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The Source Materials for Lime Production in the Monte Pisano Area (NW Tuscany, Italy)

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Abstract. In the Monte Pisano area (north-western Tuscany, Italy) several limestones outcrop and some of them are carbonate-rich rocks that were used for air-hardening lime or hydraulic lime production. Since Roman times, carbonate rocks outcropping in the Monte Pisano area have been used for that purpose. Monte Pisano is a mountainous system of modest size that is part of the Tuscan Apennine, located in the north-western part of Tuscany, and it separates the two cities of Pisa and Lucca. As an obvious consequence of the presence of good source rocks useful for the production of lime, in the surroundings of Monte Pisano there was a great use of carbonate rocks for the production of aerial lime and hydraulic lime. In fact, the monumental buildings in the Middle Ages were built making extensive use of binding materials obtained by firing rocks belonging to formations of the Tuscan metamorphic sequence: the Monte Pisano marble and the Selciferous Limestone. Several famous monuments in Pisa's Miracle Square and in Lucca's historical centre were built by using air-hardening lime and hydraulic lime obtained by firing these rocks. The aim of this work is to characterize samples from the Monte Pisano quarries, where the aforementioned carbonate-rich stones were quarried to produce air-hardening lime and hydraulic lime, by mean of chemical, mineralogical and petrographic studies and by determining their physical and mechanical properties. These same properties will also be determined on handmade mortar samples made up of self-produced binders and normalised sand to evaluate the best uses, and the optimum time and temperature of stone firing.

1. Introduction

Air and hydraulic lime are general terms for varieties of lime used to make mortars, which can set through carbonation (reabsorbing carbon dioxide from the air) or through hydration, respectively. Hydraulic lime provides a faster initial set and higher compressive strength than air-hardening lime. There are several studies on the effects of time and temperature of limestone calcination [1][2][3], the carbonation of hydrated lime [4][5], the physicochemical characteristics and mechanical properties of aerial [6] and natural/artificial hydraulic lime mortars [7][8][9], the influence of size and mineralogical composition of aggregate and of the use of additives on the microstructure of mortars and



corresponding physical and mechanical properties [10][11][12][13] and the evaluation of the hydraulic character of mortar binders [14][15][16][17][18].

Finding materials for the production of lime near the place of use has always been of fundamental importance for the construction of masonry buildings. Near the city of Pisa, the source materials useful for the production of lime are present in the mountains north of the city. In fact, on the slopes of Monte Pisano they have been extracted and worked in large quantities in two quarries near the town of San Giuliano Terme. Monte Pisano is a mountainous system of the modest size of the Tuscan Apennine located in the NW Tuscany, separating Pisa from Lucca. The geological-stratigraphic structure of the Monte Pisano is fundamentally determined by the tectonic overlap of two main units: the Monte Serra Unit [19], consisting of Triassic clastic Verrucano sediments and the Unit of Santa Maria del Giudice, also known as Metamorphic Tuscan Nappe [19][20][21][22]. In the last unit, two carbonate-rich formations, the Monte Pisano marble (MPM) Fm. and the Selciferous Limestone (SEL) Fm., were used to produce binding materials from ancient times until the middle of the last century.

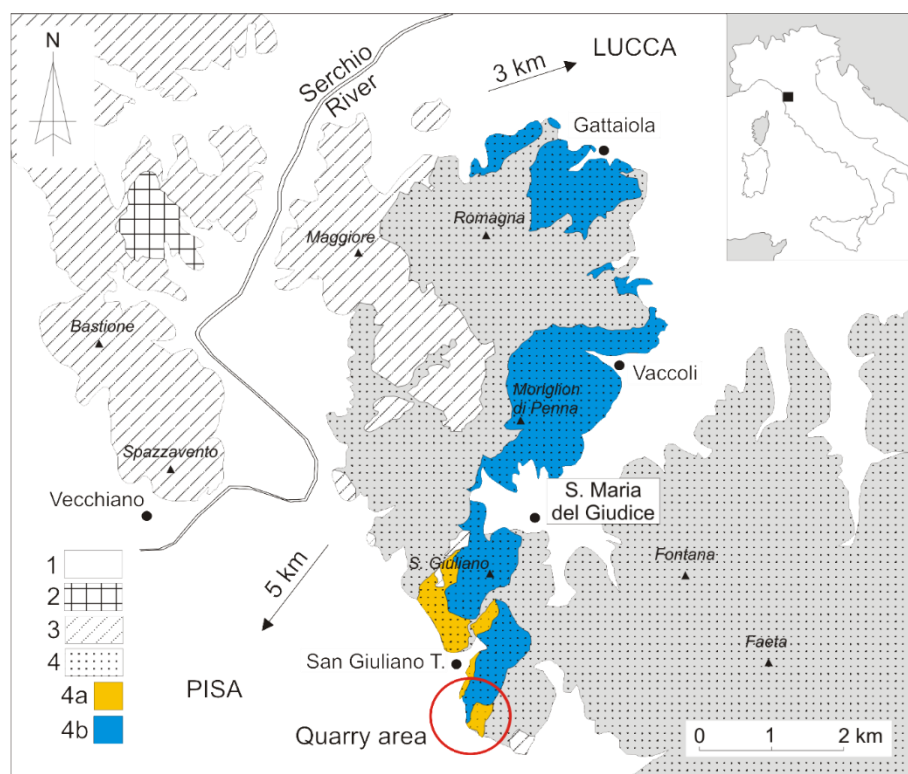


Figure 1. Geological sketch map of the Monte Pisano area (modified from Giannini & Nardi [2]). 1) Quaternary; 2) Liguride Units s.l.; 3) Tuscan Nappe; 4) S.M. del Giudice and Monte Serra Units; 4a) Selciferous Limestone Fm.; 4b) Monte Pisano marble Fm.

In literature, there are detailed studies on the MPM and SEL samples, and chemical and mineralogical compositions of these rocks are reported [23][24]. The rocks of the Monte Pisano marble Fm. consist of approximately 99% by weight of calcite and dolomite on average, and over 91% in all the analysed samples. The dolomite and calcite contents range respectively from 0.95 to 90.14 wt% and from 6.95 to 98.53 wt% [3]. The dolomite-rich levels can be found mainly in the lower part of the formation, where calcareous and dolomitic layers alternate, the less rich ones in the upper part of the formation [3]. The average dimensions of the dolomite grains vary from 50 to 100 μm and up to 200 μm in veins, while those of calcite from 35 to 80 μm . Non-carbonate minerals are muscovite,

quartz and neogenic albite. Among the accessory minerals, there are iron oxides and hydroxides that frequently grow around the dolomite crystals or form thin veins crossing the carbonate matrix [3]. The rocks of the Selciferous Limestone Fm. are mainly made up of calcite, while dolomite is rare and, if present, always in small quantities (<3.5 wt%). With the exception of the flints (made up almost entirely of quartz), the other components are quartz (<1-8%), white potassium mica (<2-15%), chlorite (<1-1.5%), albite (<1-1.5%) and traces of K-feldspar, actually found only in some samples. The most common accessory minerals are iron oxides and hydroxides; small tourmaline grains were optically identified in the insoluble residue to acid attack [4]. In the marly levels, muscovite, in addition to calcite, is the most abundant mineralogical component and can reach up to 35% of the total sample, while chlorite never exceeds 4% [4]. In this study, samples of both MPM Fm. and SEL Fm., belonging to the Metamorphic Tuscan Nappe and outcropping in the Monte Pisano area, were sampled and examined to determine the chemical and mineralogical composition and to understand whether the limes produced by heating at relatively low temperature (950°C) were hydraulic or not. For these purposes the mineralogical and elemental compositions of the rocks were determined by XRF, XRD and TG-DSC analyses. Moreover, after heating the rocks at relatively low temperature and slaking them, the mortars produced mixing these binding materials with fluvial aggregates in a 1:3 ratio were examined for measuring the main physical and mechanical properties.

2. Materials and methods

2.1 Sampling and raw materials for binder production

In this work, twenty-six samples coming from two quarries opened near San Giuliano Terme on the SW slope of the Monte Pisano have been analyzed (Figure 2). The rocks extracted from the quarries belonging to the MPM Fm. and to the SEL Fm. are made of carbonate-rich materials suitable for the production of air-hardening lime and natural hydraulic lime, respectively. The samples were collected taking into account the chemical, mineralogical and petrographic characteristics provided by Franzini and Lezzerini [23][24] that studied in detail these building materials in the framework of a research on the stones of medieval buildings in Pisa and Lucca provinces [23][24][25][26][27][28][29][30].



Figure 2. Detail of the quarrying area: in the foreground, at the bottom left, the Monte Pisano white marble separated by a fault plane from the upper right Selciferous Limestone folded layers.

Fourteen samples were granulated and milled together to form a sample representative of the pure white variety of MPM and likewise twelve samples of the two varieties of SEL, six for the brown variety and the same number of samples for the grey variety. The mixed samples were used for producing up to 1 kg of lime with which to make the corresponding lime mortars and for determining the main physical and mechanical properties of the mortar specimens during the aging (from 28 up to 112 days).

2.2 Analysis of raw materials

The chemical and mineralogical compositions of the rock samples were examined through XRF, XRD and TG-DSC analyses. Major and minor chemical elements (Na₂O, MgO, Al₂O₃, SiO₂, P₂O₅, K₂O, CaO, TiO₂, MnO, Fe₂O₃) were determined by X-ray fluorescence (XRF) on pressed powder pallets utilizing an ARL 9400 XP+ sequential X-ray spectrometer under the instrumental conditions reported by Lezzerini et al. [12]. Quantitative chemical data were obtained using correction for matrix effects based on international rock standards. The precision was monitored by routinely running well-investigated in-house standards [13]. The accuracy, evaluated using international standards, ranges from 20% (Na₂O) to 1% (CaO), with a mean value of 5% for the other elements [12]. Thermogravimetric analysis (TGA) was used to evaluate the contents of volatile compounds (essentially H₂O, CO₂) in the samples. TGA was conducted in the range 20–1000°C on about 25 mg of sample, dried (silica gel as a drying agent) at room temperature for at least a week under the following experimental conditions: open alumina crucibles, heating rate of 10°C/min and 30 ml/min nitrogen gas flow. The CO₂ content was also determined by the calcimetric technique. Qualitative mineralogical compositions of the bulk sample were performed by X-ray powder diffraction (XRPD). The experimental conditions were: Bragg-Brentano geometry, Ni-filtered Cu_{Kα} radiation obtained at 40 kV and 20 mA, 5–60 °2θ investigated range, 0.02° step, 2s counting time per step. To identify the mineralogical phases in the X-ray spectra, a search/match approach (DIFFRACPlus EVA) was used by comparing experimental peaks with PDF2 reference patterns. Real density (ρ_s) was measured through an automatic He-pycnometer on ~10g of very-fine-grained powders, dried at 105 ± 5°C for 24hr, using the following experimental conditions: ultrahigh purity compressed He, target pressure of 100 kPa; equilibrium time: automatic; purge mode: 3 min of continuous flow; maximum runs: 6; number of averaged runs: the last three. Apparent density (ρ_b) and open porosity (to water), which has been measured as water absorption at atmospheric pressure in respect to weight (Ab_w) or volume (Ab_v) of the specimens, were performed on samples with a volume of about 30 cm³, as indicated by EN1936 [31]. In particular, apparent density was calculated as the ratio between the mass of the dry sample and its volume, measured by means of a hydrostatic balance on water-saturated samples [32]. Total porosity (P) and saturation index (SI) were calculated as follows: P(%) = 100·(1–ρ_b/ρ_s) and SI(%) = 100·Ab_v / P. Uniaxial compressive strength (UCS) tests were performed on at least three cubic rock specimens with side lengths about 3 cm [33]; UCS and flexural strength tests on mortar samples were performed following the method described in EN 1015-11 [34].

Hydraulicity Index (HI) and Cementation Index (CI) values were calculated to assess the hydraulicity of the limes according to Boynton [35] and Vicat [36] formula as below:

$$HI = (\%SiO_2 + \%Al_2O_3 + \%Fe_2O_3) / (\%CaO + \%MgO) \quad (1)$$

$$CI = (2.8\%SiO_2 + 1.1\%Al_2O_3 + 0.7\%Fe_2O_3) / (\%CaO + 1.4\%MgO) \quad (2)$$

2.3 Mortar preparation

Mortar prisms of dimensions 160×40×40 mm³ were prepared using lime obtained by heating at 950°C the collected samples (MPM, SLG and SLB) and sandy aggregate in a binder/aggregate ratio of 1:3. Six specimens were prepared for each binder and all of them were cured according to EN 1015-11 [34]. Compressive and flexural strengths were measured at 28, 56 and 112 days.

3. Results and discussion

In Table 1, the average chemical compositions of the analysed rocks are reported together with Hydraulicity Index and Cementation Index. The physical and mechanical data of Table 2 shows that the analysed rocks are characterized by both low porosity (< 1% by volume) and relatively high mechanical resistance from about 130 to 160 MPa.

The chemical data of Table 1 is in agreement with that published by Franzini & Lezzerini [3][4] and shows the presence of suitable raw materials for air-hardening lime (MPM samples) and for natural hydraulic lime (SLG and SLB samples).

Table 1. Average chemical compositions (wt%) of the analysed rocks (standard deviation in italics).

Sample	LOI	Na ₂ O	MgO	Al ₂ O ₃	SiO ₂	P ₂ O ₅	K ₂ O	CaO	TiO ₂	MnO	Fe ₂ O ₃	CI	HI
MPM	43,60	0,02	1,25	0,27	0,76	<0,01	0,09	53,83	0,01	0,01	0,16	0,05	0,02
(n=14)	<i>0,55</i>	<i>0,01</i>	<i>0,38</i>	<i>0,23</i>	<i>0,72</i>	<i><0,01</i>	<i>0,10</i>	<i>0,78</i>	<i>0,01</i>	<i>0,01</i>	<i>0,14</i>	<i>0,04</i>	<i>0,02</i>
SLG	41,57	0,11	0,86	0,77	3,88	0,04	0,22	51,95	0,05	0,05	0,50	0,23	0,10
(n=6)	<i>0,34</i>	<i>0,01</i>	<i>0,14</i>	<i>0,09</i>	<i>0,63</i>	<i>0,02</i>	<i>0,03</i>	<i>0,30</i>	<i>0,01</i>	<i>0,01</i>	<i>0,07</i>	<i>0,04</i>	<i>0,01</i>
SLB	38,06	0,08	1,24	2,15	9,17	0,03	0,81	47,33	0,12	0,05	0,96	0,59	0,25
(n=6)	<i>0,76</i>	<i>0,02</i>	<i>0,17</i>	<i>0,40</i>	<i>1,10</i>	<i>0,02</i>	<i>0,14</i>	<i>1,04</i>	<i>0,02</i>	<i>0,01</i>	<i>0,11</i>	<i>0,08</i>	<i>0,04</i>

LOI = Loss on Ignition at 1000°C; Fe₂O₃ = total iron expressed as Fe₂O₃; CI = Cementation Index; HI = Hydraulicity Index.

Table 2. Main physical and mechanical properties of the analysed rocks (standard deviation in italics).

Sample	ρ_s	ρ_a	Ab _w	Ab _v	P	SI	σ_c
	g/cm ³	g/cm ³	wt%	%	%		MPa
MPM	2,72	2,71	0,19	0,52	0,61	84	127
(n=14)	<i>0,01</i>	<i>0,01</i>	<i>0,06</i>	<i>0,18</i>	<i>0,18</i>	<i>6</i>	<i>13</i>
SLG	2,71	2,70	0,13	0,34	0,37	92	162
(n=6)	<i>0,01</i>	<i>0,01</i>	<i>0,05</i>	<i>0,12</i>	<i>0,12</i>	<i>6</i>	<i>19</i>
SLB	2,71	2,69	0,25	0,68	0,74	93	151
(n=6)	<i>0,01</i>	<i>0,01</i>	<i>0,05</i>	<i>0,14</i>	<i>0,18</i>	<i>5</i>	<i>14</i>

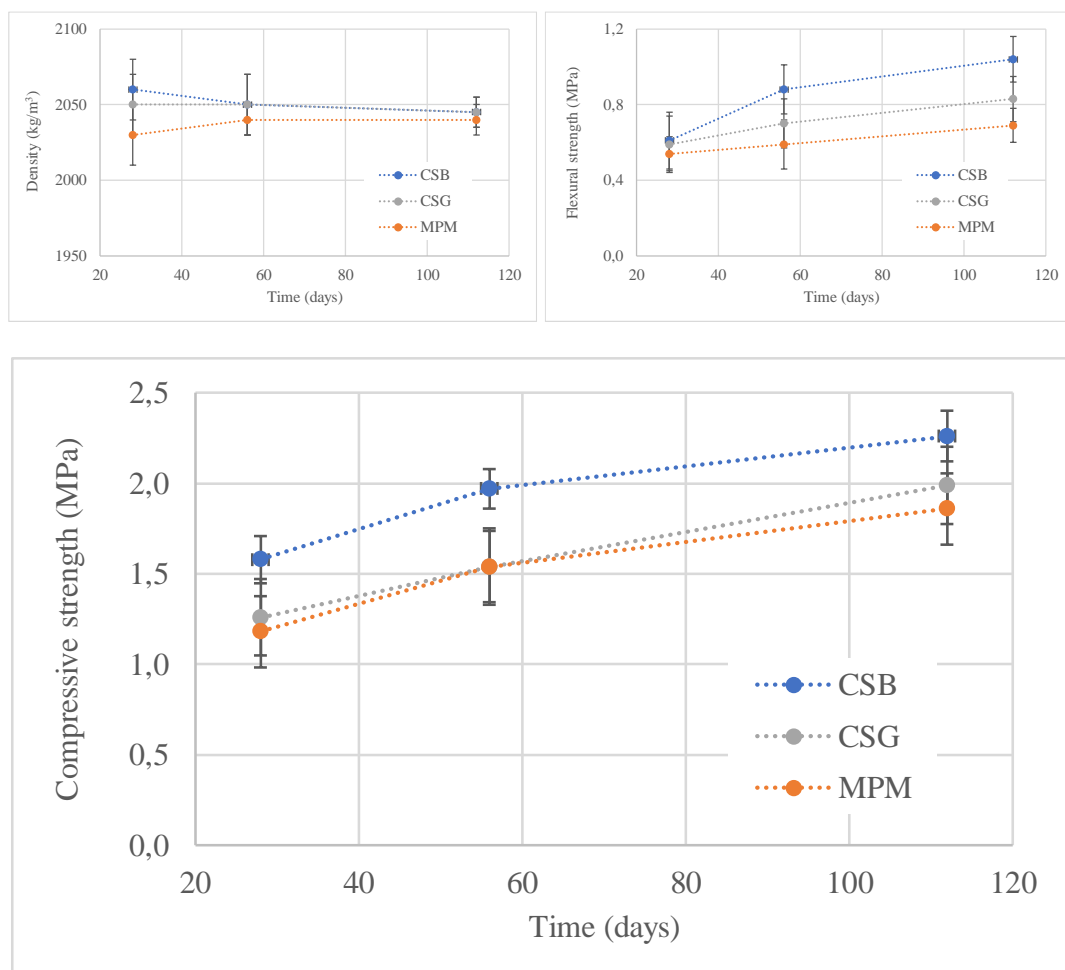
ρ_s = real density; ρ_a = apparent density; Ab_w = water absorption referred to weight; Ab_v = water absorption referred to volume; P = porosity; SI = saturation index; σ_c = uniaxial compressive strength.

According to the common classification of limes, reported by Holmes & Wingate [37] and described in Table 2, the MPM samples are useful to produce a fat lime, while SLG sample and SLB sample are raw materials for producing a slightly hydraulic lime and moderately hydraulic lime, respectively.

Table 3. Cementation Index for the various types of building limes.

Lime description	Cementation index (CI)	Amount of active clay
Fat limes	close to zero	very little clay
Slightly hydraulic limes	0.3 to 0.5	around 8%
Moderately hydraulic limes	0.5 to 0.7	around 15%
Eminently hydraulic limes	0.7 to 1.1	around 25%
Natural cement	1.7	up to 45%

After heating the rock samples at 950°C for 1, 3, 8 hours the obtained limes have been used to prepare mortars. At predetermined times, the lime mortar specimens were measured to determine their main physical and mechanical properties. As it can be seen in Figures 3, all samples show similar density (2040-2050 kg/m³) and mechanical resistance values on hardened samples according to the presence of air-hardening lime mortars and hydraulic lime mortars. In detail, flexural strengths of specimens at 28 days vary from about 0.5 to 0.6 MPa, and compressive resistance from about 1.2 to 1.6 MPa.

**Figure 3.** Density, flexural strength and compressive strength of lime mortar samples at 28, 56 and 112 days.

It is noteworthy to underline that carbonate-rich materials completely decompose to produce lime, while the other ones required more and more heating to obtain a usable product and never without residues [38][39][40]. Furthermore, it is also interesting to highlight regarding future studies on recipes for the preparation of ancient mortars that the lime produced is white when carbonate-rich rocks were used, while yellowish or yellowish-white in the case of impure carbonate rocks. Observations on the colour of the intergranular binder and especially of the lumps have been rightly observed by various authors who have studied ancient mortars produced with materials from the Monte Pisano quarrying area [8][13][18].

4. Conclusions

In this study, two carbonate-rich rocks outcropping in the Monte Pisano area were sampled and analysed for evaluating their chemical and mineralogical characteristics and physico-mechanical properties and for confirming their nature as source materials for lime production. The preliminary results of this study indicate that the binder easily obtainable by calcining stones at relatively low temperature (950°C) is essentially air-hardening lime. In fact, the calcination of impure limestones is not an easy process to carry out without suitable lime kilns and required several failed attempts before grinding finely and heating for a long time the samples over and over again. Referring to the Middle Ages and considering the kiln and fuel conditions of that time, the possibility of obtaining hydraulic lime by heating impure limestone at relatively low temperature was examined. The results show that the production of calcium silicate at a relatively low calcination temperature (950°C) is possible. Considering this result, it can be confirmed that natural hydraulic lime could be produced by using clayey limestones outcropping in the Monte Pisano area, but the difficulties related to the technological process confirm the use of both air-hardening lime and artificial hydraulic lime mortars in the buildings of Pisa and surroundings. These considerations are in good agreement with that indicated in several articles dealing with ancient mortars sampled from Pisan historical and artistic monuments that demonstrate the use of artificial hydraulic lime mortars obtained by adding pozzolanic materials to the quicklime. Further studies should be made to investigate the hydraulicity of lime under laboratory conditions by checking the flexural and compressive strengths of the mortars that were prepared using lime produced from impure limestones outcropping in the Monte Pisano area.

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