



Article Ancient Roman Mortars from Anfiteatro Flavio (Pozzuoli, Southern Italy): A Mineralogical, Petrographic and Chemical Study

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Abstract: This research is based on the characterization of ancient mortars from the Anfiteatro Flavio (Pozzuoli) dating back to the 1st and 2nd century CE through a multi-analytical approach involving macroscopic, mineralogical, petrographic, and chemical investigations. The goal that has been set is to deepen knowledge about mortar mix design, the provenance of used raw materials, and secondary minerogenetic processes that have occurred within ancient Roman mortars. Results show that: (i) raw materials for mortar preparation have a local provenance, i.e., Phlegraean Fields area; (ii) mortars can be considered as hydraulic; (iii) calcite presence could be due to a non-complete calcination process, an improper slaking or to exposition of materials to the subaerial environment; (iv) gypsum is due to calcite sulfation process; (v) halite presence is due to marine aerosol exposition. The achieved information testifies that, for at least two centuries, Roman builders considered the identified mortar mix as optimal for their buildings, but also contributes to the understanding of their technical skills and represents an important first step to planning future restoration operations.

Keywords: Roman amphitheater; Roman mortars; hydraulicity; minero-petrographic characterization; Phlegraean Fields

1. Introduction

Mortars are composite geomaterials (i.e., geological materials or deriving from technological transformations of geological materials) consisting of a hydraulic or aerial binder, aggregates, and additives reacting with the binder and undergoing modifications during setting [1]. These geomaterials are particularly interesting due to their great use in the Roman age. Roman craftsmen used to combine lime and pozzolana, (formerly Pulvis Puteolana, volcanic sand from Pozzuoli, Italy) related to Neapolitan Yellow Tuff (NYT—15 ka) formation [2,3].

The extraordinary preservation state of Roman mortars justifies several studies carried out on these geomaterials [4–12] and proves the very high technical skills of the craftsmanship. Roman buildings, i.e., monuments, roads, and aqueducts still resist for 2000 years in both aerial and underwater conditions and for this reason, the study of Roman mortars is



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Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). exceptionally important to understand the so long-aging construction technology applied by the ancient Romans [13,14].

The goal of this work is to deepen knowledge of Roman construction techniques used to produce mortar-based materials and represents the first attempt to study mortar samples from the Roman Anfiteatro Flavio of Pozzuoli (Naples, Campania, Southern Italy). For the walls of this monument, pozzolans of Phlegraean origin (such as tuff and lava) were mainly used in both bedding and coating mortars.

This research was carried out by using a standard scientific approach for the investigation of provenance and technological features of mortars [7,8,15] and it was approached with mineralogical, petrographic, and chemical analytical techniques to examine thoroughly microstructural and compositional features of mortars.

Results are presented to support the previous work of [15], which focused on building stones employed for structural uses.

2. Geological Background

The Anfiteatro Flavio (Figure 1a,b) is located in the Pozzuoli downtown within the Phlegraean Fields Area, the largest volcanic system of Southern Italy [16]. The volcanic system is the result of a subsequent series of calderic collapses [17,18]. Along with Somma-Vesuvius volcanic system, Phlegraean Fields occupy the central part of Piana Campana, structurally representing an area of tectonic collapse [16] related to the extensional tectonics which affected Tyrrhenian area since the Plio-Pleistocene [19–21] as a response to the complex geodynamic events that characterized the Western Mediterranean area leading to the opening of Tyrrhenian basin and the construction of the Apennine–Maghreb chain [16]. Extensional tectonics lowered the Apennines towards central Tyrrhenian [15] causing the sinking of the western margin and the consequent feeding of intense volcanic activity (i.e., Roccamonfina, Phlegraean Fields, Somma–Vesuvius) and the formation of large depressions (i.e., Piana Campana and Piana del Sele) filled by volcanoclastic and alluvial sediments [22].

Phlegraean volcanic activity is characterized by the production of large volumes of pyroclastic deposits by a mainly explosive type of volcanism plus sporadic effusive events represented by lava flows and domes [16]. Phlegraean Fields volcanic products are characterized by the potassium alkaline affinity typical of the Roman Magmatic Province [23,24]. The products of the nearby islands of Ischia and Procida are considered part of the Phlegraean volcanism [25,26] and the activity of the two islands is prior to the "continental" one (the "Phlegraean Fields" s.s.; [27]).

According to [28], the first activity phases of the continental Phlegraean Fields correspond to Punta Marmolite and Cuma lava domes (~47 and ~37 ka, respectively), Torre Franco Tuff Formation (~42 ka) and San Martino lava dome (~77 ka). The two main eruptive events date back to ~39 ka (40 Ar/ 39 Ar; [28,29] and ~15 ka (40 Ar/ 39 Ar; [3]). The former is represented by the Campanian Ignimbrite eruption, the most catastrophic explosive event of the Mediterranean area in the last 200 ka, the latter is represented by the eruption of Neapolitan Yellow Tuff, the most impressive event of the Phlegraean Fields in terms of thickness and areal distribution [30].



Figure 1. (a) Map of Phlegraean Fields area with location of Anfiteatro Flavio (red star) in the Pozzuoli Town; (b) 3D image of Anfiteatro Flavio.

The Anfiteatro Flavio

According to the entrance inscription, the Anfiteatro Flavio was erected around the 70s of the 1st century CE [15], but some authors (e.g., [31]) believe that it may have been edified by Emperor Nero and that inscription was placed after his damnatio memoriae.

Anfiteatro Flavio is one of the most important archaeological sites of the Campania region and one of the largest amphitheater arenas of the Roman Empire, third in size only to the Colosseum in Rome (Lazio region) and the amphitheater of Santa Maria Capua Vetere in Caserta (Northern Campania region) [31].

The building has an elliptic plan and comprises two orders of superimposed arches, thus spanning two floors, one outdoor with bleachers and an arena, and the other underground.

The amphitheater, topped by a high attic decorated with statues, was surrounded by a plateau paved with travertine slabs and bounded by a system of wooden barriers attached to a series of square pillars (approximately 174 cm high) and placed at an average distance of 277 cm ([15] and references therein). Originally, before the external facade, there was a porch positioned on pillars whose semi-columns were covered with stucco. Subsequently, in the 2nd century CE, the original pillars were reinforced with internal pillars covered with brick and under-arches plastered with red and white colors ([15] and references therein).

It is possible to access the well-retained internal hallway by an external portico. The internal hallway is connected to the highest section of the cavea staircase through twenty ramps of stairs.

Cavea was surmounted by a loggia, which consisted of Corinthian columns and capitals deposited in the subterranean during the Bourbon excavations ([15] and references therein).

The arena has an elliptical hallway, and, on its floor, there are several rectangular manholes that constitute the so-called "maneuvering shafts": this is the place from which the winches and lifting machines, positioned in the basement, came out.

In the subterranean, located about 7 m deep and accessed via two steep ramps, parts of the gears to lift the cages that carried ferocious beasts and probably other elements of the scenography of the shows are still visible ([15] and references therein).

3. Materials and Methods

For this work, 12 bedding mortar samples from Anfiteatro Flavio were investigated (Figure 2), half of which ascribable to the 1st century CE (Figure 2a) and the other half ascribable to the 2nd century CE (Figure 2b). Sampling strategy was undertaken in cooperation with archaeologists, thanks to the authorization and under supervision of Archaeological Special Superintendence of Napoli and Pompei and the Archaeological Park of the Phlegraean Fields. Considering the importance of the archaeological site, it was necessary to carry out preliminary inspections, as well as a detailed photographic survey. In this way, visual aspects were evaluated in order to identify sampling sites before their collection. This identification took into account (a) limited invasiveness, (b) representativeness, (c) limited size of samples, and (d) limited visual impact.



Figure 2. Macroscopic pictures of the (a) 1st and (b) 2nd century CE. examined mortars.

Minero-petrographic and chemical analyses were carried out on 12 selected mortars at the Department of Earth, Environmental and Resources Sciences (DiSTAR) at the University of Naples Federico II.

To implement an initial classification of samples and to better plan analyses, preliminary macroscopic observations were performed.

Thin sections analyses in optical microscopy (OM), using a Leica Laborlux 12 Pol microscope Leica Camera, (Wetzlar, Germany) were used for classical petrographic studies. Mineralogical analyses using X-Ray powder diffraction (XRPD) with a Malvern Panalytical

X'Pert Pro modular diffractometer (RTMS detector, X'Pert High Score Plus 3.0c software— Malvern PANalytical, Almelo, The Netherlands) were conducted for the identification of the crystal phases; the following conditions were used: CuK α radiation, 40 kV, 40 mA, 20 range from 4° to 70°, step size 0.02 °20, equivalent counting time 120 s per step. Representative aliquots of the samples (grain size < 10 µm) were obtained using a McCrone micronizing mill (agate cylinders and wet grinding time of 15 min; Retsch-Alle, Haan, Germany).

Microstructural and chemical analyses of the investigated geomaterials were carried out by field emission scanning electron microscopy equipped with an energy dispersive spectrometer (FESEM/EDS; Zeiss Merlin VP Compact and JEOL JSM-5310 coupled with Oxford Instruments Microanalysis Unit equipped with an INCA X-act solid state detector; Carl-Zeiss-Strasse, Oberkochen, Germany and Jeol Ltd., Tokyo, Japan, respectively).

Data sets were obtained using an INCA X-stream pulse processor (Oberkochen, Germany) (15-kV primary beam voltage, 50–100 A filament current, variable spot size, from 30,000 to $200,000 \times$ magnification, 20 mm working distance, and 50 s real-time counting) by means of INCA Energy software 5.05 (XPP array and pulse pile-up corrections). Optimization of signals was carried out using cobalt (FWHM peak height of the strobed zero = 60–65 eV) as a reference. Smithsonian Institute and MAC (Micro-Analysis Consultants Ltd., Saint Ives, UK) standard materials were used for elements calibration: diopside (Ca), fayalite (Fe), San Carlos olivine (Mg), anorthoclase (Na, Al, Si), rutile (Ti), serandite (Mn), microcline (K), apatite (P), fluorite (F), pyrite (S) and sodium chloride (Cl). Accuracies about EDS chemical analyses are reported in [6].

FESEM-EDS analysis allowed us to measure the hydraulicity index (HI) of binder and lime lumps on areas of homogeneous aspect and with spots of 10 μ m. According to [32], the semiquantitative measure of HI accounts for the (SiO₂ + Al₂O₃ + Fe₂O₃)/(CaO + MgO) ratio.

4. Results and Discussions

According to the UNI-EN 11305:2009 [33], and UNI-EN 11176:2006 [34], collected samples were characterized from a mineralogical and petrographic point of view.

4.1. Macroscopic Observations, POM and XRPD

The preliminary macroscopic analysis showed that mortar samples, belonging to the 1st century CE (Figure 2a), are characterized by several hardness conditions, varying from intact (P7-1, P8-1, P18-1, and P66-1) to friable (P15-1 and P16-1). Mortars display an overall gray–beige color, with a little brownish for a few samples (P7-1 and P15-1).

From a textural point of view, all samples show an overall sand grain size ranging from fine to coarse [35]. Aggregate size varies between 0.5 and 1.5 cm.

On the contrary, all the mortar samples belonging to the 2nd century BCE (Figure 2b) show a high hardness. Moreover, these samples are characterized by an overall gray–beige color, except sample P17-1, which shows a reddish color due to the presence of a brick fragment. Sample P64-1 is stratified, as it shows a gypsum layer due to the overlying plaster.

According to petrographic analysis, all samples show a binder with a prevailing cryptocrystalline, and subordinately micritic, texture (Figure 3a,b), except P66-1 and P12-1 samples, in which micritic matrix prevails. Matrix varies in color from beige to brownish. The binder fraction contains also subrounded lime lumps (Figure 3c,d) from millimetric to centimetric size, representing non-reacted lime. Their formation reasonably occurred during the slaking process of lime, due to insufficient seasoning of Ca(OH)₂ and/or a low water/lime ratio [1,36,37]. The aggregate fraction ranges from 30% to 50%, except for the P65-1 sample, in which the aggregate fraction is around 20% [38]. Aggregate fraction is mainly composed of pumice, scoriae, volcanic lithics, and crystal fragments. Pumice and scoriae show intensive recarbonation features and evident reaction rims (Figure 3a,b,e,f). Volcanic lithics consist of trachyte (polycrystalline glomerulus of sanidine) and tuff fragments, whereas crystal fragments within the matrix are mainly sanidine, plagioclase, clinopyroxene, and mica (Figure 3e). Ceramic fragments (Figure 3g) and marble relicts (Figure 3h) have been also detected.



Figure 3. (a) Plane polarized and (b) crossed polarized light microphotographs showing cryptocrystalline (CM) and micritic (MM) matrix types and recarbonated pumice (RR) in the P18-1 sample; (c) crossed polarized light microphotographs of sample P8-1 showing a lime lump (LL); (d) BSE micrograph of sample P65-1 showing a lime lump (LL); (e) crossed polarized light microphotographs showing recarbonated pumice (RR) with reaction rim (RR), plagioclase (pl), sanidine (san) and clinopyroxene (cpx) in the P15-1 sample; (f) BSE micrograph showing a recarbonated pumice (RP) with reaction rim (RR) in sample P15-1; (g) ceramic fragment (CF) in sample P15-1; (h) marble relict (MR) in sample P8-1.

X-ray powder diffraction (XRPD) allows us to confirm the occurrence of lime-based mortars with volcanic aggregate, as shown by semi-quantitative analyses (Figures 4 and S1). In fact, calcite is the most abundant phase of the binder fraction plus aragonite in sample P65-1. The only exception is related to the P64-1 sample where the most abundant phase is represented by gypsum, probably ascribable to the gypsum layer due to the overlying

plaster, as already evidenced by preliminary macroscopic analysis. Subordinately, gypsum was also detected in P8-1, P15-1, P16-1, P18-1, and P17-1 samples. The presence of gypsum can be related to the calcite sulphation process, probably due to a pH decrease caused by the dissolution of atmospheric SO₂ [39]. In the same samples (plus P66-1) also halite was identified.

Discrete amounts of feldspar were also detected in all the samples, along with mica and scarce or low amount of clinopyroxene and quartz likely due to the presence of brick fragments [40]. Traces of hematite were observed in P7-1, P8-1, P15-1, and P16-1 related to the samples ascribable to the 1st century CE and P64-1 and P65-1 related to the samples of the 2nd century CE. In addition, scarce to frequent amounts of halite were detected in all the samples analyzed except for the P64-1 sample. Lastly, traces of bassanite were observed in P15-1 and P17-1 (1st century CE and 2nd century CE, respectively), possibly due to the same sulphation processes justifying the presence of gypsum [41].

The ubiquitous presence of analcime and the presence of phillipsite and chabazite in a few samples typically characterize the Phlegraean Fields Neapolitan Yellow Tuff [4,42].



Figure 4. XRPD patterns of the investigated mortar samples of 1st and 2nd century CE. Where applicable, abbreviations according to [43]: Cal = calcite; Anl = analcime; Php = phillipsite; Cbz = chabazite; Fsp = feldpar; Mca = mica; Gp = gypsum; Hl = halite; Qz = quartz; Arg = aragonite; Cpx = clinopyroxene; Bsn = bassanite; Crn = corundum (20% added as standard for future quantitative analysis).

4.2. *Chemistry, Hydraulic Behavior, and Pore System Characterization* 4.2.1. Binder and Lime Lumps

EDS analysis of binder fraction was performed on both binder and lime lumps (Supplementary Material S2), in order to (1) obtain information about the type of lime used for mortar production and (2) define hydraulicity index (HI), thus obtaining a measure of the hydraulicity of the mortar.

Lime lumps contain mainly CaO + MgO (91.38–98.83 wt.% and 82.35–96.66 wt.% for mortars of the 1st and 2nd century CE, respectively). Regarding binder fraction, CaO + MgO values vary between 76.2 wt.% and 88.5 wt.% for mortars of the 1st and 2nd century CE, respectively.

Hydraulicity index (HI), calculated according to [32] is relatively small for lime lumps, varying between 0.01 and 0.05 for the P15-1 sample, between 0.01 and 0.02 for P66-1 and P64-2 samples and between 0.01 and 0.07 for P65-1 sample (Figure 5). According to [44] these values allow for the classification of lime lumps as aerial lime. Conversely, the same index is relatively high for binder fraction, showing values of 0.10 for the P15-1 sample, 0.21 for the P64-2 sample; it varies between 0.10 and 0.26 and between 0.10 and 0.19 for P66-1 and P65-1 samples, respectively, allowing the classification as slightly to moderately hydraulic lime.



Figure 5. Hydraulicity index (HI) values for binder (a) and lime lumps (b) of mortar samples.

These values of HI confirm that hydraulicity is strictly linked to the presence of pozzolanic material (i.e., volcanic aggregate), which raises the Si, Al and Ca(OH)₂ reaction allowing the formation of calcium and aluminum hydrated silicates (C-A-S-H gel). These neo-forming phases are essential for the durability of mortars as they act as fillers for the voids [7].

4.2.2. Aggregate

Major element compositions (reported in Supplementary Material S3) of mineralogical phases and glass of juvenile products (pumice and scoriae) used as aggregates for the analyzed mortars were investigated to make hypotheses about their provenance [45].

Glass analyses were plotted on the total alkali vs. silica (TAS; [45]) diagram for effusive volcanic rocks of Figure 6a. Glass analyses show a limited compositional range and plot within the trachyandesite–trachyte, and tephriphonolite–phonolite fields. They are thus ascribable to the alkaline and strongly alkaline volcanic series.

Regarding mineral phases (Supplementary Material S3), alkali feldspars (Figure 6b) are sanidine $(An_{1-5}Ab_{18-50}Or_{49-80}$ for P15-1 sample, $An_8Ab_{38}Or_{53}$ for P66-1 sample, $An_{3-5}Ab_{21-38}Or_{57-75}$ for P64-2 sample, and $An_{2-9}Ab_{20-29}Or_{55-77}$ for P65-1 sample), whereas the few plagioclases detected in the P65-1 sample are bytownite and labradorite $(An_{60-82}Ab_{16-34}Or_{2-6})$.

All pyroxenes (Figure 6c; Fe calculated following [46]) are diopside ($Wo_{53}En_{37}Fs_{10}$ for the P15-1 sample, $Wo_{50-52}En_{37-44}Fs_{4-11}$ for the P66-1 sample, $Wo_{49-52}En_{35-47}Fs_{5-14}$ for the P64-2 sample, and $Wo_{47-50}En_{37-48}Fs_{5-17}$ for the P65-1 sample).

Few phillipsite crystals (Supplementary Material S3) were detected in the P15-1 sample with the following averaged chemical formula:

$$(Na_{2.52} K_{2.79} Ca_{0.54}) [Si_{11.13} Al_{4.87} O_{32} 11.56 H_2 O]$$

recalculated on the basis of 32 oxygens. E% is the percentage error based on [47] equation. Micas (Supplementary Material S3) were also detected in P64-2 and P65-1 and their

chemistry is coherent with brown-type.

Both glass and mineralogical phase analyses fit with Phlegraean Fields analyses [42].



Figure 6. (a) Total alkali vs. silica [45] for glass analyses of juvenile products for the investigated mortars; (b) composition of the analyzed feldspars; (c) composition of the analyzed clinopyroxenes.

5. Conclusions

This work represents a first attempt to characterize mortars from one of the most important archaeological sites of Phlegraean Fields Area, the Anfiteatro Flavio, shedding some lights on the different provenance of raw materials and production technologies.

Raw materials used for mortar preparation have a local provenance, and they are well in line with the surrounding geological environment.

The pozzolanic material used consists of volcanic fragments, scoriae, pumice, and crystal fragments belonging to the pyroclastic rocks of Phlegraean Fields, which is the most important component of the recipe for producing Roman hydraulic mortars. The use of these volcanic aggregates in the analyzed mortars confers a high hydraulicity, highlighted by the presence of reaction rims around pozzolanic material. The high hydraulicity also results from a careful selection, preparation, and mixing of the local geomaterials.

The binding matrix is compositionally characterized by different secondary phases such as C-A-S-H gel, calcite, and gypsum. C-A-S-H gel resulting from the pozzolanic reaction fills the pore spaces and increases the strength of these materials [48].

Residual calcite can be due to a non-completely calcined limestone, probably resulting from a low firing temperature of the limestone or from an incorrect slaking, or it can be associated with secondary carbonation processes due to the long exposure of materials in a subaerial environment [39]. Aragonite's presence may be due to a different limestone used for mortar production [6].

The presence of gypsum and bassanite is due to calcite sulfation processes caused by a decrease in pH due to the dissolution of atmospheric SO₂ [15,39]. Finally, halite is certainly ascribable to marine aerosol exposure, given the proximity of the archaeological site to the sea.

Regarding the comparison between the two construction phases (1st and 2nd centuries), not many differences were found. It was noted that reaction rims between binder and pumice are more evident for the first construction phase, as well as a higher percentage of tuff fragments, whereas in the 2nd century samples there is a greater abundance of lime lumps.

Therefore, for at least two centuries, Roman builders considered the identified mix as optimal for their buildings, so much so that they did not make changes in the type and proportions of the used raw materials.

This research contributes to the knowledge and understanding of the technical skills achieved by the ancient Romans and represents an important first step in planning a future restoration project for the consolidation of the most degraded parts, in order to protect this important monument.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/coatings12111712/s1, S1: Qualitative X-Ray Powder Diffraction analysis. S2: EDS analysis of binder and lime lumps. S3: EDS analysis of glass and mineralogical phases.

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References

- Moropoulou, A.; Bakolas, A.; Anagnostopoulou, S. Composite materials in ancient structures. *Cem. Concr. Compos.* 2005, 27, 295–300. [CrossRef]
- Deino, A.L.; Orsi, G.; de Vita, S.; Piochi, M. The age of the Neapolitan YellowTuff caldera-forming eruption (Campi Flegrei caldera—Italy) assessed by⁴⁰Ar/³⁹Ardating method. *J. Volcanol. Geotherm. Res.* 2004, 133, 157–170. [CrossRef]
- 3. Montesano, G.; Cappelletti, P.; Caputo, D.; Liguori, B.; Campanile, A.; Rispoli., C. Mineralogical and technological characterization of zeolites from basin and range as pozzolanic addition of cement. *Materials* **2022**, *15*, 2684. [CrossRef] [PubMed]
- Miriello, D.; Barca, D.; Bloise, A.; Ciarallo, A.; Crisci, G.M.; De Rose, T.; Gattuso, C.; Gazineo, F.; La Russa, M.F. Characterisation of archaeological mortars from Pompeii (Campania, Italy) and identification of construction phases by compositional data analysis. J. Archaeol. Sci. 2010, 37, 2207–2223. [CrossRef]
- De Luca, R.; Miriello, D.; Pecci, A.; Dominguez Bella, S.; Bernal-Casarola, D.; Cottica, D.; Blose, A.; Crisci, G.M. Archaeometric study of mortars from the Garum Shop at Pompeii, Campania, Italy. *Geoarchaeology* 2015, 30, 330–351. [CrossRef]
- Rispoli, C.; De Bonis, A.; Guarino, V.; Graziano, S.F.; Di Benedetto, C.; Esposito, R.; Morra, V.; Cappelletti, P. The ancient pozzolanic mortars of the thermal complex of Baia (Campi Flegrei, Italy). J. Cult. Herit. 2019, 40, 143–154. [CrossRef]
- Rispoli, C.; de Bonis, A.; Esposito, R.; Graziano, S.F.; Langella, A.; Mercurio, M.; Morra, V.; Cappelletti, P. Unveiling the Secrets of Roman Craftsmanship: Mortars from Piscina Mirabilis (Campi Flegrei, Italy). *Archaeol. Anthropol. Sci.* 2020, 12, 8. [CrossRef]
- Rispoli, C.; Graziano, S.F.; Guarino, V.; De Bonis, A.; Di Benedetto, C.; Esposito, R.; Budetta, T.; Morra, V.; Cappelletti, P. Characterization of ancient mortars: Preliminary results from Villa del Pezzolo. In Proceedings of the IMEKO International Conference on Metrology for Archaeology and Cultural Heritage. MetroArcheo, Torino, Italy, 19–21 October 2016; pp. 151–156.
- 9. Columbu, S.; Depalmas, A.; Brodu, G.; Gallello, G.; Fancello, D. Mining exploration, raw materials and production technologies of mortars in the different civilization periods in Menorca Island (Spain). *Minerals* **2022**, *12*, 218. [CrossRef]

- Sitzia, F.; Beltrame, M.; Columbu, S.; Lisci, C.; Miguel, C.; Mirão, J. Ancient restoration and production technologies of Roman mortars from monuments placed in hydrogeological risk areas: A case study. *Archaeol. Anthropol. Sci.* 2020, 12, 147. [CrossRef]
- Columbu, S.; Lisci, C.; Sitzia, F.; Lorenzetti, G.; Lezzerini, M.; Pagnotta, S.; Raneri, S.; Legnaioli, S.; Palleschi, V.; Gallello, G.; et al. Mineralogical, petrographic and physical-mechanical study of Roman construction materials from the Maritime Theatre of Hadrian's Villa (Rome, Italy). *Measurement* 2018, 127, 264–276. [CrossRef]
- Columbu, S.; Garau, A.M.; Lugliè, C. Geochemical characterisation of pozzolanic obsidian glasses used in the ancient mortars of Nora Roman theatre (Sardinia, Italy): Provenance of raw materials and historical–archaeological implications. *Archaeol. Anthropol. Sci.* 2019, *11*, 2121–2150. [CrossRef]
- 13. Raneri, S.; Pagnotta, S.; Lezzerini, M.; Legnaioli, S.; Palleschi, V.; Columbu, S.; Neri, N.F.; Mazzoleni, P. Examining the reactivity of volcanic ash in ancient mortars by using a micro-chemical approach. *Mediterr. Archaeol. Archaeom.* **2018**, *18*, 147–157. [CrossRef]
- Ramacciotti, M.; Rubio, S.; Gallello, G.; Lezzerini, M.; Columbu, S.; Hernandez, E.; Morales-Rubio, A.; Pastor, A.; De La Guardia, M. Chronological classification of ancient mortars employing spectroscopy and spectrometry techniques: Sagunto (Valencia, Spain) Case. J. Spectrosc. 2018, 2018, 9736547. [CrossRef]
- Rispoli, C.; Fedele, L.; Di Benedetto, C.; Esposito, R.; Graziano, S.F.; Guarino, V.; Morra, V.; Cappelletti, P. Characterization of building materials from the Anfiteatro Flavio (Pozzuoli, Southern Italy): A mineralogical and petrographic study. *Ital. J. Geosci.* 2019, 138, 103–115. [CrossRef]
- 16. Fedele, L.; Morra, V. Il distretto vulcanico dei campi flegrei. In *Geoitalia, Geoitalia Fist Onlus*; MEDIAprint s.r.l.: Livorno, Italy, 2011; Volume 35, pp. 18–27.
- Perrotta, A.; Scarpati, C.; Luongo, G.; Morra, V. Stratigraphy and volcanological evolution of the southwestern sector of Campi Flegrei and Procida Island, Italy. In *Stratigraphy and Geology of Volcanic Areas*; Groppelli, G., Viereck-Goette, L., Eds.; Geological Society of America Special Paper; Geological Society of America: Boulder, CO, USA, 2006; Volume 464, pp. 171–191.
- 18. Natale, J.; Ferranti, L.; Isaia, R.; Marino, C.; Sacchi, M.; Spiess, V.; Vitale, S. Integrated on-land-offshore stratigraphy of the Campi Flegrei caldera: New insights into the volcano-tectonic evolution in the last 15 kyr. *Basin Res.* **2022**, *34*, 855–882. [CrossRef]
- 19. Rolandi, G.; Bellucci, F.; Heizler, M.T.; Belkin, H.E.; De Vivo, B. Tectonic controls on the genesis of ignimbrites from the Campanian Volcanic Zone, Southern Italy. *Mineral. Petrol.* **2003**, *79*, 3–31. [CrossRef]
- 20. Fedele, L.; Morra, V.; Perrotta, A.; Scarpati, C.; Sbrana, A.; Putignano, M.L. Note Illustrative della Carta Geologica della Regione Campana Alla Scala 1:10.000. Foglio 465 e 464 Isola di Procida; Assessorato Difesa del Suolo: Rome, Italy, 2012.
- 21. Vitale, S.; Ciarcia, S. Tectono-stratigraphic setting of the Campania region (southern Italy). J. Maps 2018, 14, 9–21. [CrossRef]
- 22. Ciarcia, S.; Fedele, L.; Morra, V.; Vitale, S. Inquadramento geologico e vulcanologico della Regione Campania. In *Le Pietre Storiche Della Campania*; de Gennaro, M., Calcaterra, D., Langella, A., Eds.; Luciano: New York, NY, USA, 2013; pp. 56–78.
- Conticelli, S.; D'Antonio, M.; Pinarelli, L.; Civetta, L. Source contamination and mantle heterogeneity in the genesis of Italian potassic and ultrapotassic volcanic rocks: Sr–Nd–Pb isotope data from Roman Province and Southern Tuscany. *Mineral. Petrol.* 2002, 74, 188–222. [CrossRef]
- 24. Peccerillo, A. Plio-Quaternary Volcanism in Italy; Springer: New York, NY, USA, 2005; Volume 365.
- 25. Di Girolamo, P.; Ghiara, M.R.; Lirer, L.; Munno, R.; Rolandi, G.; Stanzione, D. Vulcanologia e petrologia dei Campi Flegrei. *Boll. Della Soc. Geol. Ital. Roma* **1984**, *103*, 349–413.
- De Astis, G.; Pappalardo, L.; Piochi, M. Procida volcanic history: New insights into the evolution of the Phlegraean Volcanic District (Campania Region, Italy). *Bull. Volcanol.* 2004, *66*, 622–641. [CrossRef]
- Poli, S.; Chiesa, S.; Gillot, P.Y.; Gregnanin, A.; Guichard, F. Chemistry versus time in the volcanic complex of Ischia (Gulf of Naples, Italy): Evidence of successive magmatic cycles. *Contrib. Mineral. Petrol.* 1987, 95, 322–335. [CrossRef]
- Ricci, G. Il Distretto Vulcanico dei Campi Flegrei: Petrologia e Geochimica dei Depositi di Breccia e dei Prodotti Piroclastici Associati. Ph.D. Thesis, Università di Napoli, Italy, 2000.
- 29. De Vivo, B.; Rolandi, G.; Gans, P.B.; Calvert, A.; Bohrson, W.A.; Spera, F.J.; Belkin, H.E. New constraints on the pyroclastic eruptive history of the Campanian volcanic Plain (Italy). *Mineral. Petrol.* **2001**, *73*, 47–65. [CrossRef]
- Colella, A.; Calcaterra, D.; Cappelletti, P.; Di Benedetto, C.; Langella, A.; Papa, L.; Perrotta, A.; Scarpati, C.; de Gennaro, M. Il Tufo Giallo Napoletano. In *Le Pietre Storiche della Campania*; de Gennaro, M., Calcaterra, D., Langella, A., Eds.; Luciano: New York, NY, USA, 2013; pp. 129–154.
- Demma, F. Monumenti Pubblici di Puteoli: Per un Archeologia Dell'Architettura—Monografie della Rivista Archeologia Classica; L'Erma di Bretschneider: Rome, Italy, 2007; pp. 27–76.
- 32. Boynton, R.S. Chemistry and Technology of Lime and Limestone, 2nd ed.; John Wiley&Sons Inc.: New York, NY, USA, 1979.
- 33. UNI-EN 11305, Beni Culturali: Malte Storiche, Linee Guida per la Caratterizzazione Mineralogico-Petrografica, Fisica e Chimica delle Malte; SEgretariato Regionale per la Calabria: Roccelletta, Italy, 2009.
- 34. UNI-EN 11176, Beni Culturali: Descrizione Petrografica di Una Malta; SEgretariato Regionale per la Calabria: Roccelletta, Italy, 2006.
- 35. Wentworth, C.K. A scale of grade and class terms for clastic sediments. J. Geol. 1922, 30, 377–392. [CrossRef]
- 36. Bakolas, A.; Biscontin, G.; Contardi, V.; Francesehi, E.; Moropoulou, A.; Palazzi, D.; Zendri, E. Thermoanalytical research on traditional mortars from Venice. *Thermochim. Acta* **1995**, *269*, 817–828. [CrossRef]
- 37. Barba, L.; Blancas, J.; Manzanilla, L.R.; Ortiz, A.; Barca, D.; Crisci, G.M.; Miriello, D.; Pecci, A. Provenance of the limestone used in Teotihuacan (Mexico): A methodological approach. *Archaeometry* **2009**, *51*, 525–545. [CrossRef]

- 38. Terry, R.D.; Chilingar, G.V. Summary of "Concerning some additional aids in studying sedimentary formations" by M.S. Shvetsov. *J. Sediment. Petrol.* **1995**, *25*, 229–234. [CrossRef]
- de Gennaro, M.; Calcaterra, D.; Cappelletti, P.; Langella, A.; Morra, V. Building stones and related weathering in the architecture of the ancient city of Naples. J. Cult. Her. 2000, 139, 399–414. [CrossRef]
- 40. Verde, M.; De Bonis, A.; D'Uva, F.; Guarino, V.; Izzo, F.; Rispoli, C.; Morra, V. Minero-petrographic investigation on Roman pottery found in a dump in the workshop area of Cumae (southern Italy). *J. Archaeol. Sci. Rep.* **2022**, *42*, 103376. [CrossRef]
- de Gennaro, M.; Incoronato, A.; Mastrolorenzo, G.; Adabbo, M.; Spina, G. Depositional mechanisms and alteration processes in different types of pyroclastic deposits from Campi Flegrei Volcanic Field (Southern Italy). J. Volcanol. Geotherm. Res. 1999, 91, 303–320. [CrossRef]
- Morra, V.; Calcaterra, D.; Cappelletti, P.; Colella, A.; Fedele, L.; de Gennaro, R.; Langella, A.; Mercurio, M.; de Gennaro, M. Urban geology: Relationships between geological setting and architectural heritage of the Neapolitan area. *J. Virtual Explor.* 2010, 36, 1–26. [CrossRef]
- 43. Whitney, D.L.; Evans, B.W. Abbreviations for names of rock-forming minerals. Am. Mineral. 2010, 95, 185–187. [CrossRef]
- 44. Zawawi, R.; Banfill, P.F.G. Effect of burning conditions on properties of artificial hydraulic lime mortar obtained from limestone and siliceous waste materials. *Adv. Appl. Ceram.* 2006, *105*, 175–178. [CrossRef]
- Le Bas, M.J.; Le Maitre, R.W.; Streckeisen, A.; Zanettin, B. A chemical classification of volcanic rocks based on the total alkali-silica diagram. J. Petrol. 1986, 27, 745–750. [CrossRef]
- Papike, J.J.; Karner, J.; Shearer, C.K. Comparative planetary mineralogy: Valence state partitioning of Cr, Fe, Ti, and V among crystallographic sites in olivine, pyroxene and spinel from planetary basalts. *Am. Mineral.* 2005, 90, 277–290. [CrossRef]
- 47. Passaglia, E. The crystal chemistry of chabazites. Am. Mineral. 1970, 55, 1278–1301.
- 48. Jackson, M.; Mulcahy, S.; Chen, H.; Li, Y.; Li, Q.; Cappelletti, P.; Wenk, H. Phillipsite and Al-tobermorite mineral cements produced through low-temperature water-rock reactions in Roman marine concrete. *Am. Mineral.* **2017**, *102*, 1435–1450. [CrossRef]