Unit represents the more eastern palaeogeographic Ligurian succession particularly of the so-called External Ligurids or Helminthoid Flysch Units. In this frame, the Mt. Morello Formation is one of the youngest (Early Middle Eocene) calcareous-marly Helminthoid flysches, mostly of Late Cretaceous–Early Paleocene age. In particular, the External Ligurids represents the final stages of the filling of the residual part of the Ligurian oceanic basin in subduction since the Late Cretaceous.

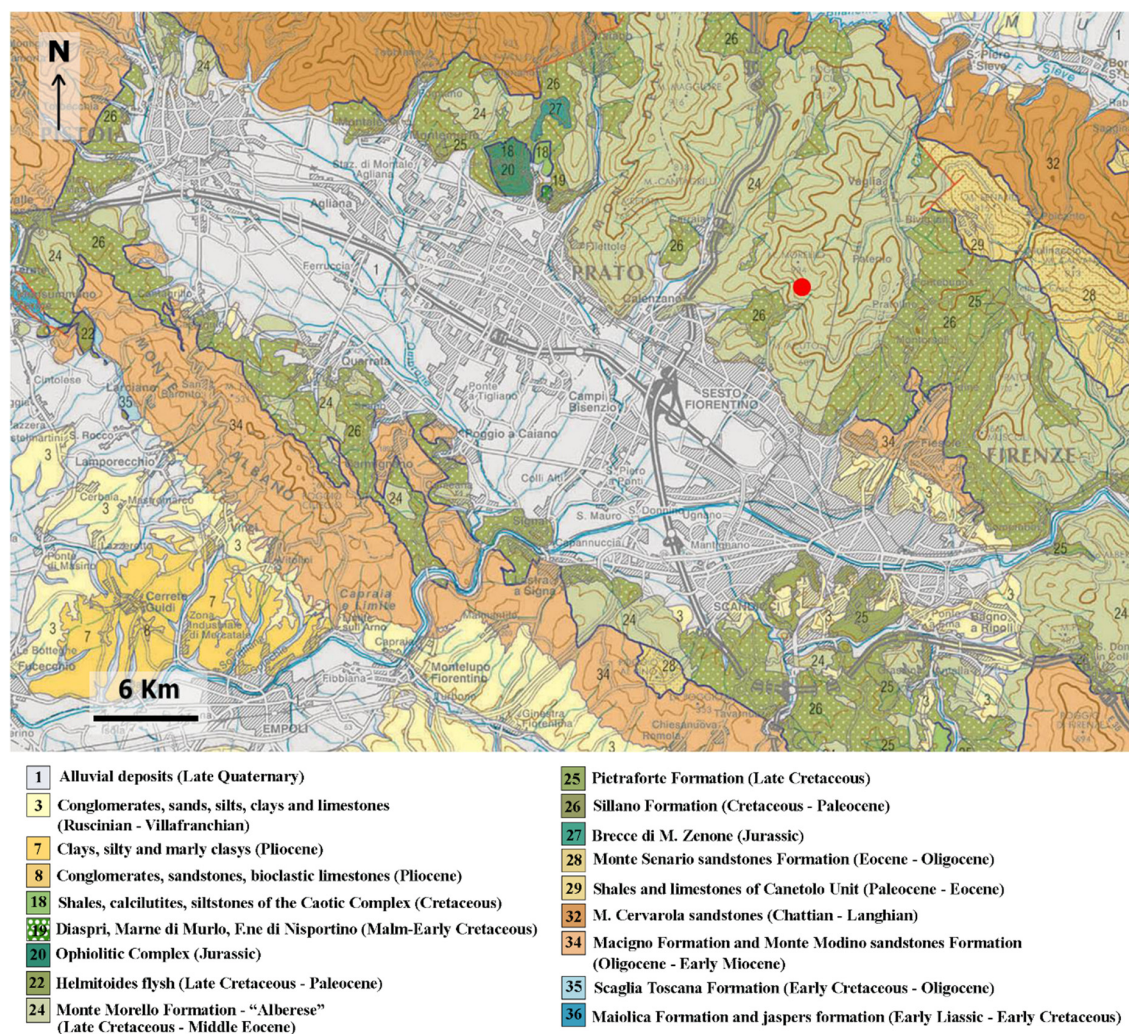


Figure 2. Geological map of the basin Florence-Prato-Pistoia with indication of the sampling area (red dot) (geological map 1:250,000, modified after Carmignani [2]).

The stratigraphic succession of the Calvana Tectonic Units includes, below the Mt. Morello Formation, a basal complex constituted by the Late Cretaceous–Early Eocene Sillano Formation with shales and calcareous-siliceous and minor arenaceous interbeds that include the arenaceous bodies of the *Pietraforte* Formation. The lowermost part of the Unit is exposed only near Figline di Prato, with basal serpentized peridotites and Jurassic gabbro that underlie a volcanic (pillow basalts) and Middle/Late Jurassic to Early Cretaceous sedimentary cover (from the base, Mt. Alpe Cherts, Calpionella limestone, Palombini shales and limestone). The stratigraphic succession of Mt. Morello Formation is closed by the Eocene shaly-marly “Pescina shales”.

The Mt. Morello Formation is made up of a sequence of marly limestones with minor marly and calcareous marly intercalations (Figure 3) [3,6,7]. In particular, the marly limestones are light grey to hazelnut in color, but whitish if weathered, and characterized by conchoidal fractures. The beds are a few centimeters to some meters in thickness, and rarely enclose bands and nodules of grey to black cherts. The minor marly and calcareous marly intercalations are represented by grey to dark grey calcareous marlstones and marlstones with “soap”-type lenticular splitting whose thickness is from a decimeter to about 15 m. The fossiliferous content of the two lithotypes is generally in the range of 6–20% with respect to the micritic-marly groundmass. Locally, grey decimetric (maximum 40 cm thick) biocalcarene beds at the base of the marly beds and rare dark grey shaly and brown grey, middle- to fine-grained sandstones also occur. The latter are generally quartz-rich sandstones with minor

feldspar grains and metamorphic lithic fragments in a micritic–micaceous matrix and an abundant sparitic cement (30–40%) according to [8]. Paleocurrents at the base of the calcarenitic and arenaceous beds point to a source located to NW [6,9,10]. The Lower to Middle Eocene (Lutetian) fossiliferous content in the calcareous-marly beds consists of microforaminifera (e.g., *Globorotalia* and *Globigerina* and calcareous nannofossils, sometimes with reworked Late Cretaceous and Paleocene species), whereas in the calcarenitic beds, macroforaminifera (e.g., *Nummulites*, *Alveolina* and *Discocyclina*) are also present [5,6]. The thickness of the formation is at least 700 m. The depositional environment is an oceanic basin and in particular the outer part of a calcareous-marly turbiditic system likely placed above the CCD (Calcite Compensation Depth) and fed by overall intrabasinal pelagic sources.



Figure 3. Mt. Morello Formation, made up of an alternance of limestones and marly limestones (light grey to hazelnut in color with conchoidal fracture) and minor marly and calcareous marly intercalations (grey to dark grey color with “soap”-type lenticular splitting).

1.3. Historical Use of Pietra Alberese as Building Material

One of the first descriptions of the use of *Alberese* in Florentine architecture comes from the Florentine Dominican Father Agostino del Riccio [11], who, in his manuscript *Istoria delle Pietre* (History of the Stones), reports that this stone was utilized in the surroundings of Florence, particularly as mill stone, while in Florence it was seldom used. Actually, the first use of *Pietra Alberese* was made by the Etruscans, as it is possible to observe it in the tombs of Mula and Montagnola in Sesto Fiorentino, located six miles northwest of Florence [12]. The Romans used it (both as stone ashlars and for the production of lime) in the aqueduct built in the 1st century B.C. that started in Val di Marina near Calenzano (about 7 miles northwest of Florence) and reached the center of Florence, collecting water from all the streams present on Monte Morello slopes [13,14]. Unfortunately, now it is almost completely destroyed. Furthermore, archaeological findings confirm the presence of *Alberese* as slabs of certain streets of the town, and this is in accordance with Villani’s *Nuova Cronica* (second book), in which the author underlined that part of the main streets of Florence were paved (glazed, he writes), particularly in front of important buildings [13,15]. Nevertheless, the use of this lithotype in the Florentine architecture is negligible with respect to the *Pietra Serena* and *Pietraforte* sandstones. The few examples are: the river pebbles in the *filaretto* masonry of the Torre dei Visdomini in Via delle Oche and in the Torre della Pagliazza in Piazza Santa Elisabetta; two long strips in the pavement of the Basilica di Santa Maria Novella and in the Cappellone degli Spagnoli (sited in the cloister of the same convent); the paving of the churchyard of the Basilica della Santissima Annunziata (Figure 4a);

rare elements in the decorated pavement of the Cattedrale di Santa Maria del Fiore (Figure 4b) and in the portal of Chiesa dei Santi Apostoli.



Figure 4. (a) Paving of the churchyard of the Basilica della Santissima Annunziata (beginning 17th century); (b) pavement of Cattedrale di Santa Maria del Fiore; (c) Certosa of Florence (14th century); (d) lintel in *Pietra Alberese* in a medieval house of Sesto Fiorentino (Florence); (e) traditional paving with slabs of *Pietra Alberese* in a courtyard of Sesto Fiorentino (Florence); (f) gable of the Chiesa di San Martino in Sesto Fiorentino (Florence) (13th century).

This sporadic use can be explained by the distance of the outcrops of this lithotype from the town while, in the case of *Pietraforte*, the quarries were a few hundred meters away, on the hills close to the left bank of Arno river. Furthermore, it must be remembered that, unlike the *Pietraforte*, the *Pietra Alberese*, in all its varieties, is a material difficult to work. In fact, the processing to obtain regular blocks from this lithotype is quite expensive because it takes so much time to quarry and requires expert stonecutters. Indeed, the material is very hard and tends to chip. Nevertheless, in the shaping of the stone ashlar, it is possible to take advantage of the beds more suitable in thickness, such as those lower than 30 cm.

The use of the *Pietra Alberese* is instead widespread in the surrounding of Florence. Six kilometers south of the town, toward Siena, it was employed as a building material in the Certosa of Florence (14th

century) (Figure 4c), while eastward it has been used in the Vallombrosan church of S. Michele a S. Salvi, as well as in many parish churches of the Florentine countryside like Abbazia di S. Bartolomeo a Ripoli, Pieve di S. Pietro a Ripoli, S. Maria a Quarto, S. Donnino a Villamagna, S. Tommaso a Baroncelli, S. Maria all'Antella, S. Francesco all'Incontro and Spedale del Bigallo. Northwestwards, it can be found in the churches of S. Stefano in Pane, S. Donato in Polverosa and S. Andrea a Brozzi. Another important village is Sesto Fiorentino, located at the slopes of Monte Morello, where the stone has been widely used as building material in dressed stones, roughly shaped blocks, pebbles, for lintels (Figure 4d), jambs, thresholds, sills, slabs for paving of courtyards (Figure 4e), stair steps, water channels [16]. The Churches of San Martino (Figure 4f), San Lorenzo al Prato, Santa Maria a Quinto, the frames of the openings in Villa Gerini and the medieval houses of Borgo Morello, are examples of the use of this lithotype. Finally, few kilometers west of Sesto Fiorentino, the fortified village of Calenzano is completely built in *Pietra Alberese*. It is to underline that all the above-mentioned churches and buildings in the surroundings of Florence are located near to outcrops of *Pietra Alberese*. Moving to Prato, 20 km northwest of Florence, the *Pietra Alberese* is the main building material because it is localized close to the slopes of the Calvana ridge, where the stone crops out extensively. In Prato, the use of *Pietra Alberese* reached a great importance in the Middle Ages as demonstrated in the Emperor Castle (1237–1245) whose imposing walls are in dressed stones (Figure 5a) as well as in the most recent part of the Palazzo Pretorio, added in the 14th century (Figure 5b). The Cattedrale di Santo Stefano (12th–14th century) in Pisan-Romanic style has an external cladding in alternating bands of serpentinite and *Pietra Alberese* (Figure 5c). However, it must be specified that some of the stone ashlar, precisely those with a yellowish alteration patina, could be associated with the siliceous limestone (lower Cretaceous) of the Calpionella Limestone Formation, present in the basal part of the Morello Tectonic Unit cropping out in Figline di Prato village (see Geological Setting, paragraph 2).

Additionally, the Renaissance masterpiece of the Chiesa di Santa Maria delle Carceri, designed by Giuliano da Sangallo at the end of the 15th century, with Greek cross plan, is clad with *Pietra Alberese* and serpentinite decorations. The same duotone serpentinite—*Pietra Alberese*—can be also found in the portals of the churches of S. Francesco, S. Domenico and S. Niccolò. The city walls are also completely built in *Pietra Alberese*, both in roughly shaped blocks and pebbles [17]. In Pistoia, sited 16 km northwest of Prato, the *Pietra Alberese* is not the main building material because close to the town there are important outcrops of *Pietra Serena* sandstone, but this limestone was utilized as dressed stone in civil buildings and in the more important Romanic religious buildings such as the Cattedrale di S. Zeno (12th–13th century) (Figure 5d) and the lower part of the façade of S. Andrea (12th century), prototype of the Pistoia Romanic style [18]. Furthermore, in Pistoia, the *Pietra Alberese* is associated in duotone with the green serpentinite. At present, the use of *Pietra Alberese* in the civil architecture in Tuscany has almost disappeared.

1.4. Historical Use of *Pietra Alberese* as Stone for Lime

As first reported by Targioni Tozzetti [1], the *Pietra Alberese* was the only calcareous stone that could be used to produce the lime in the territory from Florence to Pistoia. The evidence of the historical use of *Alberese* as a raw material for the production of lime in the Florence-Pistoia territory is given by the presence, in ancient mortars, of numerous lumps referred to under burnt rock fragments which show the petrographic characteristics of this marly limestone (Figure 6). The marly limestone beds were selected according to the main macroscopic features (hardness, grain size, color in the fresh cut, type of fracture) because it was considered empirically that these features would influence the type and quality of the lime produced.



Figure 5. (a) Emperor Castle in Prato (13th century); (b) masonry in *Pietra Alberese*, left side of Palazzo Pretorio in Prato (14th century); (c) Cattedrale di Prato (12th–14th century) in Pisan-Romanesque style, with external cladding in alternating bands of serpentinite and *Pietra Alberese*; (d) Cattedrale di San Zeno (12th–13th century) in Pistoia.

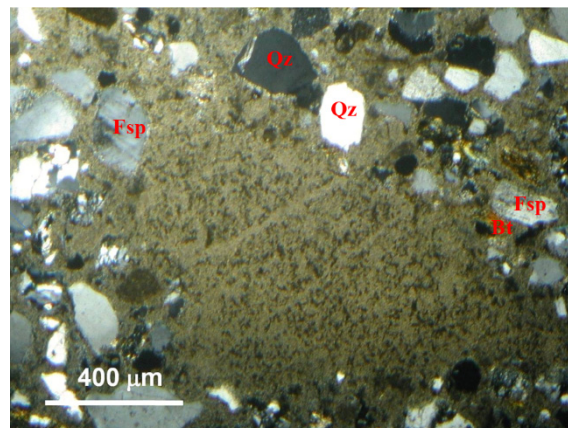


Figure 6. Image in thin section at the optical microscope (xpl) of a bedding mortar from the Prato city walls where at the center is evident an under burnt fragment of *Pietra Alberese* (Qz—quartz; Fsp—feldspars; Bt—biotite).

According to these features, Filippo Baldinucci [19] describes some varieties of *Pietra Alberese*: e.g., the *sasso albano*, *sasso coltellino*, *sasso porcino* and *sasso alberese*. In particular, the *sasso porcino*, dark-colored rock in the fresh cut (Figure 7a), was used to produce a lime called *calcina forte* (strong lime), utilized for the bedding mortars (Figure 8a) while the *sasso alberese*, light-colored in fresh cut (Figure 7b), was burned to produce the *calcina dolce* (sweet lime), a lime used for plastering mortars (Figure 8b).



Figure 7. (a) Variety of *Pietra Alberese* named *sasso porcino*, dark-colored rock in the fresh cut; (b) variety of *Pietra Alberese* named *sasso alberese*, light-colored in fresh cut.

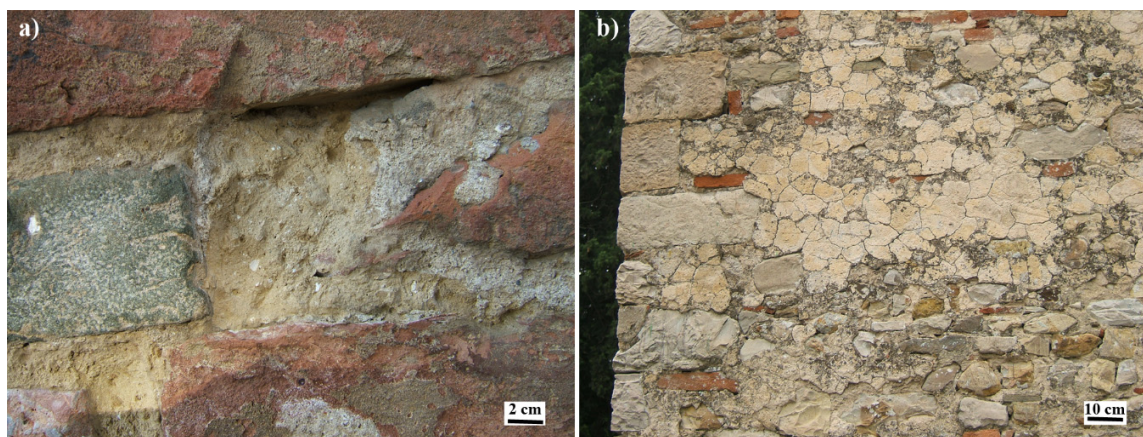


Figure 8. (a) Bedding mortar of a rural building in the surroundings of Florence; (b) old render in a rural house in the village of Quinto Alto, near Florence.

The examination of the archival documentation and scientific literature of the 17th–18th centuries has therefore shown a remarkable abundance of empirical knowledge in the selection of the stone material for the preparation of lime [20]. Today, we know that the color and aspect of the fresh cut of these marly limestones depends on the amount of clay, higher in dark stones, which gives rise to partially hydraulic limes. The burning of the light-colored variety gives rise to an air-hardening binder [21]. In Florence, both the *Pietra Alberese* taken from the outcrops and as pebbles present in the beds of the Arno and Mugnone rivers (the so-called *frombole d'Arno*) [11] were used as raw material. The lime kilns were located not far from the limestone quarries and were not unlike those used by the ancient Romans. The little quarries are not well documented, and a survey would be necessary starting from archive data. On the contrary, the quarries that supplied the cement plants are very well visible in the territory with the wounds caused to the landscape (Figure 9a).



Figure 9. (a) Cement plants, ancient kilns and recent *Pietra Alberese* quarries (yellow dots) in the Florentine territory: (1) kilns of the 19th century in La Querce (Prato); (2) cement plant in Settimello (Calenzano); (3) kiln of the 19th century in Vaglia; (4) localization of an ancient Florentine kiln of Ponte a Ema; (5) cement plant of Monte Pilli; (6) cement plant of Rignano sull'Arno; (7) cement plant of Passo dei Pecorai (Greve) (after Google Earth, modified); (b) kiln of the 19th century in Vaglia.

The kilns operated discontinuously (normally a kiln was activated once or twice a month). The average production of a kiln, such as that of Ponte a Ema (Florence, Figure 9a) used at the end of the 1500s for the production of the lime to be used in the construction of the Ponte S. Trinita, was around 90 bushels (52,623 liters) for each “firing” [14,22]. These traditional kilns had a cylindrical or conical trunk structure and in their basal part was located the fire chamber which was filled with lumber and bundles while in the upper part the limestone was placed in small pieces. The quicklime (CaO) was obtained by burning the limestone at 850–900 °C. Porous light clods were obtained. At this point, the production process followed two different directions depending on whether an almost pure *Pietra Alberese* limestone (*sasso alberese*) was burned for the production of *calcina dolce* or a more marly *Pietra Alberese* limestone (*sasso porcino*) for the production of *calcina forte*. In the first case, the clods of quicklime were wetted (slaking process) with excess water to obtain the lime putty, a dense suspension (1.2–1.4 kg/L) of calcium hydroxide $\text{Ca}(\text{OH})_2$ in water (H_2O). Free water represents 45–65% of the mass. It looks like a white paste, soft, plastic, and oily to the touch, with thixotropic behavior. This lime putty was accumulated in pits or containers, covered by a film of water or damp sand, and left for months or years in order to complete the hydration of CaO , to improve plasticity and workability and favor carbonation after use. In the case of burning the *sasso porcino*, the slaking took place by water sprinkling in order to obtain a powder to be kept in a dry place and to be used later.

Another possibility was to use an excess of water but in this case the putty had to be used immediately without being aged, otherwise it would have set before use.

Some kilns of the second half of 19th century which produced hydraulic lime are still left, although they are no more active, like those of La Querce (Prato) and Vaglia (Figure 9a,b). More recently, the marly levels of *Pietra Alberese* have been used for the industrial production of modern hydraulic binders (Portland cement). The following manufacturing plants are recorded: Peruzzi in Monte Pilli near Bagno a Ripoli, Settimello near Calenzano, Sacchi at Passo dei Pecorai near Greve in Chianti, Fabbrica Toscana in Rignano sull'Arno, east of Florence. With regard to this last plant, Molinari [23] reported that “the marly limestone extracted in Rignano sull'Arno made it possible to produce a quick-setting cement, but if the stone was burned at higher temperatures and for longer times, the final product was

a slow setting cement.” Such information suggested that outcrops of dark marly limestone (rich in clay) from Rignano sull’Arno could have been used to produce, in the second half of the 19th century, a Tuscan variety of the “Natural cement” [24,25], a quick-setting hydraulic binder, obtained from burning marly limestones with a clay content variable from 22–35% and commercialized elsewhere in Europe also with the name of Roman cement [26,27]. This possibility has been investigated in Cantisani et al. [28] verifying that a particular kind of *Pietra Alberese*, rich in clay and very fine grained, could have been used to produce a kind of “Natural cement.”

1.5. The Use in the Artistic Production

The *Pietra Alberese* was also used in the artistic production thanks to the presence of a particular variety. In fact, in the fields and along the bed of the streams, it is possible to find pebbles or blocks of this stone, from hazelnut to dark brown in color, rich in sub-millimeter to millimeter-thick calcite veins, that allows a complex internal geometric subdivision of the beds into parallelepipeds or polygonal splinters. The cutting and polishing of these blocks show the presence of a microcrystalline structure with grey/grey greenish to light blue colors (similarly to images of skies and bodies of water) in the inner part, whereas the external part is characterized by small polygonal to rectangular varicolored areas (generally yellowish to brown and locally to dark red, green and violet), similar to faulted millimetric bandings, such as to evoke landscapes with ruined houses, turreted castles, trees, canyons and peaks. The varicolored banding is typically developed parallel to the external boundaries of the stone (e.g., the bedding). These areas are divided by numerous thin fractures filled by calcite or calcite + iron oxides/hydroxides veins at a high angle to the bedding or laminations and simulate fault structures. A part of the veins is cut by oxide-rich stylolites that, in turn, are crossed by later calcite veins. It is the so-called *Pietra Paesina* (Figure 10a). These stones can also be found in other geological formations of the Ligurian Units (e.g., S. Fiora Unit, Caio Flysch of the Trebbia Unit, Formation of the Vara Unit).

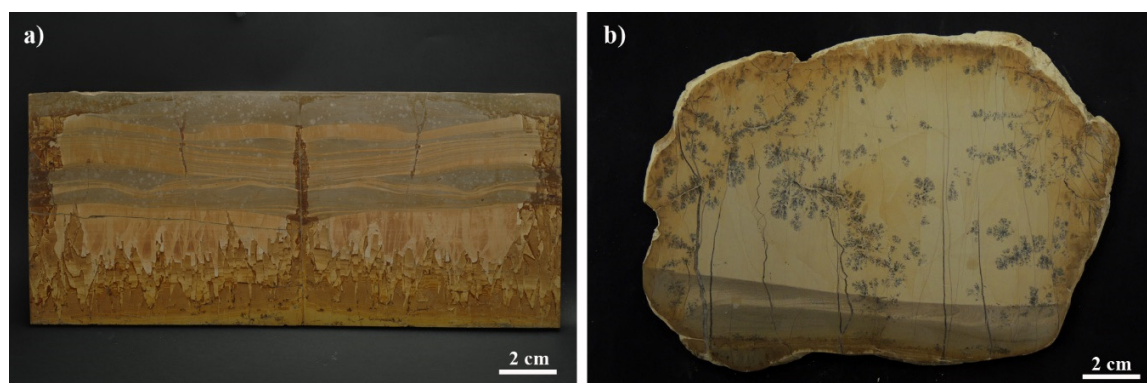


Figure 10. (a) *Pietra Paesina*, courtesy of Museum of Natural History—University Museum System University of Florence; (b) *Tigrato d’Arno*, courtesy of Fondazione Giovanni Pratesi, Figline Valdarno (Florence).

Regarding the genesis, in the past, the discontinuities between one polygon and the other were considered small faults both of direct and reverse type, but this structural association is not justifiable with any dynamic model of fracturing and deformation of the rocks. In addition, the sedimentary structures present within the beds appear without displacements or offsets in correspondence with the fractures and veins. Therefore, different hypotheses have been suggested. For some authors [29] this process developed through the infiltration of meteoric water along the fractures and then perpendicularly to them within the carbonate rocks; this process produced the “faulted stratified” structures in the external parts of the beds due to the different degree of oxidation of iron from Fe^{2+} to Fe^{3+} and a partial substitution of Mg with Ca, giving origin to the varicolored bandings.

Serra et al. [30] also pointed to the variable content of Fe and Mn oxides/hydroxides in the formation of the varicolored bandings and to the presence of three different non-tectonic generations of joints, the first two syn-diagenetic and the last one exogenic (during weathering).

Moreover, they underlined the importance of the capillary forces, variations of grain size, sedimentary structures, e.g., laminations and organic content in the different parts of the sediment during the infiltration of the fluids for producing the variable width and thickness of the banding due to iron and manganese periodical precipitation in the single polyhedral bodies. Other authors believed that the formation processes of the *Pietra Paesina* is to be associated with the tectonic forces that led to the formation of the Apennine chain [31]. In addition to the *Pietra Paesina*, the alteration of the different types of *Pietra Alberese* gave rise to other varieties of stone such as the *Lineato d'Arno* (characterized by a structure with parallel laminations, whitish to dark grey in color), the *Verde d'Arno* (when the fracturing is absent and the color is a pale green tending to grey), the *Tigrato d'Arno* (characterized by widespread bush figures made of micro beads of oxides and hydroxides of manganese) (Figure 10b) and the rare *Terra bruciata di Rimaggio* (yellow and brown with areas intensely colored in red that seem to be produced by the fire action).

The first description of *Pietra Paesina* was made by Kircher [32] in his *Mundus subterraneus*. In Tuscany, the use of this stone began at the end of the 16th century with Cosimo II de' Medici. At that time in the *Galleria dei Lavori* (Opificio delle Pietre Dure with the unification of Italy), already founded by Ferdinando I de' Medici in 1588, all types of this stone were used in the production of the so-called *commesso in pietre dure*. This is an art of ancient Florentine tradition still in use, involving the realization of a mosaic using various stones "committed together" in the inlays and in the encrustations of a furniture. Starting from the 17th century, the decorative use of the *Pietra Paesina* spread also in France, England and Germany due to the contacts that the Medici family had with the royal courts of all Europe; everywhere it was appreciated for its uniqueness and rarity. For the landscape it evokes, the *Pietra Paesina* was also called *marmo ruinario* in Italy, or *ruin marble* in England; it was called *ruinenmarmor* in Germany and its success was due to the Renaissance taste first, with Baroque and neoclassical following, for ruins and craggy landscapes.

In France, Louis XIV, the Cardinals Richelieu and Mazarino were great admirers of this stone and founded some factories with artists taken from the Medici laboratory. Among the reasons for this attraction, there was certainly the awareness of the ornamental value already present hidden inside a humble, unworked material. In addition to the simple use of the polished stone, e.g., in the varieties with wavy laminations recalling the seaside, artists began to draw little fishes, birds, boats (in the Museum of the *Opificio delle Pietre Dure* there is an exposition of suggestive marinas) up to more complex drawings [33]. The religious use of the *Pietra Paesina* in the Baroque age should also be mentioned; it stems from the idea that the Providence imprisoned the shape of the ruins in the rock for the perpetual admonition to man, *pulvis es et in pulverem reverteris* (you are dust and to dust you will return).

2. Materials and Methods

Samples of *Pietra Alberese* with different macroscopic features were taken from Monte Morello Formation, precisely in the slopes of Monte Morello, the locality of the typical outcrop (see Figure 2). The samples are characterized by a color ranging from light hazel to dark grey and with different compactness and fracturing shape to be referred to the two varieties, *sasso alberese* and *sasso porcino* (see Figure 7a,b). For each variety, 5 samples were analyzed.

A mineralogical, chemical and petrographic characterisation of samples was performed.

Mineralogical analyses of the bulk samples were carried out by X-ray diffraction (XRD), utilizing a Philips PW 1050/37 diffractometer with a Philips X'Pert PRO data acquisition and interpretation system, operating at 40 kV-20 mA, with a Cu anode, a graphite monochromator and with 2°/min goniometry speed in a scanning range between 5–70° θ for the bulk sample and 5–32° θ for the clay fraction. The diffractometer analyses were performed on the <63 μ m grain-size fraction of the bulk samples, previously crushed and powdered, as well as on the <4 μ m clay fraction, extracted after

washing and settling according to the Stokes law [34–36]. The slides of the <4 µm clay fraction were analyzed untreated, after a treatment with ethylene glycol, and after heating either at 450 °C or 600 °C.

The amount of CaCO₃ was determined with a gasometric method [37] using the Dietrich–Frühling calcimeter. The percentage of calcite was calculated with reference to a calibration curve constructed by linking the volume of CO₂ developed by acid attack of the powdered rock with the amount of pure CaCO₃.

The amount of the total clay minerals has been evaluated as a difference with respect to the amount of calcite determined with the previously reported gasometric method.

The samples were reduced to a thickness of 30 µm and observed under a light transmitted microscope. For the petrographic observation in thin sections, a Zeiss Axioscope A.1 microscope, with a camera to obtain images and a dedicate software for the image elaboration and measuring of main characteristics of materials (AxioVision), was used.

Thermogravimetric analyses (TGA) were also performed. The thermogravimetric analysis measures the change in the percentage by weight of a material when heated, as a result of the decomposition of the various components. The sample was analyzed in special ovens where the atmosphere can be controlled.

In many instances, the carbonates may decompose below 600 °C, due to compounds, which promote decomposition, especially soluble salts, or other compounds, or even because of defects in the crystal lattice [38].

Analyses were performed by heating 3.70 mg of powder of the samples with a Perkin Elmer Pyris 6 TGA. The program set provided the heating of the sample from 100 to 580 °C with a heating rate of 40 °C per minute. Once the temperature of 580 °C was reached, the sample was left for 2 minutes at this temperature, followed by a heating rate of 1 °C per minute and, from 730 to 950 °C, by a rate of 40 °C per minute. When the temperature of 950 °C was reached, the sample was left at this temperature for 1 minute.

The chemical composition of the samples was obtained through X-ray fluorescence using a Philips PW 1480 instrument. The elements were determined using a Rh anode in accordance with Franzini method [39]. Accuracy and precision were verified using international standards (NIM-G, G2, W2, GS-N, GH, W1, GA, AC-E). For the particularity of the carbonatic matrices, a calibration using international carbonate standards (NCS DC 60108a, NCS DC 60110, NCS DC 14021a, NCS DC 14014a, 400, 401, 402, 393, SGT-BCS) was performed.

Further, the main physical parameters of *Pietra Alberese* samples were evaluated. Samples of 1.5 × 1.5 × 3 cm were dried at 60 °C and the dry weight W_d was determined. The real volume V_r and the bulk volume V_b were determined using, respectively, a Quantachrome helium pycnometer and a Chandler Engineer mercury pycnometer. Then the samples were dipped into deionized water and weighed after saturation (constant wet weight W_w). With these data, the following parameters, real density (γ), bulk density (γ_s) and total porosity ($P\%$), were determined:

$$\gamma = W_d / V_r \quad (1)$$

$$\gamma_s = W_d / V_b \quad (2)$$

$$P\% = \frac{(V_b - V_r)}{V_b} \times 100 \quad (3)$$

The effective (or water accessible) porosity ($P_w\%$) was determined using a hydrostatic balance (Mettler Toledo balance). The following formulas were applied, based on Archimedes' Law:

$$V_w = \frac{(W_w - W_d)}{\gamma_w} \quad (4)$$

$$V_a = \frac{(W_w - W_h)}{\gamma_w} \quad (5)$$

where Wd is the dry weight, Ww is the wet weight at the saturation point, Wh is the hydrostatic weight, Va is the volume of samples, Vw is the volume of water inside the pores, γ_w is the density of water at the measurement temperature; the effective porosity ($P_w\%$) was calculated as:

$$P_w\% = \frac{Vw}{Va} \times 100 \quad (6)$$

3. Results

The analysed samples were gathered in the two varieties *sasso alberese* and *sasso porcino*, which show different macroscopic characteristics: the *sasso alberese* variety includes samples which are light hazel/hazel in color with a red ochre patina in the exposed surface, a smooth fresh cut surface and a conchoidal fracture; the *sasso porcino* variety includes samples with a whitish bluish alteration of color of the surface, a grey/dark grey color of fresh cut surface, a rough shape, and a scaly fracture.

The mineralogical data of the two varieties are reported in Table 1: the main differences are related to the calcite and clay minerals amount. The calcite content ranges are from about 88% to 70% and the clay minerals from about 7% to 26%, proving the presence of limestone (*sasso alberese*) and marly limestone (*sasso porcino*) lithotypes.

Table 1. Main mineralogical composition (by XRD and calcite by gasometric analysis) expressed as weight percentage (wt %).

Sample	Calcite	Quartz	Feldspars	Clay Minerals
<i>sasso alberese</i>	89 ± 2	traces	traces	8 ± 5
<i>sasso porcino</i>	70 ± 3	traces	traces	27 ± 8

In addition, other differences can be related to the clay minerals association: the *sasso alberese* variety shows the presence of illite, chlorite and chlorite-vermiculite, while in the *sasso porcino* variety there are kaolinite, illite, chlorite and illite-smectite (Table 2).

Table 2. Clay mineral association (Kln = kaolinite, Ill = illite; Chl = chlorite; Ill-Sme = illite-smectite; Chl-Vrm = chlorite-vermiculite) of the samples belonging to *sasso alberese* and *sasso porcino* varieties. The amount is expressed as weight percentage (wt %).

Sample	Kln	Ill	Chl	Ill-Sme	Chl-Vrm
<i>sassoalberese</i>	-	50	25	-	25
<i>sassoalberese</i>	-	10	40	-	50
<i>sassoalberese</i>	-	25	30	-	45
<i>sassoalberese</i>	-	15	35	-	50
<i>sassoalberese</i>	-	20	30	-	50
<i>sassoporcino</i>	30	45	15	10	-
<i>sassoporcino</i>	15	55	10	20	-
<i>sassoporcino</i>	30	45	15	10	-
<i>sassoporcino</i>	40	25	25	10	-
<i>sassoporcino</i>	15	60	5	20	-

Microscopically, the samples belonging to the *sasso alberese* variety appear as fine-grained micrites with small percentages of fossils (3–5%). These latter ones range from 40 to 80 µm in size and consist of *Globigerinae*, *Globorotaliae*, and calcified *Radiolarian*, within a mainly micritic/microsparitic mass. So, these samples can be classified as mudstone [40] or micrite [41]. The material is often crossed by numerous thin veins of spatic calcite and sometimes has weak concentrations of ochre pigments in dendritic structure (Figure 11a).

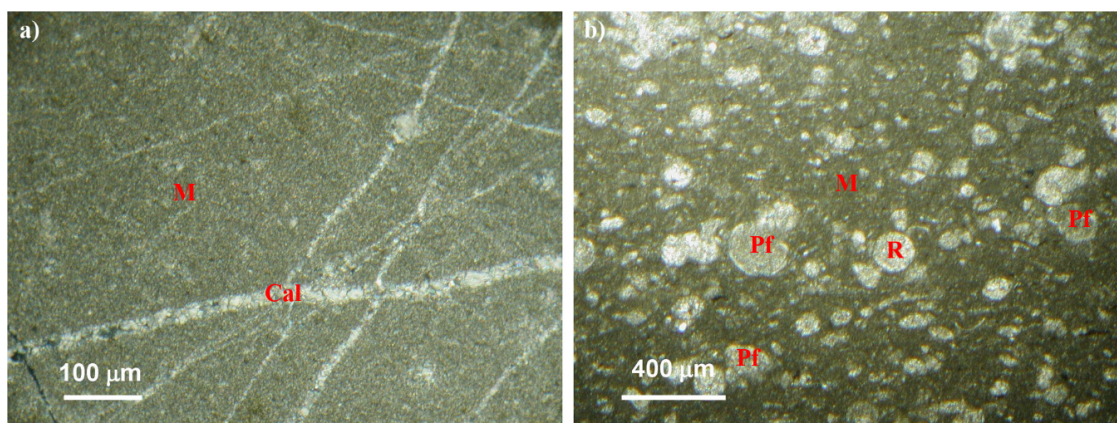


Figure 11. (a) Image in thin section at the optical microscope (xpl) of a sample belonging to the *sasso alberese* variety characterized by a fine-grained micrite (M) with small percentages of fossils and veins of calcite (Cal); (b) image in thin section at the optical microscope (xpl) of a sample belonging to the *sasso porcino* variety, with a percentage of fossils ranging between 20 and 25% consisting of *Globigerinae*, *Globorotaliae* (Pf = Planktonic foraminifera) and *Radiolarian* (R).

The samples belonging to the *sasso porcino* variety, instead, appear as biomicrites with a percentage of fossils ranging between 20 and 25%. Their size ranges from 40 and 200 µm, and consist of *Globigerinae*, *Globorotaliae* and *Radiolarian* of which the shell shows a microsparitic to sparitic structure (Figure 11b). These samples can be classified as wackestone [40] or biomicrite [41]. A dispersion of semi-opaque materials referable to clay components is often observable in the micritic mass. There are also sparitic lenses with a thickness of about 40 µm and small clay pockets with a thickness of 60 µm (possible intraformational pelitic clasts). Muscovite, quartz and feldspar are sometimes present in the carbonatic framework with dimensions of 40 µm. The stone is crossed by rare veins of calcite, sometimes anatomising, containing concentrations of ochre pigments.

TGA analysis indicates that the decomposition of the calcium carbonate takes place at 686 °C with a mass loss of 38.6% for the *sasso alberese* variety and at 684 °C with a weight loss of 37.3% for the *sasso porcino* variety.

The XRF analysis was performed only on a representative sample of each group (1 and 2). The data reported in Table 3, highlight, above all, differences related to the amount of CaO and SiO₂ between the two groups.

Table 3. Chemical composition (XRF) expressed as weight percentage (wt%) (bdl = below detection limit).

Samples	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃ TOT	MnO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	SO ₂	L.O.I.
<i>sasso alberese</i>	12.4	bdl	1.7	0.9	0.1	1.0	45.4	0.1	0.3	bdl	bdl	38.0
<i>sasso porcino</i>	15.7	0.2	5.1	1.7	bdl	1.6	39.2	bdl	0.9	0.3	0.04	35.0

For the physical parameters, the samples belonging to the *sasso alberese* variety show a lower value of total open porosity (4.7% the mean value) and even lower of water accessibly porosity (1.6% mean value) with respect to samples belonging to the *sasso porcino* variety (mean value of open porosity 6.2%, and 3.6 of water accessibly porosity (Table 4). It is important to underline that the total open porosity includes micro meso and macro porosity, therefore it is always higher than water accessible porosity.

Table 4. Physical parameters (γ = real density; γ_s = bulk density; P = total open porosity; P_w = water accessible porosity).

Sample	γ (g/cm ³)	γ_s (g/cm ³)	$P\%$	$P_w\%$
<i>sasso alberese</i>	2.69 ± 0.01	2.56 ± 0.01	4.7 ± 0.5	1.6 ± 0.7
<i>sasso porcino</i>	2.69 ± 0.02	2.53 ± 0.02	6.2 ± 0.4	3.6 ± 0.2

4. Discussion

The mineralogical, petrographic, chemical, and physical analyses performed on the two varieties of *Pietra Alberese* highlight that the samples, already distinguishable with the naked eye for color and type of fracture, have also different characteristics. The content of calcite (higher in the *sasso alberese* variety), the amount of clay minerals (higher in the *sasso porcino* variety), the paragenesis of the clay minerals, the petrographic textures, the total open porosity, and water accessible porosity values are the main parameters useful to distinguish them.

In general, the *Pietra Alberese*, belonging to the *sasso alberese* variety, utilized for monumental buildings, shows a very high durability against the action of atmospheric agents, as demonstrated by the good condition of conservation of ashlar exposed since the Middle Ages. This excellent behavior can be explained by the lower value of the water accessible porosity that is $1.6 \pm 0.7\%$ and by the micritic texture which guarantees a remarkable cohesion because the single calcite grains are strictly joined thanks to a mild recrystallisation in the diagenetic phase.

Sometimes slight exfoliation phenomena can be observed such as those present in the external wall of the left nave of the Cattedrale di Pistoia, particularly when the ashlar is put in place perpendicularly to the stratification (Figure 12a). Moreover, cases of fracturing along calcite veins are reported like that present in the frame of the gable of San Francesco in Prato (Figure 12b). In these cases, dangerous situations can arise because large fragments can detach, as it happens for the *Pietraforte* sandstone [42,43].

A chromatic alteration is instead always present with a whitening (Figure 12c) or with the formation of a yellowish patina (Figure 12d).

Despite this high durability observed in high-quality masonries, in vernacular architecture, sometimes ashlar with evident decay phenomena like “soap” flaking, are evident (Figure 12e). In fact, these ashlar come from marly beds, therefore they are characterized by greater sensitivity towards water due to the high amount of clay minerals (variety with characteristics similar to *sasso porcino*). The presence of the clay minerals is also the great problem which affects the durability of the *Pietra Serena*, as discussed in Fratini et al. [44]. Therefore, it is necessary to underline how the petro-physical study of the building stone materials can help to improve the state of the art about the problems of conservation and to establish the more suitable restoration interventions [42–47].

Regarding the *Pietra Alberese* used as stone for lime, [48,49], it is possible to obtain a different kind of lime, from an air-hardening lime, (from burning slightly marly limestones—*sasso alberese*) to hydraulic lime until a cement (from burning marly limestone, *sasso porcino*) [28]. In relation to the hydraulic limes, it is worth mentioning the exceptional qualities of the bedding mortars utilized for the building of the Cupola di Brunelleschi [50] and Campanile di Giotto [51].

Therefore, the binder produced by burning the stone with a greater amount of clay minerals develops, after setting, calcite, hydrated calcium silicates, amorphous carbonate and vaterite able to confer to the mortar good performance and durability. This binder shows the presence of the same non-hydrated calcium silicate (C2S) and calcium alumino-silicate (CAS) phases observed in the natural cement (e.g., so-called “Natural cement”).

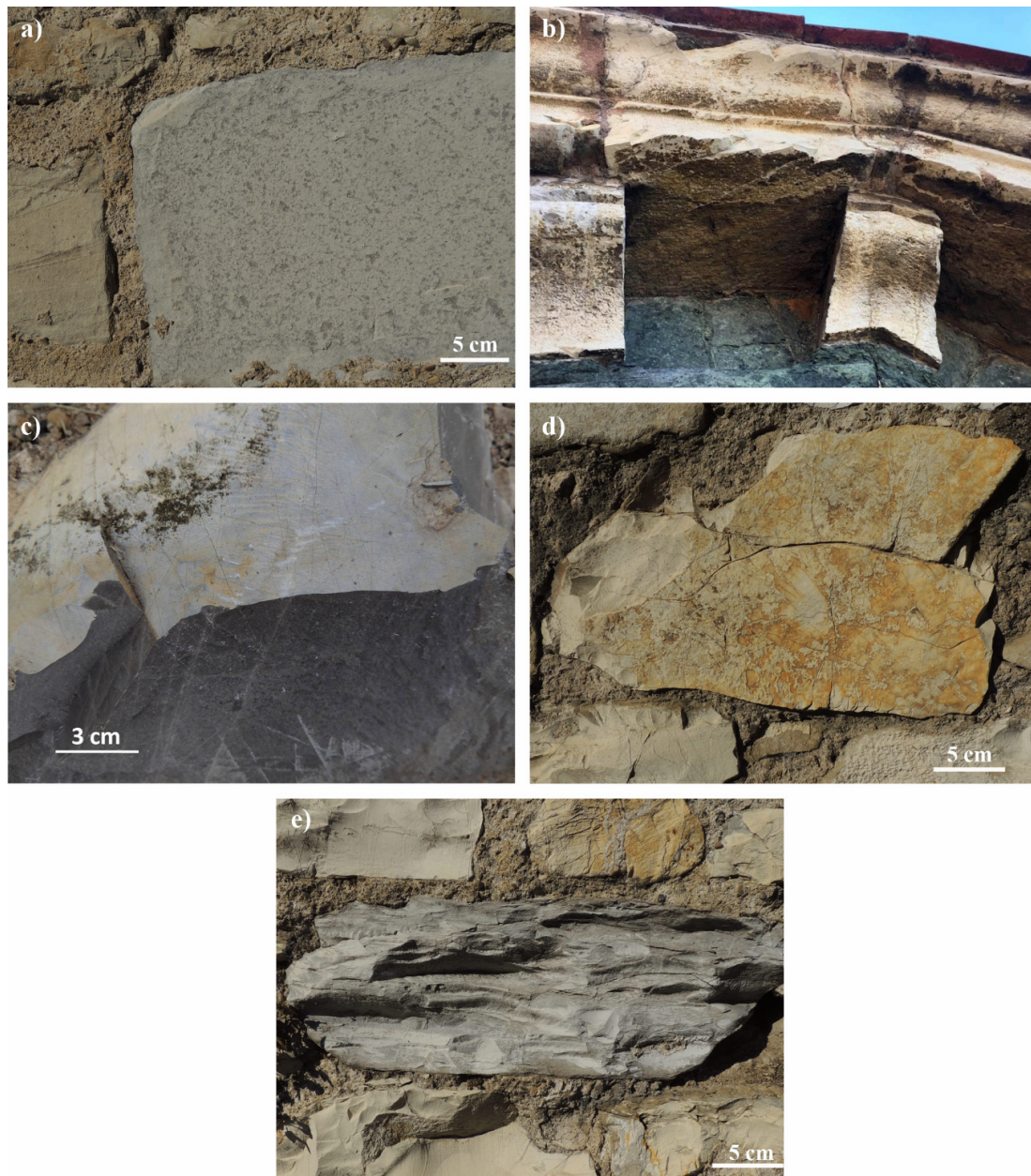


Figure 12. (a) Very slight exfoliation developed in *sasso alberese* variety, when the ashlar is put in place perpendicularly to the stratification (Cattedrale di San Zeno—Pistoia); (b) fracturing along calcite veins in *sasso alberese* variety, the frame of the gable of San Francesco in Prato (courtesy of A. Casciani and P. Rosa); (c) evident whitening in *sasso porcino* variety, with respect to the fresh cut; (d) formation of a yellowish patina in *sasso alberese* variety; (e) “soap” flaking” decay in an ashlar realized in a marly bed of *sasso porcino* variety.

5. Conclusions

Mineralogical-petrographic, chemical, and physical characterisation has been carried out on two different varieties of *Pietra Alberese* used to produce lime, the *sasso porcino* and the *sasso alberese*. The first one, dark-colored in the fresh cut, shows a greater amount of calcite and a higher content of clay responsible for higher water accessible porosity (3.6%); it was used to produce a lime called *calcina forte* (strong lime) with hydraulic properties, employed in the bedding mortars. The *sasso alberese*, light-colored in the fresh cut, was burned to produce the *calcina dolce* (sweet lime) used for plastering; it shows a higher amount of calcite and a lower amount of clay with a corresponding

lower water accessible porosity (1.6%). These characteristics make this variety compact and durable so that it was used also as building material in the villages surrounding Florence, in Prato, where it is the main building material and in Pistoia, where it was utilized together with *Pietra Serena* in public and religious buildings. The high durability is demonstrated by the ashlar exposed since the Middle Ages that do not show decay phenomena except a strong chromatic alteration with a whitening or with the formation of a yellowish patina.

This research confirms the importance played by the mineralogical-petrographic, chemical, and physical characterisation of the stone materials of the historical architecture in order to understand their use, the role played in the urban development, and the durability towards atmospheric agents in view of conservation purposes.

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