



Georesources in Cultural Heritage: the Mg/Ca Ratio in Lime as a Marker of Variations in the Exploitation of Lime Stones in the Vercelli Area (Piemonte, Italy) over the Centuries

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Abstract

Archaeological investigations in the rural settlements of the Po Valley in the Piedmont region of Northern Italy, particularly in the Monferrato area, have revealed a wide range of structures dating from the Roman to the Early Medieval periods. This rural architecture is of great heritage value, as it provides insights into the historical development of Piedmont.

This paper focuses on the analysis of lime, one of the oldest and most important building materials, used as binder of bedding mortars of three archaeological rural buildings sites dating from the Early Roman imperial Period to the Late Antique phases of medieval fortified centers of Piedmont region.

A low-cost and efficient diagnostic geochemical-based method based on the characterization of two oxides present in the lime of mortars and in carbonate rocks of the area (MgO and CaO) is presented. Exploited limestone quarries exploited often have a fairly constant chemical composition and therefore a typical geological Mg/Ca ratio. The variation in this ratio is useful for the relative dating of building walls and for identifying of geological formations and quarries possibly used during the different architectural phases. This paper focuses on this second objective: the study of potential supply areas across the ages related to the ancient communication routes.

Keywords Georesources · Archaeological research · Lime · Mortar · Quarry exploitation

Introduction

The rural settlements found in the western sector of the Po Valley (Piedmont region, Northern Italy) are characterized by a wide range of buildings and infrastructures dating back between the Roman period and the early Middle Ages. These architectural elements were characterized by wooden walls with cobblestone bases or brick fragments, parts of older and more recent walls built with cast and mortared materials, the typology of which does not allow an architectural dating.

Earlier structures were often reused, especially in the late antique (TA) and early medieval (AM) phases, to create a considerable irregularity in texture and height which prevents a chronological characterisation of the walls.

Furthermore, bricks, pebbles and stones found in the local area were often reused once a building had been demolished and/or renovated. Mortar were the sole architectural material that remained concurrent with the construction phase.

Since ancient times, mortars were an artificial and man-made product made up of natural materials typically obtained by the firing of a carbonate or gypsum. By this process, the binder forms and, only after the mixing with an aggregate and water, it hardens becoming a mortar (Pecchioni et al. 2018). Currently, mortars are defined as a mixture of binders (organic or inorganic), aggregates (mainly of fine grain size) and water, to which it is possible the addition of one or more organic or inorganic additives, in order to improve and/or control the laying conditions of the mix, its physical (e.g. porosity, water permeability) and mechanical (resistance, deformability, adherence to surfaces etc.) characteristics.

Several techniques are used to characterize mortars: wet chemical analysis, instrumental methods for characterization of inorganic and organic materials as thermal analysis (DTA, TGA, DSC) (Moropoulou et al. 1995, 2000; Pires

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and Cruz 2007; Todor 1976) and infra-red spectroscopy (FTIR) (Derrick et al. 1999), physical and mechanical testing for durability and performance assessment, radiocarbon dating (Bendisoli and Panzarasa 2022; Hale et al. 2003) and X-ray diffraction (XRD) (Montesano et al. 2022; Rispoli et al. 2024). In addition, in order to investigate the technology and supply areas, several papers focused on the study of ancient mortars (Miranda et al. 2012; Lezzerini et al. 2018; Maragh et al. 2019; Gambino et al. 2022; Milanesio et al. 2022; Cuevas et al. 2023).

Lime is undoubtedly one of the most important building and decorative materials used from ancient times to the present day. This paper deals with the study of this material, used as binder component in the bedding mortars of three rural archaeological sites, ranging from the Early Roman Imperial Period to the Late Antique periods of medieval fortified settlements. Since in Piemonte, particularly in the Monferrato area, lime was extensively used in architecture, so it was considered appropriate to integrate the archaeological studies with an analytical procedure.

This study presents a low-cost and efficient diagnostic method based on the geochemical characterization of two oxides present in the lime of mortars and in carbonate rocks of the area: MgO and CaO. The exploited limestone quarries often have a fairly constant chemical composition and therefore a typical Mg/Ca ratio of the geological formation. The chemical composition of the carbonate fractions of limestones and dolomites provides valuable mineralogical, petrographic and geological information on the environmental, lithological and chemical characteristics of the formations studied. The Mg/Ca ratio is one of the two factors, along with salinity, that controls the precipitation and structure of carbonates (Folk and Land 1975), which is why it has been assumed within the same depositional environment, and therefore at the outcrop scale, this ratio does not vary greatly.

The variation in this ratio is valuable for determining the relative age of building walls and for identifying geological formations and potential quarries used during different architectural periods. This research focuses on the study of potential resource locations in different historical periods linked to ancient transport networks.

Geographic and Geological Setting

The research area is situated in the central and eastern part of the Piedmont region (Fig. 1). In this paper three rural settlements from the Roman and medieval periods located in the plain area along the alluvial belt of the Po River—BRUSASCO, TRINO, and TICINETO (Figs. 2 and 3) were analysed (Fig. 4).

The Trino Vercellese site, located at San Michele (VC), is a settlement with a very long history, from the Augustan

period to the 13th century AD (Negro Ponzi Mancini 1999a, 1999b, 1999c).

The site of Ticineto, locality il Villaro (AL), shows a Roman rural settlement (1st–4th century AD) and a later funerary church and early medieval necropolis (Negro Ponzi Mancini 1980, 1983).

In addition, the location of Brusasco is also of great importance. Brusasco is situated on the right bank of the Po, at the junction of the Dora Baltea river, on the slopes of the Monferrato Hill. The settlement dates back to the Medieval period of the 10th and 11th centuries AD, followed by later Low Medieval and post-medieval phases (16th and 17th centuries) (Negro Ponzi Mancini 1987).

The medieval village was located close to the current hamlet of Ghiaro and was probably a rural agglomeration surrounded by a hedge or a wall, consisting of peasants' dwellings, a few craftsmen's houses, granaries, stables, a mill, an oven and some simple workshops (Negro Ponzi Mancini 1983).

Towards the south of the river belt, on the hydrographic right of the Po River, the hilly region of northern Monferrato within a strip approximately 20 km wide, has been investigated and sampled for ancient limestone quarries. In this area, limestones suitable for producing lime are present in sparse and differentiated outcrops.

The Monferrato region is a tectonic-sedimentary domain that is part of the Piemonte Tertiary Basin (BTP). This basin contains successions of Cenozoic age (Upper Eocene—Messinian) that outcrop in the hilly area of Southern Piemonte. In the Monferrato area, Alpine metamorphic units and Ligurian sedimentary units are discordantly covered by deposits of the Piedmont Tertiary Basin (BTP) (Bicchi et al. 1994, Forno et al. 2009). This basin was formed as a result of the collisional double vergence evolution of the Alpine chain (Piana and Polino 1995; Piana et al. 2017a; Mosca et al. 2010).

The BTP is delimited—to the S and SW by the arc of the western Alps ('Ligurian Alps');—to the NE by the north-western end of the northern Apennines;—to the N and NW by the deposits of the Po Valley. Based on the type of substrate, tectonic evolution and sedimentary characteristics of the successions, the BTP has been subdivided into two main tectonostratigraphic domains (Fig. 5): the Monferrato to the north and the Piedmont Tertiary Basin s.s. (composed in turn of the sectors named respectively: Collina di Torino CT, Langhe LG, Alto Monferrato and Borbera-Grue Areas, Forno et al. 2009).

The Monferrato succession's stratigraphic features exhibit significant lateral and vertical variability owing to complex Cenozoic kinematic evolution. A geological description of the Monferrato area can be provided by referring to two maps (Figs. 6 and 7).

Fig. 1 Location of the study area

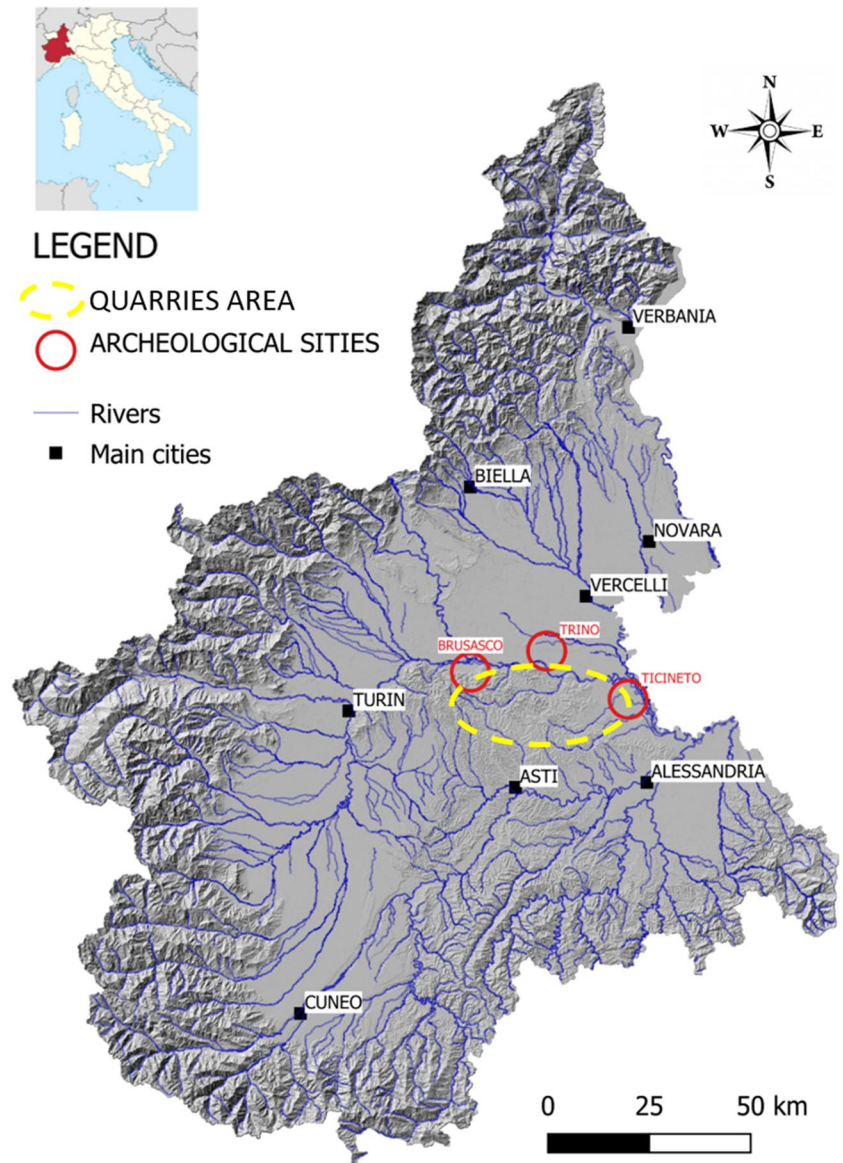


Fig. 2 a Aerial view of the Roman complex, west side, 1989 (Negro Ponzi Mancini 1999a) **b** View of the medieval building from the south (Negro Ponzi Mancini 1999a)



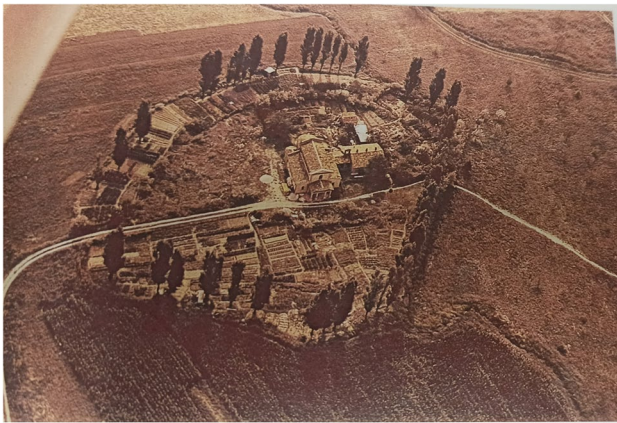


Fig. 3 Infra-red aerial view of Trino site, West side (1982) (Negro Ponzi Mancini 1999a)

The lithologies in the area mainly consist of arenaceous, arenaceous-pelitic, marly and sandy-gravelly Middle Eocene-Miocene successions (BTP) and pelitic and arenaceous Pliocene successions; conglomerate and chaotic siliceous mudstone successions (Ligurian units of Monferrato). In the past, dimension stones were extracted from the cemented arenites and greywackes of the Cenozoic sedimentary successions of the BTP (Barale et al. 2020; Piana et al. 2017b; Fig. 5).

In the study area, hilly area of "Monferrato" (Fig. 6), the geological formations and complexes show suitable rock resources for lime production.

Fig. 4 Ticineto il Villaro archaeological site (Negro Ponzi Mancini 1980)



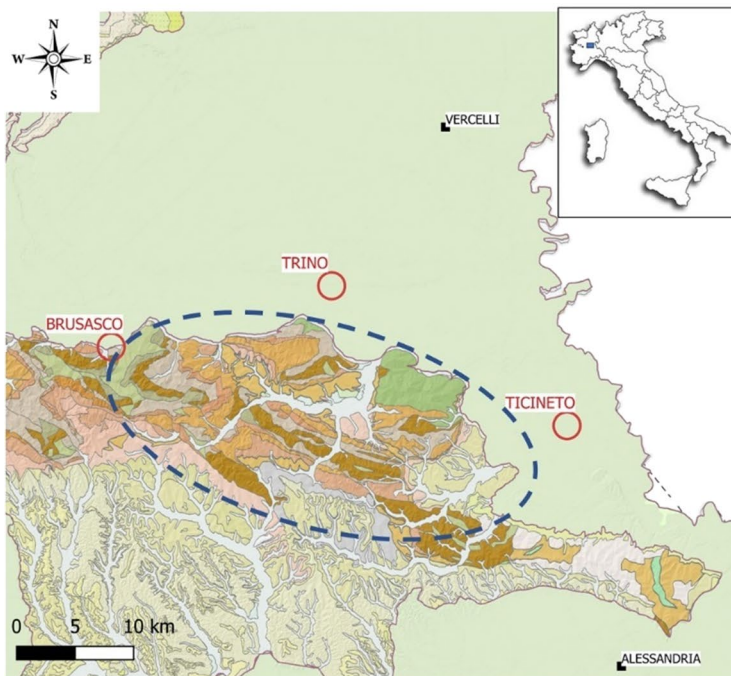
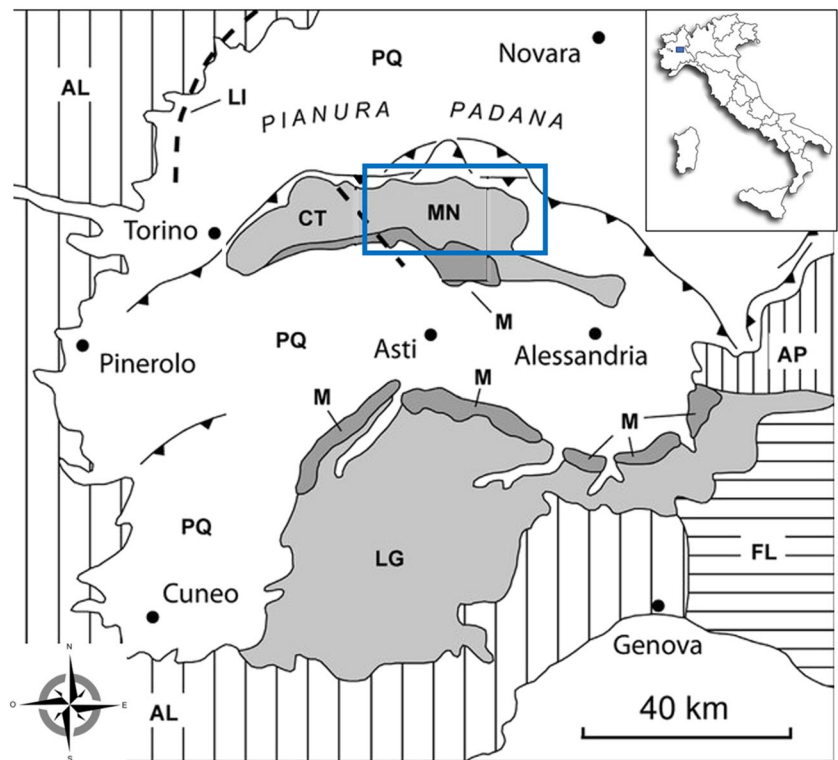
The majority of samples were obtained from Pietra da Cantoni, consisting in fossiliferous carbonate of platform successions. It was likely used as a mortar binder and also in the construction of significant structures such as churches, Romanesque towers, and other important buildings dating back to the 12th and 13th centuries. Additionally, Pietra da Cantoni is characterised by hypogeal architecture, which pertains to underground architecture intended for the storage of food and wine—known as the *infernòt*. Currently, this architectural style is recognised as part of Unesco's global cultural heritage (Consiglio Regionale del Piemonte 2003).

Furthermore, in the Monferrato area, sandstones and soft limestones are specific to this area and were often reserved for the construction of churches or important buildings. Due to their easy workability, they were used for the construction of several of architectural elements, which allowed their use beyond the local area (Fig. 7).

The Fig. 6 shows the lithological map of ornamental rocks. In the study area the rocks are divided into three categories:

- Cenozoic terrigenous rocks: arenaceous, arenaceous-pelitic, marly and sandy-gravelly successions ranging in age from the middle Eocene to the upper Miocene (BTP)
- Ortochemical rocks: primary and resedimented evaporitic gypsum of Messinian age (BTP).
- Cenozoic allochemical rocks: predominantly carbonate successions, calcarenites and calcirudites of the BTP

Fig. 5 Geological scheme of the Piedmont Tertiary Basin. *AL*: Alpine chain. *AP*: Apennine chain. *FL*: Ligurian Nappes. Paleogene-Neogene sedimentary basins on Alpine basement: *CT*= Turin Hills; *LG*= Langhe. Paleogene-Neogene sedimentary basins on Apennine basement: *MN*= Monferrato. *M*: Messinian succession. *PQ*: Pliocene-Quaternary succession. *LI*: Insubric line (modified from Forno et al. 2009)



SIMPLIFIED GEOLOGICAL MAP

- Main cities
- Archaeological site
- Study area

Geological successions

- Alluvial and fluvioglacial deposits of Piedmont Plain (Pleistocene-present)
- Pliocenic successions:**
 - Marly-silty and sandy succession (Zancleano-Piacenziano)
- Tertiary Piedmont Basin (BTP) succession:**
 - Valle Versa chaotic complex (Messinian)
 - Casale Monferrato Formation (Messinian)
 - S. Agata Fossili Marls (Tortonian-Messinian)
 - Tonengo Arenites (Langhian)
 - Pietra da Cantoni (Burdigalian)
 - Pteropodi Inferiori Marls (Acquitanean- Burdigalian)
 - Antognola Formation (Rupelian-Acquitanean)
 - Cardona Formation (Rupelian)
 - M. Piano Marls (Priabonian)
- Ligurian units of Monferrato**
 - La Pietra chaotic complex (Cretacico sup. – Eocene)

Fig. 6 Simplified geological asset of the study area (modified from Piana et al. 2017a, Journal of Maps; e Piana et al. 2017b, Servizio WebGIS: Geoportale Arpa Piemonte—GeoPiemonte Map 2021)

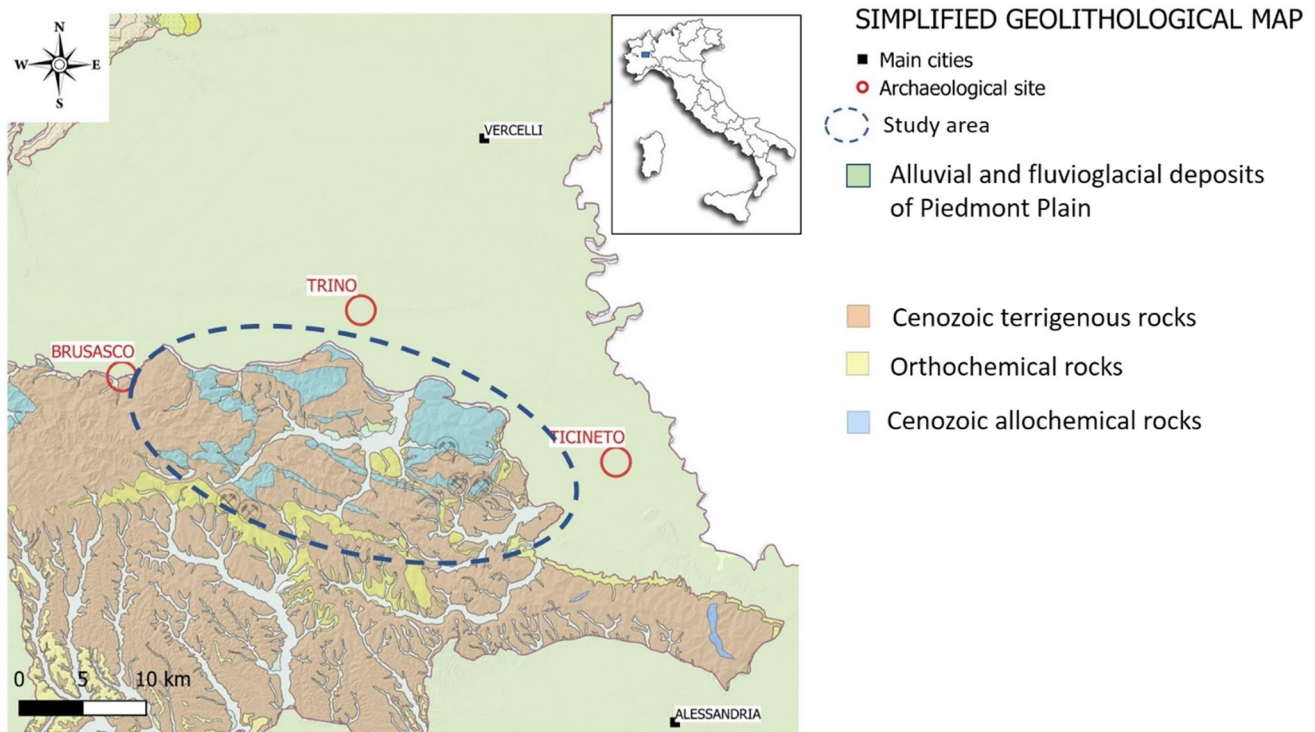


Fig. 7 Simplified geolithological map of the study area (modified from Fig. 2 – Simplified geological asset of the study area (modified from Piana et al. 2017a, Journal of Maps; e Piana et al. 2017b, Servizio WebGIS: Geoportale Arpa Piemonte—GeoPiemonte Map 2021)

and calcareous marly turbidite successions of Eocene age (Ligurian units or Monferrato).

The studies that led to the drafting of the geolithological map of ornamental stones (Barale et al. 2020), were also based on the census of numerous historical quarries, often consisting of small quarrying units. Some of these quarries, endowed with suitable chemical characteristics, were also used for the procurement of the lime needed to prepare the binder for mortars.

Materials and Method

Ancient quarry sites have been identified and based on geological and historical investigations representative samples have been collected. The exploited limestone quarries frequently show a fairly constant chemical composition and therefore a typical Mg/Ca ratio. The variation of this ratio was useful to identify the geological formations and the potential quarries exploited during the different architectural phases and ages.

Sampling and Analysis Methodology

Mortar samples were collected during excavation campaigns in Ticineto, Brusasco and Trino. 31 mortar samples were analysed from rural constructions at the Brusasco site, dating back to the Medieval (M) and Late Medieval (BM) phases; location of each sample is reported in Fig. 8.

At the Ticineto site, 18 mortar samples were analysed from the remains of rural constructions dating back to the Roman (RM), Medieval (M), and Late Medieval (TA) phases.

For the Trino site, 30 samples were obtained from the Medieval (M) phase of the Church of S. Michele, and 52 samples were collected from rural constructions and boundary walls from the Roman (RM), Early Medieval (AM), and Medieval (M) phases.

The field survey of the area surrounding the archaeological sites took place before the rock sampling. It was carried out in the hilly strip to the south of the Trino site, between Brusasco (west side) and Ticineto (east side). The main objective was to identify the limestone formations that could have been employed in the production of limestone. The survey paid special attention to the routes of the ancient

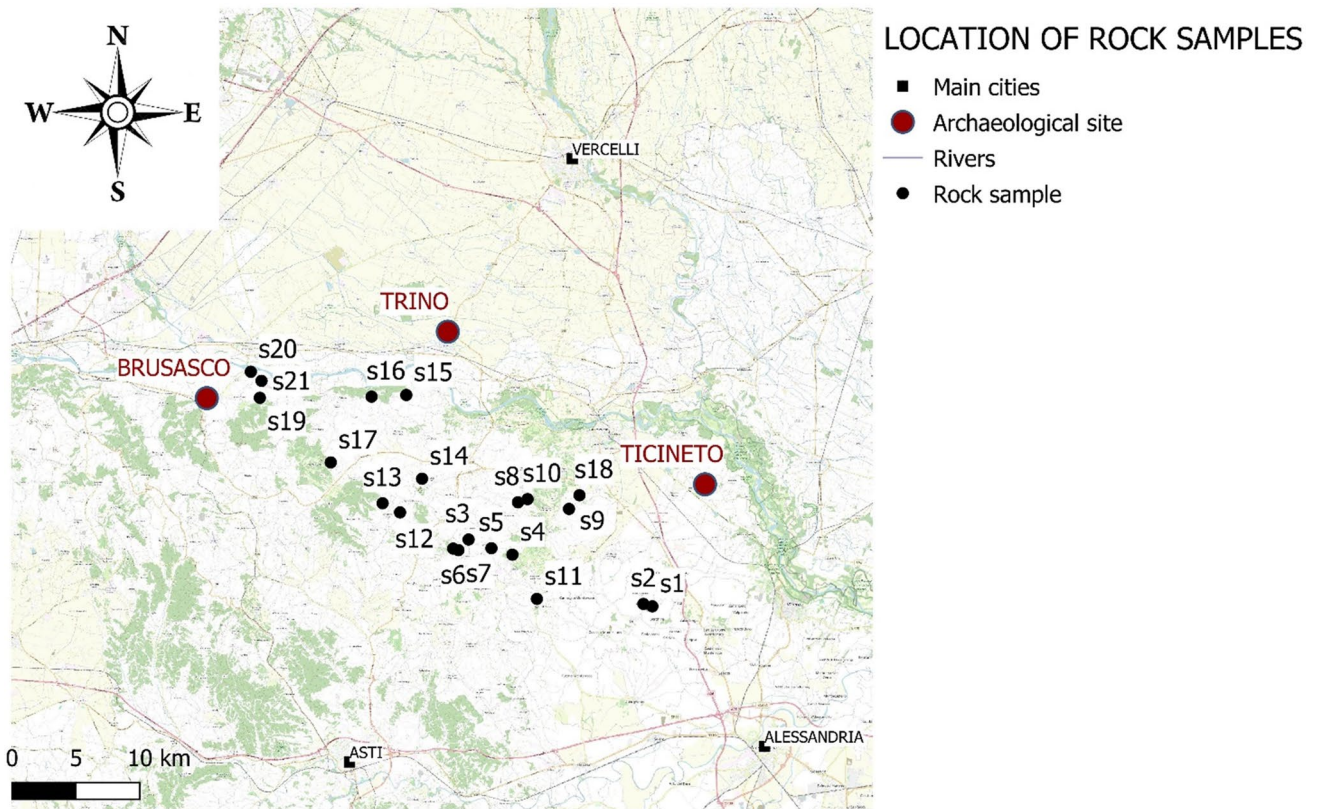


Fig. 8 Location of rock sampling points

roads and to the areas that showed traces of past excavation activities, which could be attributed to ancient quarries.

The sedimentary rocks of the Cenozoic age successions, specifically from the Upper Eocene to Messinian, within the BTP (Piedmont Tertiary Basin) contain geological formations that may hold potential for the extraction of limestones suitable for the production of lime. These include a wide variety of sediments, mainly carbonates, such as carious limestone, yellow arenaceous limestone and grey, organogenic limestone. Each sample has been described macroscopically, and associated with the specific geological formation/complex specified in Table 1.

21 rock samples were collected and subjected to Ca and Mg analyses using the same method applied for mortars characterisation.

Based on a macroscopic description of the samples and sampling points, it was feasible to associate them with five geological formations mainly characterised by marls, calcarenites and carbonate successions. These formations belong to the Cenozoic successions of the BTP (Tonengo Arenites, Pietra da Cantoni, Antognola Formation, Cadorna Formation) and one, from an earlier time, belonging to the Ligurian Unit (La Pietra Chaotic Complex).

An analysis on the mortar and rock samples followed a specific procedure, which included:

- leaching of the mortar samples; selective leaching of mortar samples is a process used to dissolve the lime and leave the inert fraction (sand consisting almost entirely of quartz and silicates) as a residue. Leaching was carried out using a weak acid (dilute hydrochloric acid).
- determination of Mg and Ca. The amounts of calcium and magnesium were determined by atomic absorption after sedimentation of the suspended solids.

Mg/Ca ratio calculation. The value of this ratio is unique and remains constant for each mortar, even when the amount of binder used to prepare the mortar varies. To make the results easier to read, the ratio values are multiplied by one thousand.

Results

To distinguish between different types of lime, the ratio of Ca and Mg has been proven to be a valuable method. These two elements are consistently present in both limestone samples and the binders used in wall and building mortar.

Typically, quarries used for lime production are sourced from the same geological formation, resulting in a relatively uniform chemical composition of the limestone.

Table 1 Summary description of rock samples

SAMPLE SITE	LITHO-UNIT	UNIT DESCRIPTION	AGE	LITHOLOGY
s1	LU	Cardona Formation—arenaceous and arenaceous-pelitic successions (BTP)	Rupeliano	carious limestones; carbonate rich mudstone
s2	LU	Caotic complex of La Pietra (Ligurian Unit)	Upper Cretaceous-Eocene	Undifferentiated complex composed by limestone, sandstone and conglomerate
s3	OTTIGLIO	Cardona Formation—arenaceous and arenaceous-pelitic successions (BTP)	Rupeliano	carious limestones; carbonate conglomerate
s4	MOLETO	Antognola Formation (BTP)	Rupeliano-Aquitainiano	organogenic limestones carbonate rich mudstone
s5	OTTIGLIO	Antognola Formation (BTP)	Rupeliano-Aquitainiano	organogenic limestones carbonate rich mudstone
s6	OTTIGLIO	Tonengo sandstone (BTP)	Langhiano	yellow calcareous sandstone; arenite
s7	OTTIGLIO	Tonengo sandstone (BTP)	Langhiano	yellow calcareous sandstone; arenite
s8	ROSIGNANO M.TO	Cantoni Rocks (BTP)	Burdigaliano-Langhiano	yellow calcareous sandstone; arenite
s9	ROSIGNANO M.TO	Cantoni Rocks (BTP)	Burdigaliano-Langhiano	yellow calcareous sandstone; arenite
s10	ROSIGNANO M.TO	Cantoni Rocks (BTP)	Burdigaliano-Langhiano	yellow calcareous sandstone; arenite
s11	VIGNALE M.TO	Tonengo sandstone (BTP)	Langhiano	yellow calcareous sandstone; arenite
s12	PONZANO M.TO	Cantoni Rocks (BTP)	Burdigaliano-Langhiano	yellow calcareous sandstone; arenite
s13	PONZANO M.TO	Cantoni Rocks (BTP)	Burdigaliano-Langhiano	yellow calcareous sandstone; arenite
s14	PONZANO M.TO	Cantoni Rocks (BTP)	Burdigaliano-Langhiano	yellow calcareous sandstone; arenite

Table 1 (continued)

SAMPLE SITE	LITHO-UNIT	UNIT DESCRIPTION	AGE	LITHOLOGY
s15	PALAZZOLO Cantoni Rocks (BTP)	Biocalcarenes and biocalcirudites; hybrid glauconia sandstones	Burdigaliano-Langhiano	yellow calcareous sandstone: arenite
s16	PALAZZOLO Cantoni Rocks (BTP)	Biocalcarenes and biocalcirudites; hybrid glauconia sandstones	Burdigaliano-Langhiano	yellow calcareous sandstone: arenite
s17	ODALENGO GRANDE Cantoni Rocks (BTP)	Biocalcarenes and biocalcirudites; hybrid glauconia sandstones	Burdigaliano-Langhiano	yellow calcareous sandstone: arenite
s18	ROSIGNANO M.TO Antognola Formation (BTP)	Silty marls with interbedded arenaceous-conglomeratic and paraconglomeratic bodies	Rupeliano-Aquitainiano	grey organogenic limestones
s19	VERRUA Cardona Formation—arenaceous and arenaceous-pelitic successions (BTP)	Alternating conglomerates, microconglomerates and bioturbated arenites, with rare marly-pelitic levels	Rupeliano	carious limestones: carbonate rich mudstone
s20	VERRUA Caotic complex of La Pietra (Ligurian Unit)	Varicoloured clays incorporating Mesozoic limestone blocks, calcarenites, serpentinites and lenticular bodies of carbonate pebble orthoconglomerates	Upper Cretaceous-Eocene	Undifferentiated complex composed by limestone, sandstone and conglomerate
s21	VERRUA Caotic complex of La Pietra (Ligurian Unit)	Varicoloured clays incorporating Mesozoic limestone blocks, calcarenites, serpentinites and lenticular bodies of carbonate pebble orthoconglomerates	Upper Cretaceous-Eocene	Undifferentiated complex composed by limestone, sandstone and conglomerate

The values of the MgO/CaO ratio in the 152 analyses carried out (131 mortars and 21 limestone samples) vary over a rather wide range of values, from 4 to 300, corresponding to limestone ranging from pure limestone to dolomitic limestone. This means that the lime studied were obtained from limestone of different nature and origin, as it is very rare for a single deposit to have such a wide range of values within it.

Analysis of Rock Samples

The values of the Mg/Ca ratio in the sampled rocks range from a minimum of 7 to a maximum of 303.

In most cases, the quarries from which the rocks were extracted to produce lime and which belong to the same geological formation showed a generally rather constant Mg/Ca ratio.

Different formations can be individuated:

- **Cardona Formation (s1, s3, s19)**. The rocks of this formation display a compact structure and form irregular, isolated bodies in clays and marls. The rocks contain a high amount of CaCO_3 (>90%). Rocks extracted from outcrops related to this complex have exhibited Mg/Ca ratio values ranging from 8.7 to 15.6;
- **La Pietra Chaotic Complex (s2, s20, s21)** comprises clusters and beds of calcarenites, arenaceous calcars, and conglomerates with dolomitic limestone, black limestone,

and marly limestone elements. The formation contains bodies with high carbonate content, which are suitable for producing lime and Mg lime. The rocks taken from the outcrops associated with this complex display the highest values of the Mg/Ca ratio (ranging between 207 and 303).

- **Antognola Formation**. This formation shows CaCO_3 contents around 80–85%. The Antognola calcarenites (samples **s4** and **s5**) have a compact structure with a microcrystalline texture and average Mg/Ca ratios around 15.3, while sample **s18** was taken from a marly-clayey outcrop with a higher Mg/Ca ratio of 94.3.
- **Tonengo Arenites (s6, s7, s11)**. This formation is characterised by yellowish calcareous sandstones with CaCO_3 contents below 80%. Rocks taken from outcrops associated with this complex showed Mg/Ca ratios between 7.0 and 9.2.
- **Pietra da Cantoni (s8, s9, s10, s12, s13, s14, s15, s16, s17)** is a fairly extensive formation in the Monferrato area and consists of compact, amorphous organogenic limestones forming irregular, discontinuous beds with CaCO_3 contents above 90% within subordinate calcareous sandstones. Rocks from outcrops associated with this complex showed Mg/Ca ratios ranging from 7.3 to 27.1.

Figure 9 shows the spatial distribution of the results according to the lithologies (and geological formations) sampled.

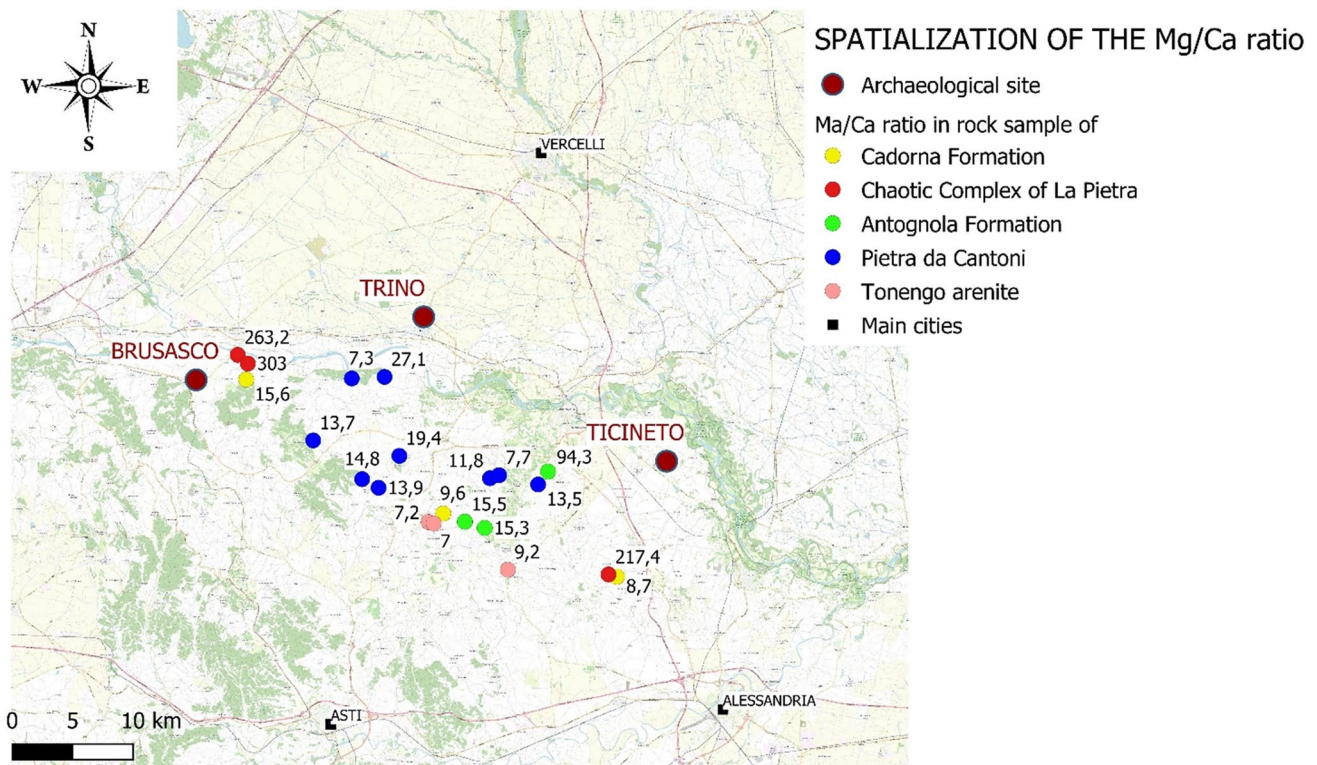


Fig. 9 Spatial distribution of results (Mg/Ca ratio) for rock samples

Pink dot = Tonengo arenites (Langhian), blue dot = Pietra da Cantoni group (Burdigalian-Langhian), green dot = Antognola formation (Rupelian-Aquitainian), yellow dot = Cardona formation (Rupelian), red dot = La Pietra chaotic complex (Late Cretaceous-Eocene).

Sampling and Geochemical Analysis of Mortars, and Stratigraphic Correlation of Buildings

The results of the geochemical characterisation, based on the Mg/Ca ratio, of mortars found in rural buildings and churches date back to the early Roman, late antique, and medieval phases of fortified centres.

In particular, in the archaeological sites analysed, the following historical phases were distinguished in Tab. 2.

Brusasco Archaeological Site

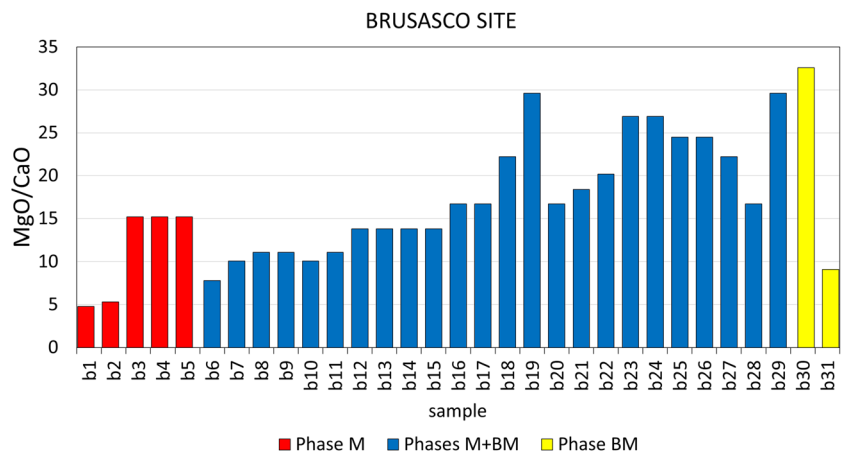
The results of the chemical analysis (Mg/Ca ratio) belong to the mortars sampled from the remains of rural constructions at the Brusasco site and the corresponding archaeostratigraphic dates. The detected archaeological phases belong to the Medieval M and the Late Medieval BM.

The mortar samples taken from Brusasco display Mg/Ca values that range between 4.8 and 32.6 (refer to Fig. 10 and Table 3).

Table 2 Abbreviations of historical phases

Historic Period	Abbreviation
Late Antique phase	Phase TA
Roman and Early Medieval phases	Phases RM + AM
Roman and Medieval phases	Phases RM + M
Early Medieval phase	Phase AM
Medieval phases	Phase M
Medieval and Low Medieval phases	Phases M + BM
Low Medieval phase	Phase BM

Fig. 10 Histogram showing the values of the Mg/Ca ratio of the mortar samples belonging to the different phases (M, M + BM, and BM)



In the samples belonging to the M-phase, the Mg/Ca ratio values vary between 4.8 and 15.2, with an average of 11.11.

For the M + BM phases, the Mg/Ca ratio values range from 7.8 to 29.6, with a mean value of 17.8.

In the case of BM phases, the Mg/Ca ratio values exhibit a range from 9.1 to 32.6, with a mean value of 20.9.

The range of Mg/Ca ratio values in the M phase is more restricted than in the samples of the later phases.

Trino Church Archaeological Site

The results of the chemical analysis (Mg/Ca ratio) belong to the mortars sampled from the remains of rural constructions at the Trino church site and the corresponding archaeostratigraphic dates.

The detected archaeological phases belong to the Medieval phases.

The mortar samples taken from Trino Church all belong to Medieval phase and show Mg/Ca values that range between 4.0 and 29.6 (refer to Fig. 11 and Table 4).

50% of the samples fall within the interquartile range from 7.3 to 15.4.

Trino Rural Buildings Archaeological Site

The results of the chemical analysis (Mg/Ca ratio) belong to the mortars sampled from the remains of rural constructions at the Trino rural buildings site and the corresponding archaeostratigraphic dates. The detected archaeological phases belong to phases from the Roman to the Medieval ones.

The mortar samples taken from Trino rural buildings display Mg/Ca values that range between 4.0 and 15.2 (refer to Fig. 12).

In the samples belonging to the RM + AM phases, the Mg/Ca ratio values vary between 13.8 and 15.2, with an average of 14.5.

Fig. 11 Histogram showing the values of the Mg/Ca ratio of the mortar samples belonging to the historical phase M

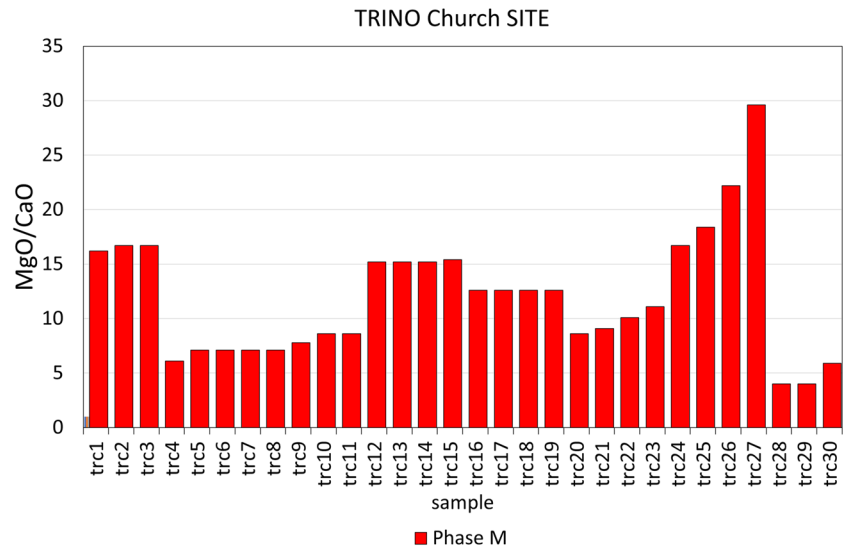
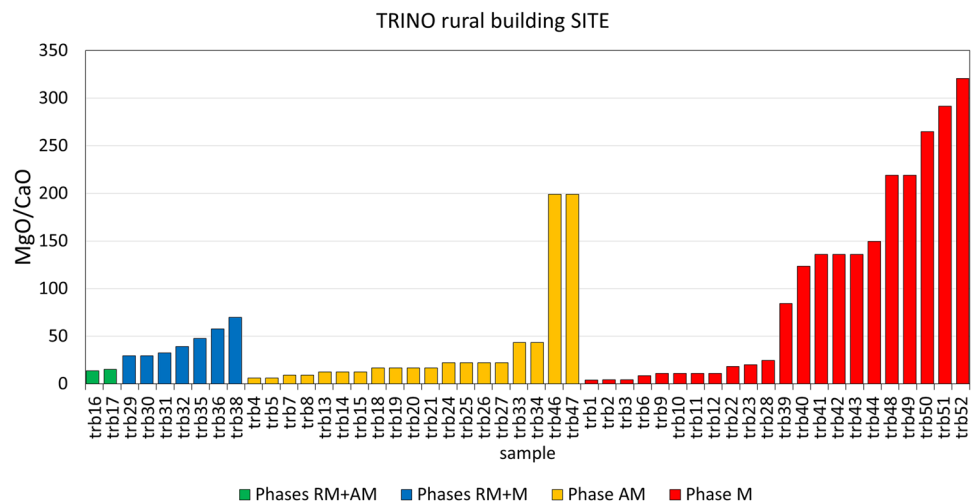


Fig. 12 Histogram showing the values of the Mg/Ca ratio of the mortar samples belonging to the different phases (RM + AM, RM + M, AM and M)



For the RM + M phases, the Mg/Ca ratio values varies from 29.6 to 69.8, with a mean value of 43.7.

In the case of AM phase, the Mg/Ca ratio values exhibit values from 6.1 to 199.1, with a mean value of 37.3.

The range of Mg/Ca ratio values in the M phase range from 4.0 to 320.7, with a mean value of 100.4.

Ticineto Archaeological Site

The results of the chemical analysis (Mg/Ca ratio) belong to the mortars sampled from the remains of rural constructions and walls at the Ticineto site and the corresponding archaeostratigraphic dates.

The detected archaeological phases belong to phases from the Late Antique to the Medieval ones.

The mortar samples taken from Ticineto display Mg/Ca values that range between 4.0 and 15.2 (refer to Fig. 13).

In the samples belonging to the RM + AM phases, the Mg/Ca ratio values vary between 13.8 and 15.2, with an average of 14.5. For the RM + M phases, the Mg/Ca ratio values varies from 29.6 to 69.8, with a mean value of 43.7. In the case of AM phase, the Mg/Ca ratio values exhibit values from 6.1 to 199.1, with a mean value of 37.3. The range of Mg/Ca ratio values in the M phase range from 4.0 to 320.7, with a mean value of 100.4.

Discussion

Brusasco Archaeological Site

Figure 14 shows the Mg/Ca ratio values of the rock samples and those of the mortars belonging to the different phases (M, M + BM and BM).

Fig. 13 Histogram showing the values of the Mg/Ca ratio of the mortar samples belonging to the different phases (TA, RM + AM, RM + M and M)

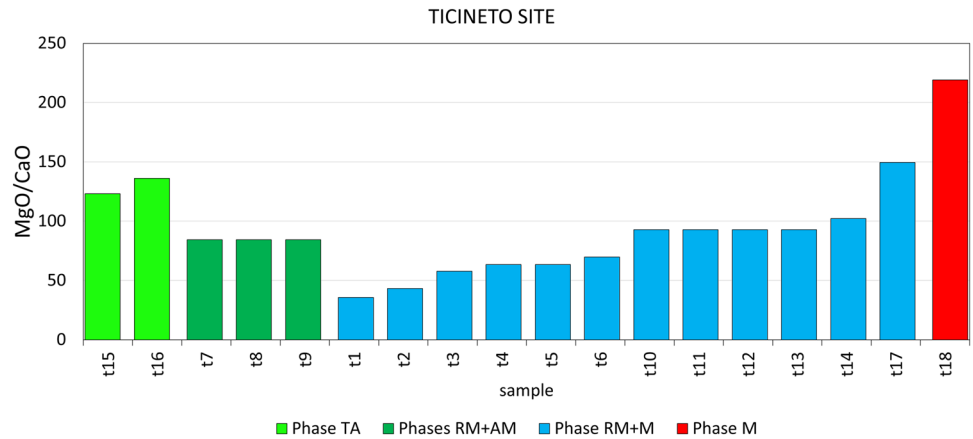
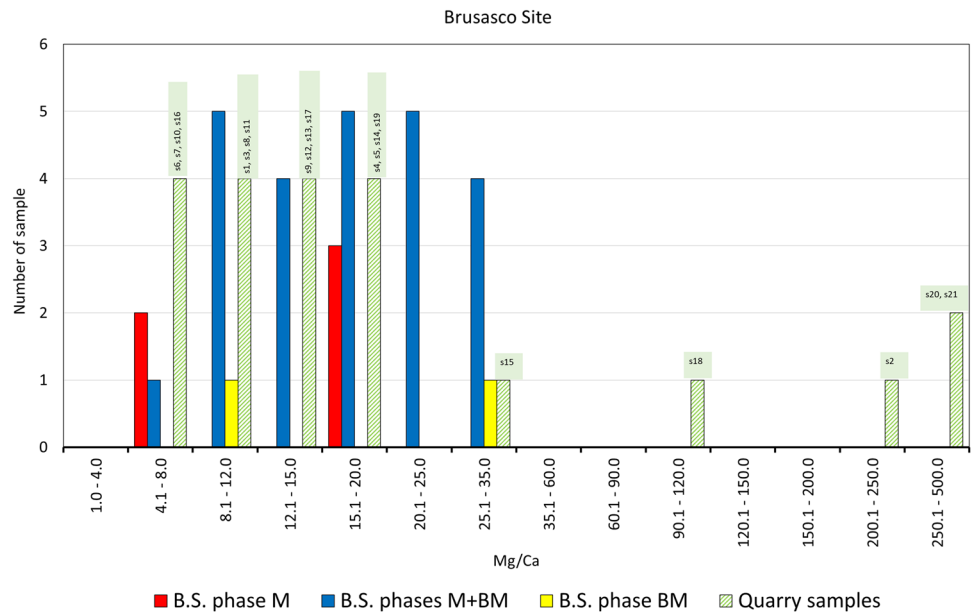


Fig. 14 Histogram showing the values of the Mg/Ca ratio of the rock samples and those of the mortars belonging to the different phases (M, M + BM and BM)



The rock samples s18, s2, s20 and s21, collected respectively in the quarries of Rosignano Monferrato, Lu and Verrua show values of the Mg/Ca ratio above 90 that differ from those of the mortars sampled at the site. These quarries can be reasonably excluded from the supply sources of the Brusasco site studied.

As far as phase M is concerned, observing the trace of ancient communication routes (see Fig. 1) and the correspondence between the values of the mortars and those of the rock samples, the quarries of Verrua (s19), closest to the site, and those of Palazzolo (s16) are noted as possible supply sites. The quarries of samples s4, s5, s6, s7, s10 and s14 (Ottiglio and Rosignano area) could also be supply sites as the results show. With this in mind, it is likely that there were one or more secondary communication routes used for this purpose.

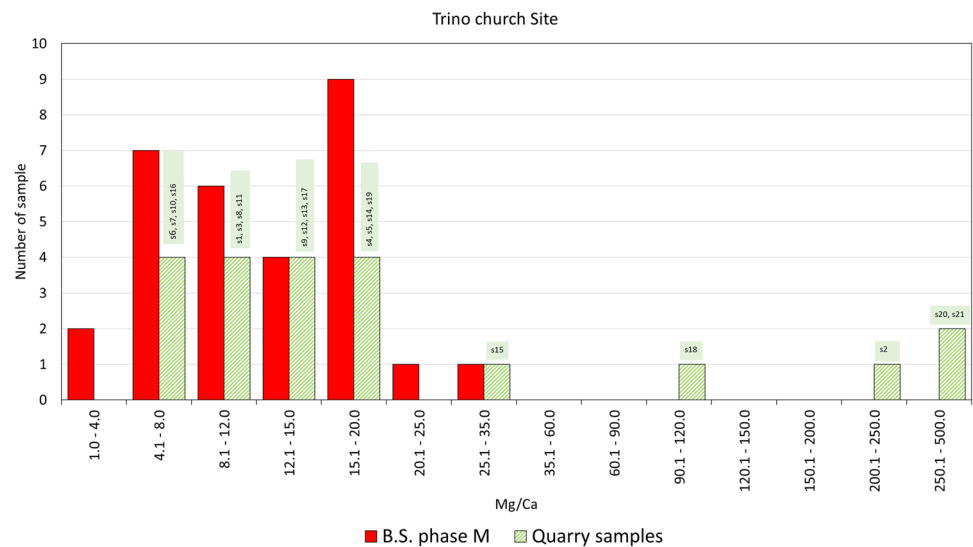
As for phase BM, the probable supply site was the Palazzolo quarry (s15) located along the ancient communication route.

The M + BM phases cover a wide time span and see the supply of raw material more widely spread over the territory, as shown by the wide variability of the values.

Phase M sees correspondence with samples taken from quarries s6, s7, s10, s16, s4, s5, s14 and s19.

Observing the trace of the ancient communication routes (see Fig. 17) and the correspondence between the values of the mortars and those of the rock samples, the quarries of Verrua (s19), closest to the site, and those of Palazzolo (s16) are noted as possible supply sites.

Fig. 15 Histogram showing the values of the Mg/Ca ratio of the rock samples and those of the mortars belonging to M phases



Trino Church Archaeological Site

The diagram in Fig. 15 shows the values of the Mg/Ca ratio of the rock and mortar samples belonging to the M phase of the Trino church building only.

The rock samples s18 (located in Rosignano area), s2 (located in Lu area), s20 and s21 (both located in Verrua area, in La Pietra Caotic Complex) show Mg/Ca ratio values greater than 90 that differ from those of the mortars sampled at the site. One can reasonably exclude these quarries from the supply sources of the Trino Church site.

Based on the traces of ancient communication routes (see Fig. 17) and the correspondence between the values of the mortars and those of the rock samples, the quarries probably used were located in Verrua (s19) and Palazzolo (s15 and s16). However, it cannot be excluded that the supply of raw

materials during the M period for the construction of the church at Trino covered a large part of the area investigated.

Trino Rural Buildings Archaeological Site

The diagram in Fig. 16 shows the values of the Mg/Ca ratio of the rock and mortar samples belonging to the different phases (RM + AM, RM + M, AM and M).

The mortar samples of the RM + AM phase correspond to samples s9, s12, s13, s17 and s4, s5, s14, s19, in areas further away from the plain area, except for sample s19 taken in the Verrua quarry. This hypothesis can be confirmed by the presence of an ancient communication route from Trino towards the south, i.e. towards the hilly area (Fig. 17).

Some mortar samples from the RM + M phase correspond to the values of sample s15 taken at the Palazzolo quarry,

Fig. 16 Histogram showing the values of the Mg/Ca ratio of the rock samples and those of the mortars belonging to the different phases (RM + AM, RM + M, AM and M)

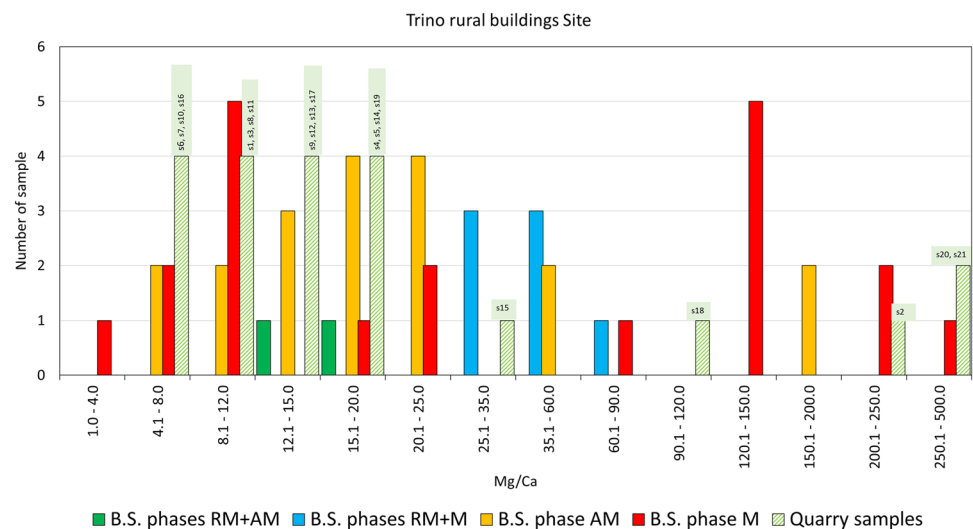
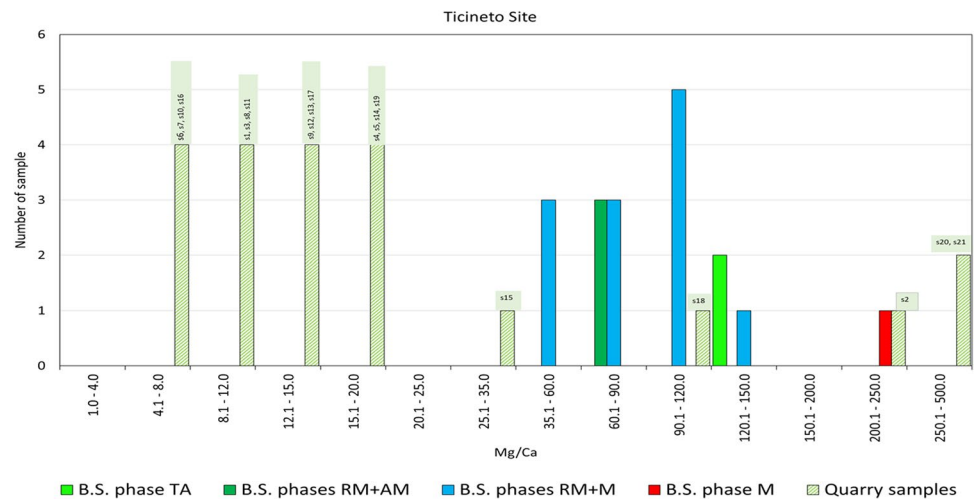


Fig. 17 Histogram showing the values of the Mg/Ca ratio of the rock samples and those of the mortars belonging to the different phases (TA, RM + AM, RM + M and M)



located near Trino. For the other samples, belonging to the AM and M phases, the raw material supply is very widespread in the area, as shown by the wide variability of the Mg/Ca ratio values.

Ticineto Archaeological Site

The diagram in Fig. 17 shows the values of the Mg/Ca ratio of the rock samples and those of the mortars belonging to the different phases (TA, RM + AM, RM + M and M).

All rock samples, except s18 and s2, show Mg/Ca ratio values that deviate from those of the mortars sampled at the Ticineto site. These quarries can be reasonably excluded from the sources of supply of the studied site.

The mortar samples of the M phase show correspondence with the s2 sample taken from the Lu quarry at the La Pietra chaotic complex, which shows an Mg/Ca ratio of 217.4. On the other hand, several samples from the RM + M phases correspond to the values of sample s18 taken from the Rosignano quarry and belonging to the Antognola Formation.

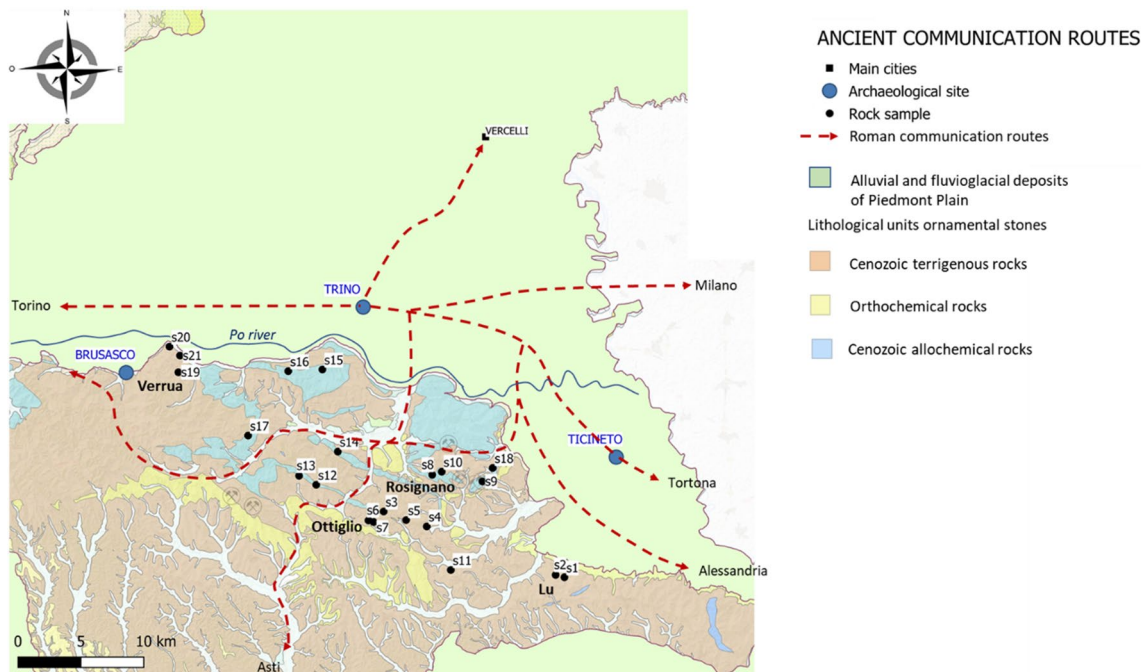


Fig. 18 The most important medieval settlements and the most important Roman communication routes were also used in later periods

In summary, samples s2 and s18 were taken from quarries close to Ticineto, in Lu and Rosignano M.to respectively, so it is plausible that a large part of the materials extracted for lime production came from these quarries.

Conclusions

Rural architecture is worthy of consideration as a cultural heritage because it testifies to the development of Piemonte's territory over time.

In this work, the MgO/CaO ratio was analysed in rock samples from limestone quarries in the area and in lime binders of mortars from three rural settlements of Roman and Medieval origin, located in the lowland area along the alluvial belt of the River Po—Brusasco, Trino and Ticineto, in the Piedmont region (Italy). Mortar analyses, fast and economical method, are an important diagnostic archeometric tool for identifying the original quarries used for limestone production and the period of exploitation. Indeed, the analysis of the MgO/CaO ratio in the limestone rocks of the ancient quarries can also be used as an element of spatial and temporal correlation with the historical phases identified in the different archaeological sites.

In this context, it was useful to learn about the traces of ancient communication routes (Battistoni and Lombardini 2007). In fact, medieval settlements continued to be located along the ancient Roman roads (Fig. 18).

The analyses show a wide range of MgO/CaO ratios in all the rock samples (ratios ranging from 7 to 303). However, in almost all cases the MgO/CaO ratios of the rock samples analysed show values typical of quarries from the same geological formations. Furthermore, analysis show that the MgO/CaO ratio allows the samples to be divided into classes corresponding to the different origins of the limestone. The correlation between the classes and the archaeological stratigraphy confirms the use of limestone of different origins in all the sites in the different chronological phases.

The MgO/CaO ratio was variable in the different phases, but not very variable in the same group of buildings: The MgO/CaO ratio in the mortars is mainly between 7 and 35 in Brusasco, between 50 and 150 in Ticineto, while it is very variable in the rural buildings of Trino.

Samples with very close MgO/CaO values have a good chance of coming from the same quarry, and in cases where, as in Trino, different sources were used over time, samples with similar values also have a good chance of being contemporary.

In the case of the medieval church of Trino, the mortar samples show MgO/CaO ratios between 6 and 27, values comparable with rock samples taken from quarries closer

to the site and more easily accessible due to the presence of good communication routes.

The comparative analysis of the MgO/CaO ratio in rock and mortar samples, combined with the archaeostratigraphic and local context analysis of historical infrastructures, has proved to be a useful tool for the spatial correlation between different sites and the temporal correlation with respect to the extraction phases.

Rural architecture deserves to be considered a cultural heritage because it testifies to the development of Piedmont's territories over the centuries.

In this context, mortar has proved to be an important diagnostic tool for identifying the original limestone quarries and the period of exploitation. The study showed that quarries exploited in an earlier period (i.e. the Roman period) were often no longer exploited in more recent periods (i.e. the Medieval or Late Medieval periods). The reasons for this may be related not only to the inability to quarry, but also to political and road-related changes.

The provenance of limestone can therefore provide interesting information about the network of trade routes and their changes over time.

The characterisation of ancient mortars and the comparison and correlation with their sources of supply are certainly the starting point for opening up new, innovative and multidisciplinary lines of research on geomaterials in the field of cultural heritage. In particular, detailed analyses of such materials and research protocols are also useful for characterising and systematising the production of 'alternative' mortars, compatible with the mortars of these sites and formulated with waste materials (construction and demolition waste and extractive waste) with a view to a circular economy.

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