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Archaeometric Analysis of Encrustations Adhering to Pietra Ollare Fragments from the Medieval Village of Nogara

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Abstract: The aim of this study was to analyze a set of pietra ollare fragments that presented burnt encrustations to further understand the use of pietra ollare vessels during the Middle Ages. The fragments were obtained from Nogara (Vr) and date to the 9th–10th centuries CE. To obtain a variety of data, scanning electron microscopy (SEM) with energy-dispersive X-ray spectroscopy (EDS) and pollen analyses were performed. The SEM-EDS enabled the microscopic observation and the understanding of the chemical composition of the encrustations; the pollen analysis was performed to find possible pollen trapped in the encrustations. The pollen was scarce, but notable specimens were found. The results SEM-EDS analysis provided data possibly linked to meat preparation. Further analysis will be conducted to deepen our understanding of the use of the pietra ollare in cooking practices. These results are relevant because they match other data that have emerged from the excavations at Nogara (archeozoological and paleobotanical) and because the use of this kind of vessel remains poorly studied.

Keywords: encrustations analysis; soapstone; pietra ollare; food; SEM-EDS; pollen analysis; Middle Ages

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1. Introduction

In 2005, excavations were conducted at Nogara. During the digging, pietra ollare vessels fragments with encrustations were found. These encrustations were probably the result of food cooking or preservation. The aim of the SEM-EDS analysis conducted in this study was to find possible food traces. The artefacts were found along the bank of the Tartaro River, where a part of the Nogara settlement developed during the Middle Ages, near the castle in the town. The fragments were found in the ground and the fireplaces of a couple of houses that were excavated. Therefore, we could analyze materials from within a well-known and well-dated context (using radiocarbon and dendrochronology) that allowed us to gain perspective on the ordinary lives of the inhabitants of these Medieval houses in Nogara.

1.1. Context

1.1.1. Pietra Ollare in Italy during the Early Middle Ages

Dario Monaco

Pietra ollare is a commodity-related Italian term for a variety of metamorphic rocks, with different colors, look, and composition that are subdivided in 11 groups based on the geological and petrographic characteristics by the classification by Mannoni et al. [1].

All the metamorphic rocks called pietra ollare present some common physical and mechanical properties [1,2]:

- High thermal refractoriness;
- Low porosity (not prone to liquid absorption);

- Chemical stability;
- Very low hardness (from 1 to 4 on the Mohs scale), so they are easily carved.

The conditions for the formation of deposits of pietra ollare limit their presence in western Europe to Alpine areas from the Maritime Alps to the Rhaetian and Orobic Alps. From a mineralogical point of view, the physical and mechanical properties of the pietra ollare [3] derive from mainly olivine and/or pyroxene rocks that were originally located in the Earth's mantle at a depth of 50 km under the continents and 5 km under the oceans [1]. The main areas in which these rocks were extracted and carved were in the western Alps (Aosta Valley and Piemonte) and central Alps (Lombardy, in particular Chiavenna Valley) [2,4]. During the Early Middle Ages, the western Alps contributed fewer artifacts; from the middle of the seventh century, these artefacts were almost exclusively produced in the central Alps.

The physical and mechanical properties of pietra ollare made it suitable for carving vessels and crucibles to use on fire. Pietra ollare extraction and carving are documented in the Roman period but were relegated mainly for local use near the production zones. During the Early Middle Ages, the use of pietra ollare vessels spread to the whole Po Valley and central Italy; archeological findings document their use in coastal or near coastal centers in southern Italy [2–10]. The commercial diffusion followed fluvial and maritime courses. In our case, the pietra ollare in Nogara was probably river-related [7] (Figure 1).

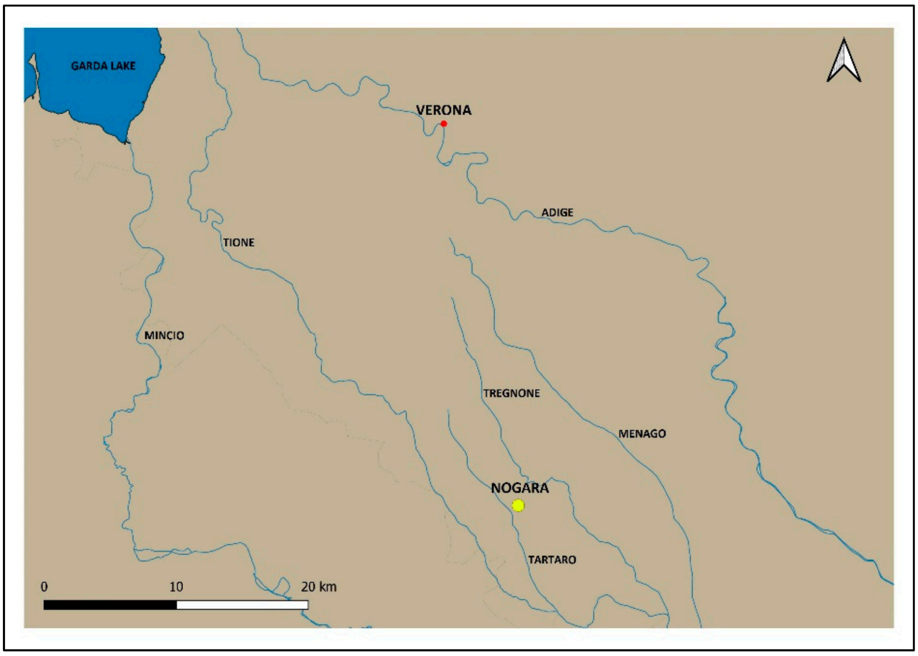


Figure 1. Nogara and main water courses in the area.

Notably, the English term "soapstone" refers only to stones containing predominantly talc and magnesite [9]. Because many types of pietra ollare exist in addition to the magnesite–talc–schists (such as chlorite schists, serpentine schists, etc.), we use the broader term pietra ollare.

1.1.2. Nogara: Medieval Village in Po Valley

Dario Monaco, Fabio Saggioro

Nogara is and has been an important center in the low plains south of Verona (Figures 2 and 3); the investigations conducted in the early 2000s acknowledged the genesis and development of this center in the Middle Ages [9]. A fundamental event in the history of Nogara is the foundation of the castle in 906, supported by a diploma of King Berengario, which also granted the rights for a market and port, among others. The main objective of the construction of the castle was defense from the incursions from the Hungarians and the desire to increase the strategic importance of a center on a strong rise, such as Nogara. Moreover, the area was in the hands of deacon Audiberto, a trusted collaborator and friend of the count of Verona Anselmo and Berengario. As discovered through the excavations, the history of this center began well before 906: the area of the bank of the Tartaro River was probably frequented since the end of the eighth century. During the ninth century, we can see how the true and proper structuring of the area developed, with the construction of equal-sized lots, followed by the partial drainage of the area, with annexed arrangement of the bank, and the planting of a road paved with wood. This phase of settlement development between the 9th and 10th centuries is part of a wider and more articulated demographic and economic recovery of the areas of the lower plain, in which public actors intervened in the redefinition of landscape, community structures, and the economy [11,12].

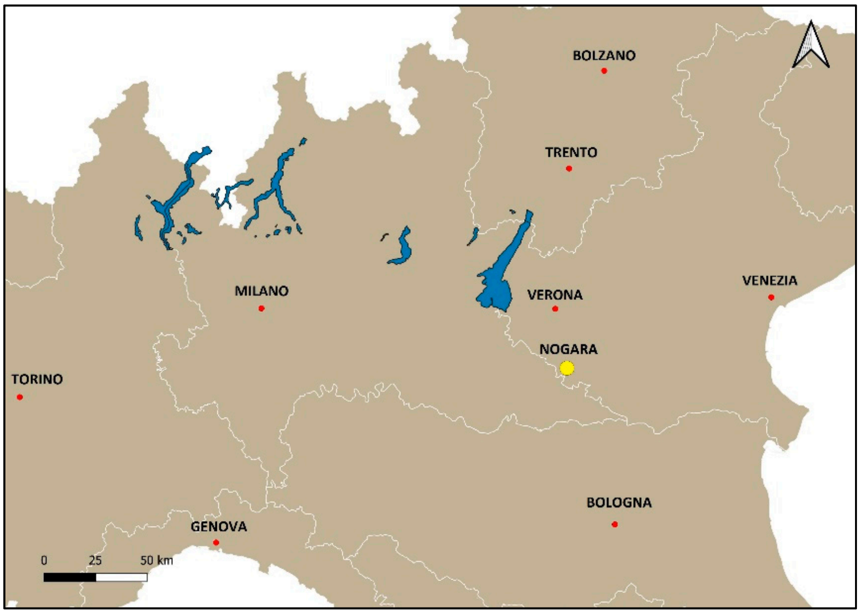
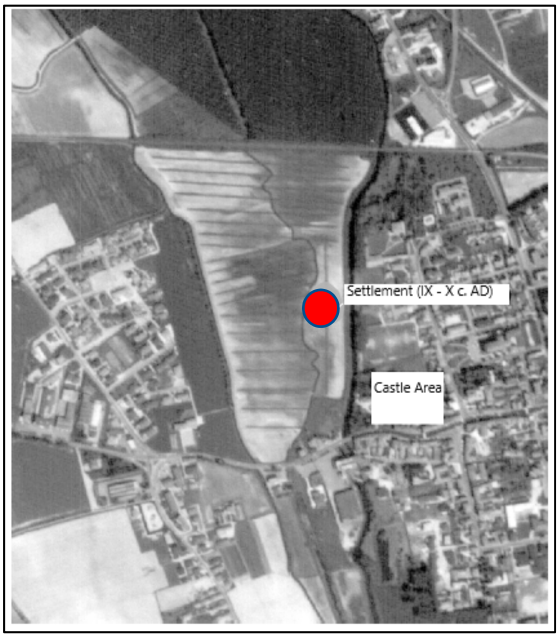


Figure 2. Nogara position in Po Valley.

The materials analyzed were found in the digging sectors 1, 2, 3, and 5, which represented the most important excavation area (Figures 4 and 5). In this area (as mentioned before), the remains of a couple of houses, identified in the digging documentation as buildings A and B, were found (Figure 5a). The two structures are dated to the 9th–10th century (phase 2 of the relative chronology), and each one presents different phases of use and fireplaces. During their lifetime, the structures experienced different internal reorganizations and renovations. Before the first half of the 10th century, building B was abandoned (Figure 5b), and the area it once occupied was probably converted for agricultural purposes. Building A had a longer life cycle, but from the beginning of the 11th century (to the 13th century), the whole area once occupied by the two houses was no longer present as any residential structure. The area was probably converted to a dumping and working site, as evidenced by the huge darker organic deposits that contain ceramics, carbons, casting dross, and other materials. The post holes recorded in this phase (phase 3 of the relative chronology) indicate structures that likely did not have a housing function. In the following 14th to 16th centuries (phase 4 and 5), the area became a swamp, and people more sporadically frequented the area; visits were limited to riverbank use, and no structural elements were present. The only infrastructure was a small canal that was probably excavated during the modern age for the partial agricultural restoration of the area [11].



(a)

(b)

Figure 3. (**a**) Aerial view of Nogara. The marked area is the Medieval settlement, that area was investigated during the excavations. (**b**) Aerial view of digging sector. Images adapted with permission from [11]. 2011, F. Saggioro.

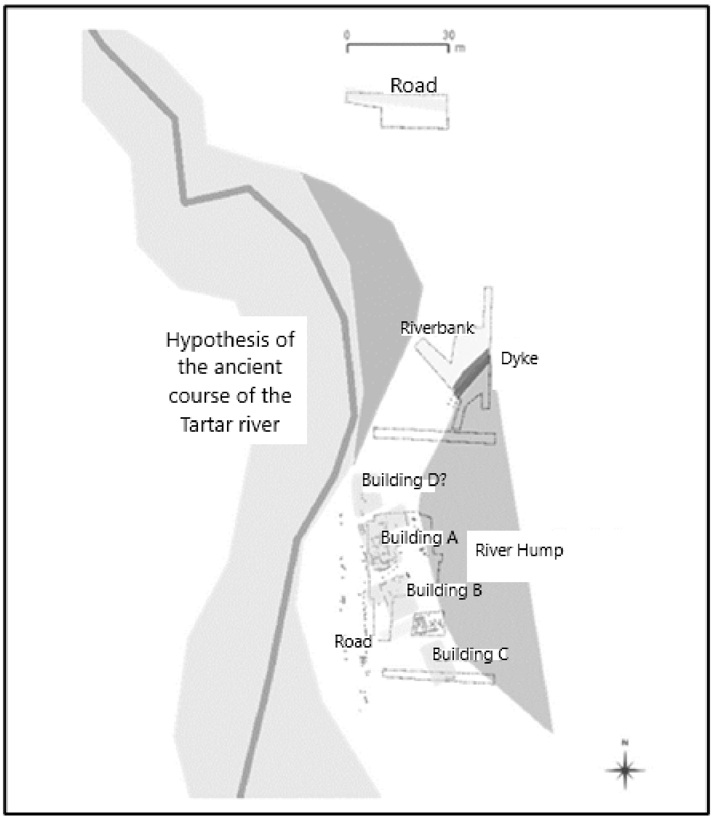
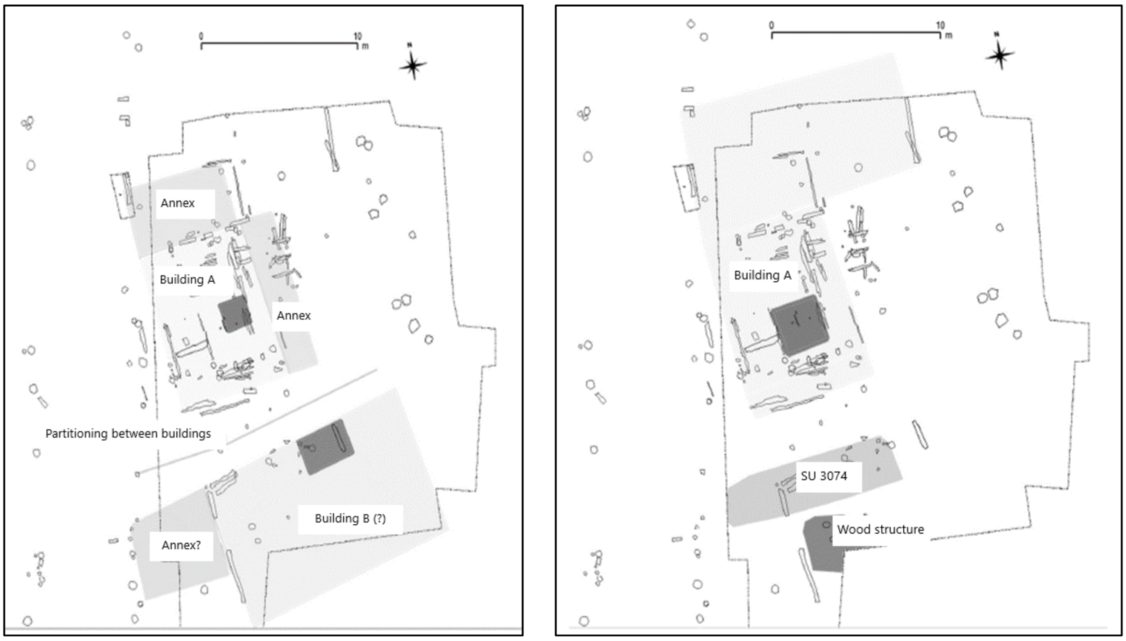


Figure 4. Morphological and hydrological recostruction.



(**a**) (**b**)

Figure 5. (**a**) Phase 2a (814–824 CE: first quarter of 9th century) and phase 2b ((1) 824–847 CE; (2) 847: end of 9th century); (**b**) phase 2c (late 9th, first half of 10th century). Images adapted with permission from [11]. 2011, F. Saggioro.

2. Materials and Methods

2.1. Materials

Dario Monaco

Initially, we had 31 fragments; after a selection process, 10 were chosen to be further analyzed. (See images of the fragments in the Appendix A, Figure A1.)

The fragments, in concordance with the previous studies conducted by Chiara Malaguti [13], present plain walls that link to a truncated cone form of the vessels; this form was useful for vessels intended for cooking by hanging on the fire. This type of application is also suggested by the convex form of the vessel bottoms.

Because the objective of this study was not a discussion on the pietra ollare per se, but the use of vessels made with it, we chose to mainly investigate the encrusted remains on the fragments. The mineralogical characteristics of the shards were observed on 4 representative samples, verifying if the elements we identified in the encrustation originated not from vessel use but from the chemical composition of the vessel. For a more comprehensive examination regarding the petrographic characteristics and commercial diffusion of the pietra ollare, we referred to other specific studies on these topics [1–10].

Table 1 indicates the relevant information for each fragment and the analysis applied to each sample.

Table 1. "Chronological and contextual information" column adapted with permission from [11]. 2011, F. Saggioro. which provides more details about these phases.

Sample	Stereo Microscope	SEM-EDS (Encrustation)	SEM-EDS (Stone vs. Encrustation)	Pollen Analysis	Material	Chronological and Contextual Information	Stratigraphic Unit
1	X	X			Wall 1 ("parete 1") (inner part)	?	3071
2	X	X	X	X	Wall 3 ("parete 3") (outer part)	PHASE 2B: (1) 824–847 CE; (2) 847-end of 9th c., use level (p. 61)	3064

Table 1. *Cont.*

Sample	Stereo Microscope	SEM-EDS (Encrustation)	SEM-EDS (Stone vs. Encrustation)	Pollen Analysis	Material	Chronological and Contextual Information	Stratigraphic Unit
3	X	X			Bottom with wall (“fondo con parete”) (outer part)	PHASE 2C: late 9th to first half of 10th c., use level (p. 61)	3008
4	X	X	X	X	Bottom (“fondo”) (outer part)	PHASE 2B: (1) 824–847 CE; (2) 847-late 9th c., use level (p. 61)	3064
5	X	X		X	Big Bottom (“fondo grande”) (inner part)	PHASE 2B—(1) 824–847 CE (2) 847-late IX c—use level/growth level (p. 61)	3065
6	X	X	X	X	Rim (“orlo”) (outer part)	PHASE 2B—(1) 824–847 CE (2) 847-late IX c—use level/growth level (p. 61)	3065
7	X	X		X	Bottom with the wall’s base, (“Fondo con base parete”) (inner part, corner between the bottom and wall base)	PHASE 2C: late 9th to first half of 10th c., use level (p. 61)	3038
8	X	X	X	X	Little bottom (“Fondo piccolo”) (inner part)	PHASE 2B: (1) 824–847 CE; (2) 847-late 9th c., use level/growth level (p. 61)	3065
9	X	X			Bottom with wall (“Fondo con parete”) (outer part)	PHASE 2B: (1) 824–847 CE; (2) 847-late 9th c.—growth level caused by fireplace use (p. 61)	3057
10	X	X		X	Bottom with a little carbon (“Fondo con carboncino”) (inner part)	PHASE 3: beginning of 11th–13th c.—growth level (pp. 65–66)	3044

2.2. Methods

2.2.1. Stereo Microscope Observations

Dario Monaco, Carmela Vaccaro, and Elena Marrocchino

The first step in the study was to observe the 31 encrusted fragments with a stereo microscope. The observations were performed at the Physics and Earth science Department at the University of Ferrara. After these observations, 10 fragments among the 31 were chosen for further analysis with the SEM-EDS. The selection was based on two criteria:

- Considerable encrustation presence;
- Chronologic collocation between the 9th and 10th centuries, with two exceptions, Samples 1 and 10. Sample 1 does not have a clear dating, but the considerable encrustation presence motivated the sampling. Sample 10 is chronologically collocated between the 11th and 13th centuries but also contained considerable encrustation.

For the selection of 4 representative samples for the comparison of the compositions of the stone and encrustations, we applied the same criteria. Samples 1 and 10 were excluded from the chronology criterion, as described above. After the selection of the shards, we removed a small sample (1–2 cm^2) from each one of them using pincers, paying particular attention to ensuring that the crystalline structure of the stone and the encrustation on the surface were visible in the section. Then, we proceeded with SEM-EDS analysis.

2.2.2. SEM-EDS Analysis

Dario Monaco, Carmela Vaccaro, Elena Marrocchino, and Negar Efthekari

We analyzed the encrustations on the samples with the aim of identifying food remains. Using SEM-EDS, we characterized the 4 representative samples, verifying if the elements that we identified in the encrustation originated from vessel use or the chemical composition of the vessel.

The encrustations were manually sampled with the use of a lancet, and the material was deposited on the SEM’s STUB. The analysis was performed by Negar Efthekari at the

Department of Engineering at the University of Ferrara, under the direction of Carmela Vaccaro and the collaboration of Elena Marrocchino, using previously reported methods [14]. Before the observation of the 4 representative samples, we dried them in an ARGOLAB TCN 115 oven for three days at 50 °C to enhance the vacuum performance of the SEM-EDS.

We used a scanning electron microscope (model SEM Zeiss EVO 40 Aztec Oxford nano analysis). The high-brightness thermionic cathode LaB6 can conventionally operate in high vacuum conditions and with air inserted in the sample chamber (variable pressure). With the variable pressure modality, we can observe isolated samples without covering and materials that cannot resist vacuum conditions. This instrument was equipped with energy-dispersive X-ray spectroscopy (EDS) for analyzing the chemical composition, with light elements ($Z < 11$) included. A backscattered electrons detector was also present. The analysis parameters were as follows:

- Source: LaB6.
- Maximum acceleration tension: 30 kV.
- Electrons emitted were detected in the presence of gas.
- Energy-dispersive X-ray spectrometry (EDS) for X-ray microanalysis.
- Could conventionally operate in high vacuum and with variable pressure (SEM XVP), with maximum pressure: 6 torr.

We obtained the following information:

- Superficial morphology and topography (millimeter to submicrometer scale).
- Chemical element identification in areas selected by the user; chemical element identification in particles (only particles with dimension greater than 1 micron).
- Elemental quantitative analysis (also $Z < 10$ elements) and compositional maps.

In addition to conductive materials, we can also observe isolated samples, for example, resin-incorporate samples, ceramics, paper, polymers, ambient dust, vegetal fragments, and fixed and dehydrated animal tissues (without metallic film deposition).

The obtained images were three-dimensional and colored on a grey scale; the variation in this scale indicated the diverse chemical nature of the components, where the brighter the color, the higher the element atomic number.

We acknowledge the limits of sole SEM-EDS analysis for the petrographic study of the pietra ollare samples; so, the analysis is useful for an indicative look at the stone composition but not for a detailed petrographic characterization. We judged this level of detail as sufficient for our study, as our focus was the study of the encrustations not the characterization of the pietra ollare.

For detailed and comprehensive petrographic information on the Nogara samples, we suggest referring to the work currently being conducted by the University of Verona [2]. This work, framed within a Ph.D. thesis, involves a systematic study of the mineralogical characterization of pietra ollare quarries in the Piuro area (important extraction and production zone during the Middle Ages, situated in Sondrio province, in the central Alps in Lombardy). The analysis is currently underway, being performed by Elisa Maccadanza and coordinated by Marco Zanatta (UniTN Physics Department), which involves the use of spectroscopic techniques aimed at the detailed mineralogical identification of the various sampled quarries. Micro-Raman spectroscopy is being used to identify the mineralogical phases of the material by analyzing its vibrational spectrum (i.e., the spectrum of the vibrational frequencies of the atoms and molecules that compose the sample). This will expand the existing spectra database with specific data on the pietra ollare outcrops in Valchiavenna and Val Bregaglia [9] and facilitate the determination of the provenance of the pietra ollare products that are widespread in Italy and have been analyzed following the same protocol. Of the reference samples currently being analyzed, many are from Nogara.

2.2.3. Pollen Analysis

Dario Monaco, Marco Marchesini

The pollen was analyzed at the laboratory of the Centro Agricoltura e Ambiente Giorgio Nicoli (San Giovanni in Persiceto (BO)). Seven samples were obtained from seven fragments that had already been analyzed by SEM-EDS (Table 1), which were subjected to various chemical steps to obtain material from each one that was as free as possible from organic matter and other components other than pollen [15]. Once the pollen samples were obtained, they were observed under a transmitted-light optical microscope (OPTECH B5) usually at 40X magnification, and the palynomorphs were identified with the help of pollen atlases [16]. For more details on the chemical procedure, please see the supplementary material.

Considering the context in which the pot shards were found, as shards mixed with waste soil, we studied only the encrustations present on the pot shards to detect any pollen that could indicate the use and/or content of the pots. The study of the soil in which the pot shards were scattered contained pollen that belongs to another event, so the soil was not studied because it was not considered relevant for understanding the use or content of the original pots.

3. Results

3.1. SEM-EDS

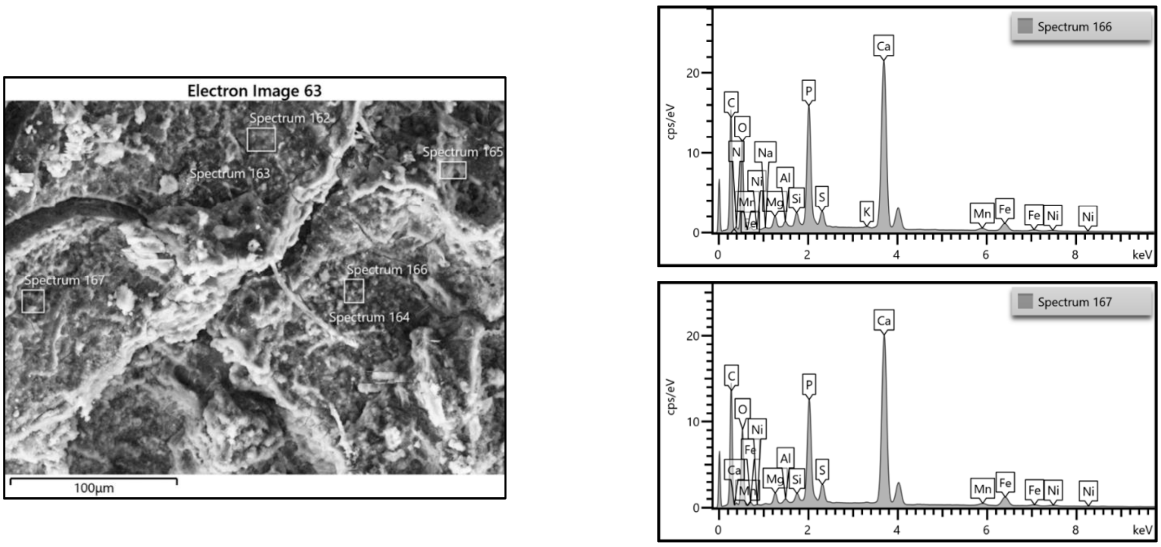
3.1.1. Dario Monaco, Carmela Vaccaro, and Elena Marrocchino

SEM-EDS: Pietra Ollare and Encrustations

We performed the SEM-EDS analysis on the pietra ollare stone samples to obtain a general view of the chemical composition, not a detailed characterization but enough to exclude the presence of pietra ollare material in the sampled encrustations.

The chemical compositions of the samples were similar. Table 2 lists some representative composition spectra from the four analyzed samples.

A fundamental finding that emerged from the SEM-EDS analysis of the encrustations was the wide presence of Ca and P, particularly in samples 5, 7, and 8, (Figure 6). All the SEM-EDS data and images used are available in the Supplementary Material.



Wt%	C	N	O	Na	Mg	Al	Si	P	S	K	Ca	Mn	Fe	Ni	Tot.
Sp. 166	1.04	4.39	42.82	0.18	1.3	0.51	1.17	12.3	1.78	0.23	29.16	1.05	3.67	0.4	100
Sp. 167	18.79		62.19		0.47	0.13	0.27	3.99	0.76		11.22	0.31	1.66	0.2	100

Figure 6. Electron image, spectra, and chemical data from sample 8.

Table 2. Representative spectra from the four analyzed samples.

								Sample 2									
Wt%	**C**	**O**	**Na**	**Mg**	**Al**	**Si**	**P**	**S**	**Cl**	**K**	**Ca**	**Cr**	**Mn**	**Ti**	**Fe**	**Ni**	**Tot.**
Sp. 18	2.07	49.5	0.41	17.73	1.69	21.96		0.4	0.34	0.28	0.74				4.53	0.34	100
Sp. 19	46.38	36.61	0.17	6.62	0.49	7.28		0.18	0.13	0.08	0.36				1.71		100
Sp. 20	2.8	46.66	0.44	17.16	1.96	22.15		0.53	0.32	0.25	1.03	0.35			5.83	0.51	100
								Sample 4									
Wt%	**C**	**O**	**Na**	**Mg**	**Al**	**Si**	**P**	**S**	**Cl**	**K**	**Ca**	**Cr**	**Mn**	**Ti**	**Fe**	**Ni**	**Tot.**
Sp. 27	8.87	41.37		16.4	0.37	26.41	0.13	0.11			0.44				5.5	0.41	100
Sp. 28	14.36	44.42		13.66	1.75	10.37	0.28	0.28			2.53	0.58	0.23		11.53		100
Sp. 29	18.91	42.25		11.86	1.13	5.9	0.48	0.28			4.64	0.28	0.49		13.77		100
Sp. 30	22.09	36.99		11.62	0.38	17.8	0.64	0.27			5.53				4.25	0.44	100
								Sample 6									
Wt%	**C**	**O**	**Na**	**Mg**	**Al**	**Si**	**P**	**S**	**Cl**	**K**	**Ca**	**Cr**	**Mn**	**Ti**	**Fe**	**Ni**	**Tot.**
Sp. 58	15.29	46.98		14.62	3.35	14.78	0.13	0.23	0.07		0.19				4.11	0.26	100
Sp. 59	22.86	42.9	0.19	11.1	0.49	15.92	0.11	0.25	0.25	0.15	1.37			0.27	3.89	0.24	100
Sp. 60	32.11	40.69	0.16	8.79	0.6	11.09	0.1	0.37	0.1	0.09	0.55				5.08	0.27	100
Sp. 61	30.99	40.71	0.96	9.61	0.17	13.41		0.48	0.64	0.34	0.59				2.09		100
								Sample 8									
Wt%	**C**	**O**	**Na**	**Mg**	**Al**	**Si**	**P**	**S**	**Cl**	**K**	**Ca**	**Cr**	**Mn**	**Ti**	**Fe**	**Ni**	**Tot.**
Sp. 69	12.87	45.22		15.35	0.26	23.57		0.27			0.12					2.33	100
Sp. 70	24.52	42.17		11.99	3.33	9.71	0.15	1.03			0.16	0.69				6.04	100
Sp. 71	18.78	43.44		13.49	0.66	19.38	0.14	0.54			0.13	0.21				3.24	100
Sp. 72	26.64	39.46		11.15	0.35	16.57	0.24	1.19			0.37	0.2				3.83	100
Sp.73	20.7	40.01		11.38	0.34	17.76	0.5	2.58			2.39	0				4.34	100

Other interesting finding was the presence of pyrite framboids, which is a finding in agreement with the observation and discussion on the micromorphology of the soil in Nogara by Cristiano Nicosia [17].

3.2. Pollen

Dario Monaco and Marco Marchesini

In general, the appearance of the slides was uniform (only samples 10 and 5 were more readable, and some slides of samples 6, 7, and 8 were not very visible), being extremely similar to what was previously observed by Arobba and Murialdo in the pollen analysis conducted on fragments of pietra ollare found in S. Antonino (SV) [18]. In the slides, we observed many irregular and semitransparent yellow-brownish masses (Arobba and Murialdo suggested in their case, which is also applicable to ours, that these masses could be burnt food residues), woody fibers, spores, fungal hyphae, carbonaceous remains, and a small quantity of pollen. The pollinic charts are reported in Tables 3 and 4.

Table 3. Pollen chart.

Pollen		**Total Number**	**Sample 1**	**Sample 2**	**Sample 3**	**Sample 4**	**Sample 5**	**Sample 6**	**Sample 7**
AMARANTHACEAE	*Chenopodium* indiff.	3	/	/	/	/	/	/	3
CICHORIOIDEAE	*Cichorioideae* indiff.	5	4	/	/	/	/	1	/
BRASSICACEAE	*Crucifera sinapis tipo*	2	/	/	/	/	1	/	1

Table 3. *Cont.*

Pollen		Total Number	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Sample 6	Sample 7
FABACEAE	*Fabaceae* indiff.	1	/	/	/	/	/	/	1
	Leguminosa lotus o onix tipo	2	2	/	/	/	/	/	/
LAMIACEA	*Mentha*	1	/	/	/	1	/	/	/
PINACEAE	*Pinus* indiff	1	1	/	/	/	/	/	/
POACEAE (Graminacee)	*Poacee spontanee* group	10	5	/	/	2	/	/	3
	Poll Indet.	3	/	/	/	1	1	1	/
URTICACEAE	*Urticaceae* indiff	1	1	/	/	/	/	/	/

Table 4. Spore chart.

Spore	Total Number	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Sample 6	Sample 7
Ascospora	41	/	/	/	/	/	/	41
Cladosporium	1	1	/	/	/	/	/	7
Epicoccum	5	/	/	/	/	/	/	5
Equisetum	1	/	/	/	1	/	/	/
Generic spores	29	2	2	1	1	1	1	21

4. Discussion

4.1. Pollen

Dario Monaco and Marco Marchesini

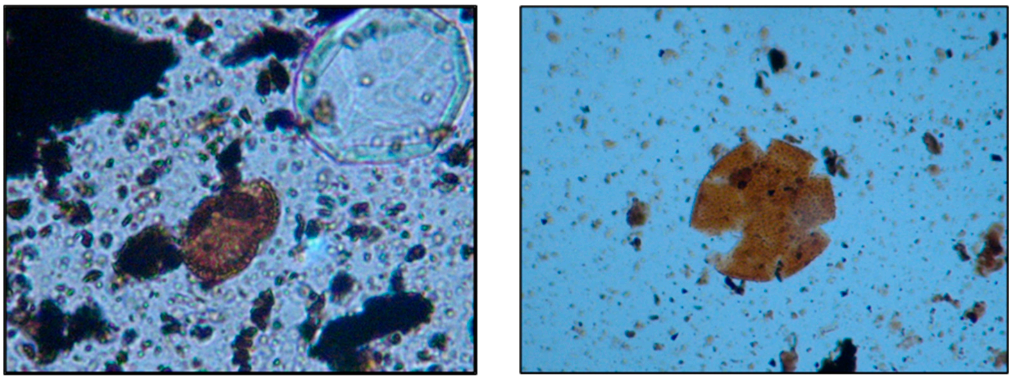
In general, little pollen was found, which, for the most part, was from spontaneous species. Therefore, the pollen was as follows:

- Most probably present in the sediment in which the fragments of the containers were preserved.
- Suspended in air (especially *Poaceae*) and then deposited in the containers during or shortly after cooking.
- Present in the water used during cooking; therefore, it would not be pollen directly indicative of the food prepared in the containers.

Arobba and Murialdo [18], with materials very similar to those analyzed in this study (but from a different, hilly location), found that the main source of pollen in one of their samples (the only one with a statistically relevant amount of pollen) was the water used during cooking, not the food.

The scarcity of pollen was therefore expected, considering the context of the origin (these encrustations before the burial were probably exposed to the open air and therefore to weathering) and the finding of similar studies [18], but the absence of large quantities of pollen could be a finding, especially if combined with the SEM-EDS observations. We discuss this in the conclusions. However, this does not mean that findings cannot or have not emerged related to spores and some pollen. Based on the low quantity of palynomorphs and their uncertain origins, the considerations that can be drawn are therefore hypothetical and speculative.

The pollen of most interest are those of *Cruciferae Sinapis tipo* (Figure 7a), which (assuming a culinary origin) could indicate the use of pietra ollare for the preparation of long-cooking vegetable soups, such as that required for the preparation of turnips. Although quantitatively insufficient to form real hypotheses, the presence of a *Lamiacea*, maybe *Mentha* (Figure 7b), is remarkable because the *Lamiaceae* are a wide family of plants that includes species with a long story in cooking and popular medicine practice, such *Salvia* (sage) or the aforementioned *Mentha* (mint) [19–21]. This may be an incidental presence, but the analysis of the other fragments (also ceramic) could be deepened to search for other evidence of this type of plant.



(**a**) (**b**)

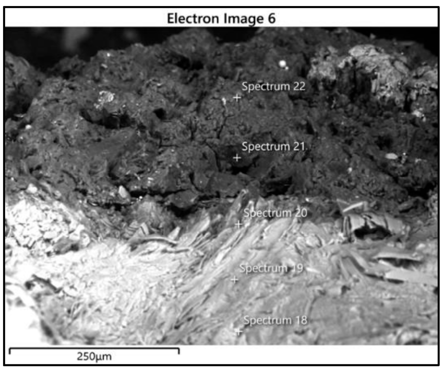
Figure 7. (**a**) *Crucifera Sinapis tipo* (27.36 µm diameter); (**b**) *Lamiacea Mentha tipo* (109.44 µm diameter).

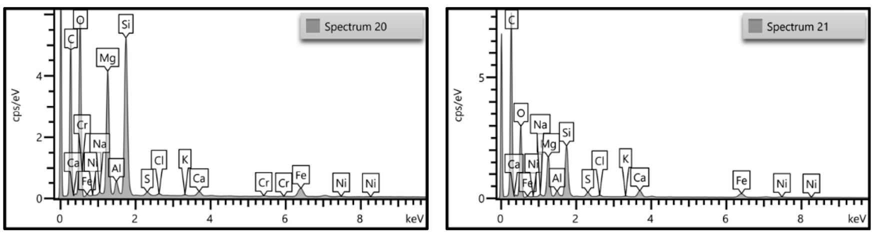
The most remarkable plant indicated from the pollen analysis, *equisetum*, was indicated by the spores. However, in this case as well, the quantities available necessitate caution in terms of drawing conclusions. If the equisetum is actually related to its use and not to a random deposition, this would be a notable finding. In this regard, in the pollen studies conducted in the past at Nogara [11], despite the large number of studied pollen and spores of pteridophytes, not a single spore of this plant was found. Finding it by chance is therefore curious as being found not due to its use but inside the encrustation of a container. Equisetum is a dioecious plant (with male and female specimens); the male specimens have been used in the past up to few decades ago in the Po Valley countryside as a sponge. Equisetum has plant structures that are rich in silica and has abrasive properties. The use of equisetum for cleaning metal containers was previously reported; the same assumption could be made for use on pietra ollare containers during the Middle Ages. If so, this finding provides additional information on the daily habits of the people of the period.

4.2. Pietra Ollare

4.2.1. Pietra Ollare with Encrustations

The chemical composition of the pietra ollare samples (Figure 8) is generally different from that of the encrustations (Figure 8b–d), with traces of possible contamination between the two, limited to the interface zone between them (Figure 8a). This confirmed that the findings in the encrustations are, in general, unrelated to the stone of the vessels.

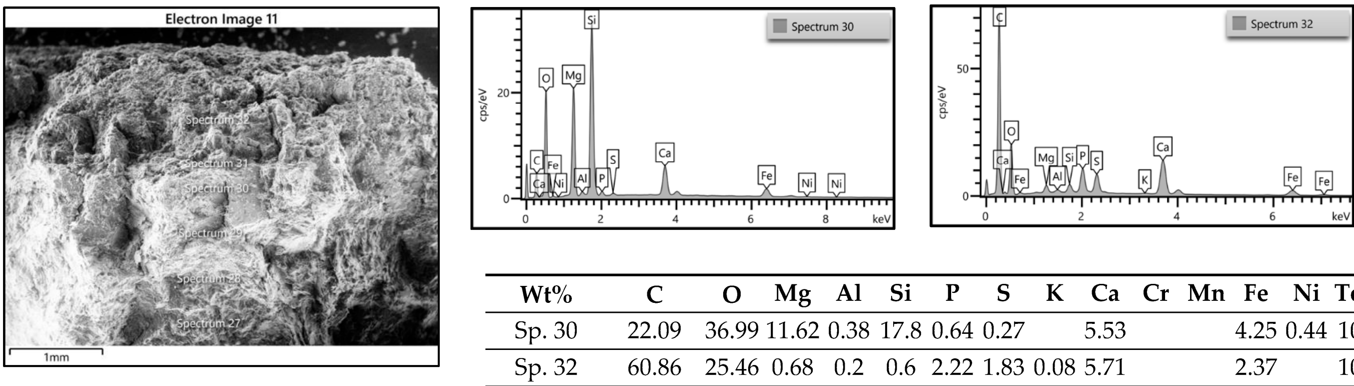




Wt%	C	O	Na	Mg	Al	Si	P	S	K	Ca	Cr	Fe	Ni	Tot.
Sp. 20	2.8	46.66	0.44	17.16	1.96	22.15		0.53	0.32	0.25	1.03	0.35	5.83	100
Sp. 21	6.51	48.91	0.82	13.26	1.58	15.95		1.57	0.58	0.41	3.37		5.67	100

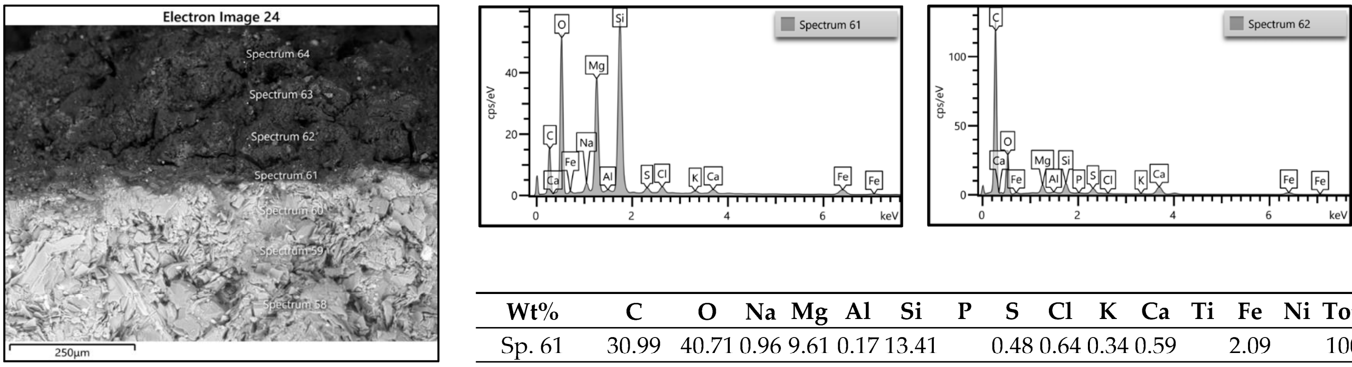
(**a**)

Figure 8. *Cont.*



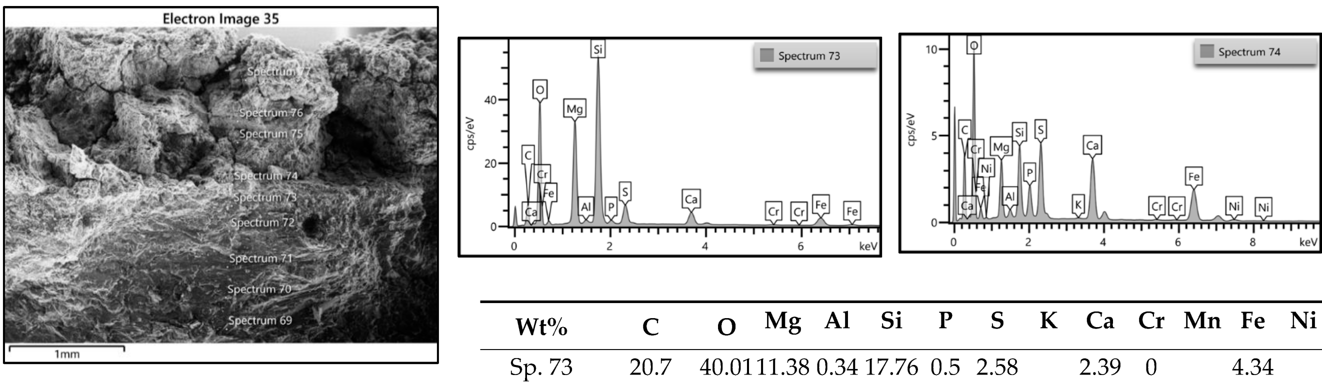
Wt%	C	O	Mg	Al	Si	P	S	K	Ca	Cr	Mn	Fe	Ni	Tot.
Sp. 30	22.09	36.99	11.62	0.38	17.8	0.64	0.27		5.53			4.25	0.44	100
Sp. 32	60.86	25.46	0.68	0.2	0.6	2.22	1.83	0.08	5.71			2.37		100

(**b**)



Wt%	C	O	Na	Mg	Al	Si	P	S	Cl	K	Ca	Ti	Fe	Ni	Tot.
Sp. 61	30.99	40.71	0.96	9.61	0.17	13.41		0.48	0.64	0.34	0.59		2.09		100
Sp. 62	65.81	28.04		1.09	0.12	1.13	0.08	0.71	0.04	0.06	1.67		1.25		100

(**c**)



Wt%	C	O	Mg	Al	Si	P	S	K	Ca	Cr	Mn	Fe	Ni	Tot.
Sp. 73	20.7	40.01	11.38	0.34	17.76	0.5	2.58		2.39	0		4.34		100
Sp. 74	28.79	37.89	4.14	0.48	4.13	2.13	5.12	0.09	6.61	0.14		9.89	0.58	100

(**d**)

Figure 8. (**a**) Electron image, spectra, and chemical data from sample 2; Sp. 20 captured on pietra ollare; Sp. 21 captured targeting encrustations. (**b**) Electron image, spectra, and chemical data from sample 4; Sp. 30 captured on pietra ollare; Sp. 32 captured targeting encrustations. (**c**) Electron image, spectra, and chemical data from sample 6; Sp. 61 captured on pietra ollare; Sp. 62 captured targeting encrustations. (**d**) Electron image, spectra, and chemical data from sample 8; Sp. 73 captured on pietra ollare; Sp. 74 captured targeting encrustations.

Comparing our chemical data with those in the literature [8,9,22], we found a general provenience from the central Alps (Valchiavenna and Valmalenco). However, considering the differences in terms of analytical and instrumental aspects with those studies, we consider our assessment as purely indicative. Further analyses are required for a valid assessment (See Section 2.2.2).

4.2.2. Pyrite

Dario Monaco, Carmela Vaccaro, and Elena Marrocchino

We found the presence of iron sulfides, observed with various crystalline structures, idiomorphic (octahedron), and with a framboid structure. The presence of this sulfide is coherent with the findings of Cristiano Nicosia [17], who identified the presence of pyrite framboids in the soil of the excavation area, associated with carbon and vegetal fragments and, in some cases, with bone material. So, in our case, we hypothesized that the presence of an oxidative environment (as described by Nicosia [17]), organic matter in the encrustations or in the strata (see Section 4.2.3), and iron (probably from the pietra ollare) favored the formation of these minerals.

4.2.3. Ca and P quantities

Dario Monaco, Carmela Vaccaro, and Elena Marrocchino

Among the findings that emerged from SEM-EDS analysis, one of the most notable is the wide presence of Ca and P. All samples showed traces of these elements, some more than others. In particular, samples 5, 7, and 8 contained very high levels of P.

Vast amounts of the literature, both agronomic and archaeological, deal with the presence of phosphorus in the soil, both from geological and organic origin [23–26]. This is because of the importance of the phosphorous cycle for the balance of soil components and, from an archaeological point of view, because its presence characterizes human settlements and surrounding areas, leaving traces that last for centuries [25]. The presence of high levels of P accompanied by Ca and K has been linked to traces of food preparation and consumption [25,27,28]. In our case, because we focused on the encrustations adhering to inner and outer sides of pots, we advance a preliminary hypothesis for a similar origin, in particular, the possible presence of bone material, because the ratio of Ca to P that we found in the samples is close to that of apatite and hydroxyapatite.

The possibility that the origin of these traces is the strata must also be considered; the shards were found in highly anthropized layers (house use and growth levels), so the hypothetical traces of food, organic matter and bones could be the result of the dirt and the dumpings inside and outside of the dwellings. The findings of a micromorphological study of the layers in this sector of the digging also support this hypothesis, revealing the wide presence of meal remains (bone material, eggshells, and fish) and ash from fireplaces [17]. Currently, we also cannot exclude a geological origin of the apatite, considering the complexity of the soil chemistry and dynamics [26], so further analyses are needed for a valid assessment of this aspect.

The highest values of P were registered in samples 7 and 8, for which the encrustations were attached to the inside of the container (particularly in the angle between the bottom and wall of the vessel). So, for these two specimens, the bone origin linked to food preparation in the vessel may be more reliable.

An index widely used to characterize bones is the ratio of the amount of calcium to phosphorus (Ca/P ratio). With this index, hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$), a fundamental constituent of bone tissue, can be identified. This mineral has a theoretical stoichiometric molar ratio for both humans and animals of 1.67 [29], which is complemented by the value of the theoretical stoichiometric ratio by weight of Ca and P, namely 2.15 [30]. In our case, therefore, our reference value was 2.15. Therefore, for a whole series of factors and processes (e.g., age, species, bone type, sex, and, in our case, diagenetic factors) [31], the actual ratio is different from the theoretical one. This is found in both human and animal bones [30].

No case similar to ours has been reported in the literature, i.e., looking for bone material inside encrustations using SEM-EDS. The literature contains general cases (archaeological and others) directly starting with bone material analysis with SEM-EDS as well as cases in which the analysis of the surface of objects revealed bone presence [32]. Therefore, once the quantities of Ca and P are obtained in weight percentage (Wt%) or atomic percentage (At%) to identify possible bone material, we proceeded as follows. Using all the data would not have been logical, as we would have included data unrelated to the presence of bone. This would have risked inappropriate increases or decreases in the average Ca/P ratio of the individual samples. We therefore opted for a selection of data, choosing those only within a range considered reliable: 0.98–2.85, as previously reported [33]. This range was obtained by the researchers by comparing data from multiple studies on Ca/P ratio in human bones. A certain overlap exists between the data that can be obtained from animal and human remains. In addition, this range was wide enough to allow us to consider many of the data we obtained.

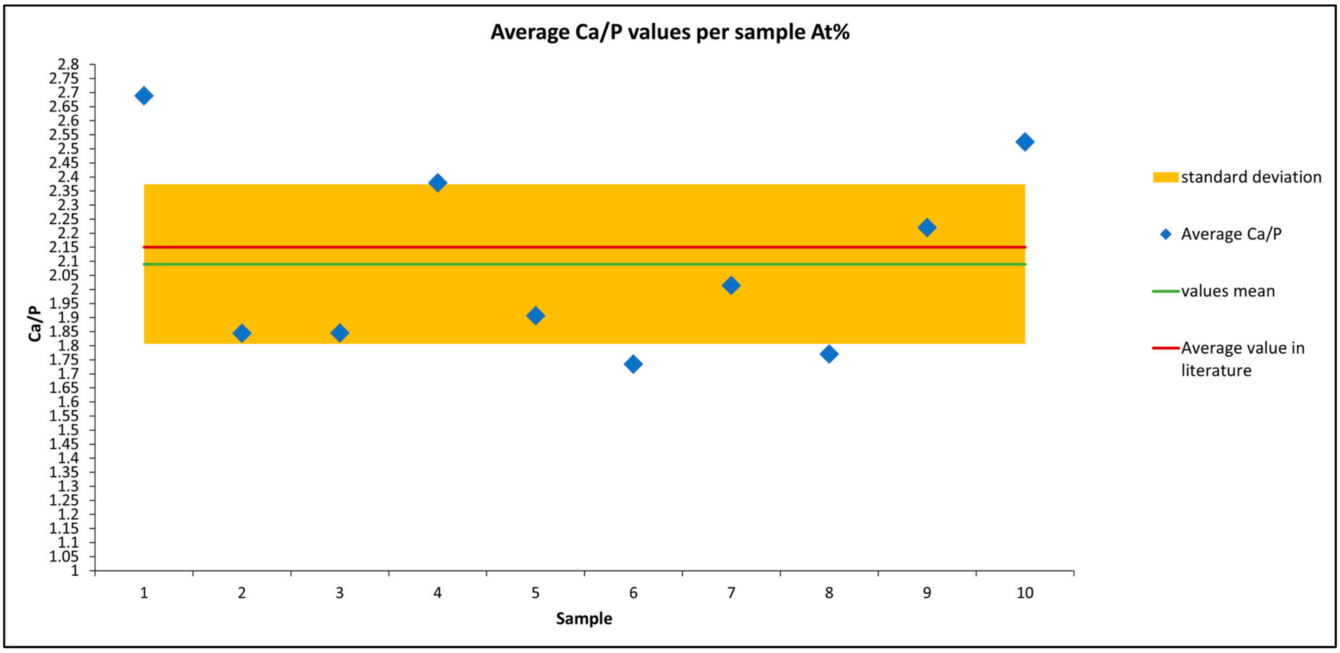
Tables 5 and 6 and Figure 9 provide the Ca/P ratio data. In particular, the total average ratio calculated is close to 2.15 (Figure 7). Deviations from this value could be explained by diagenetic factors and by differences in the age of the individuals at the time of death. The data are within the values reported in the literature from the analysis of bone material of both human and animal origin [33–37], which also fall within the range 1.6–2.58, indicative of the presence of bone material [36]. Lastly, exposure to heat (i.e., firing) does not seem to cause changes in the quantities of the elements [36], so the firing of this bone material did not alter the ratio.

Table 5. Data of average Ca/P ratio in all samples and total average ratio in At%.

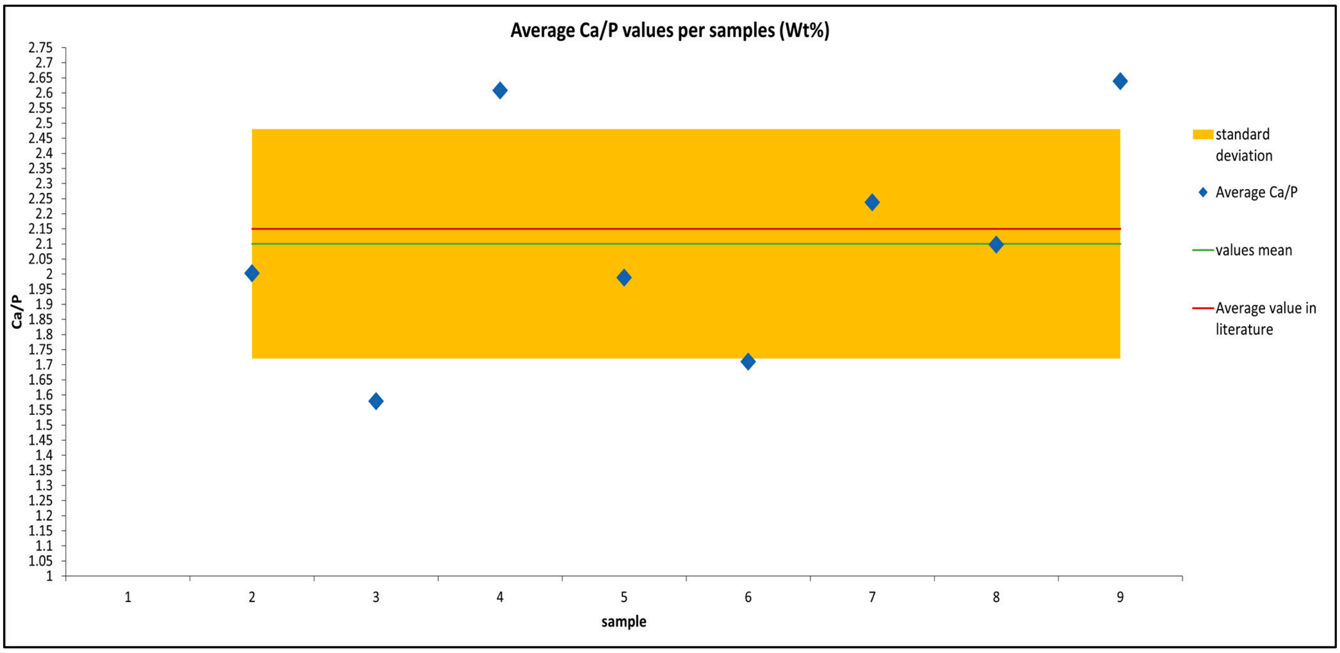
Sample	Ca/P Median	Standard Deviation	Standard Deviation of Average, At%
1	2.688	/	0.283
2	1.844	0.531	
3	1.845	0.544	
4	2.379	0.327	
5	1.906	0.574	
6	1.734	0.552	
7	2.014	0.404	
8	1.769	0.393	
9	2.220	0.353	
10	2.524	0.214	
	2.092	average of averages	

Table 6. Data of average Ca/P ratio in all samples and average ratio in Wt%.

Samples	Ca/P Median	Standard Deviation	Standard Deviation of Average, Wt%
1	/	/	0.380
2	2.002	0.504	
3	1.579	0.463	
4	2.608	/	
5	1.988	0.583	
6	1.709	0.514	
7	2.238	0.268	
8	2.097	0.417	
9	2.639	0.153	
10	/	/	
	2.101	average of averages	



(**a**)



(**b**)

Figure 9. (**a**) Graph with the Ca/P values expressed in At% and the mean value that goes very near to the reference value 2.15 [30]; (**b**) Same as the figure a but with the data expressed in Wt%, samples 1 and 10 are excluded because we did not find relevant data.

The presence of bone remains in the encrustations, if confirmed, could be a notable finding because this information would show that part of the diet was based on the consumption of meat. However, even if traces of bone material cannot be confirmed at the current level of analysis, the use of the pietra ollare containers for the preparation of meat dishes remains probable owing to its thermal properties [1] that make it well-suited for the preparation of long-cooking dishes such as stews and boiled meat.

Meat was often prepared by boiling or by double/multiple-step cooking [19]: boiling followed by another type of cooking (roasting, frying, stewing, etc.). Boiling was a fundamental technique for the preparation of meat in ancient times, showing continuity between ancient and Medieval cooking. This technique was used not because it was the only one available but because of its several advantages: tenderizing meats that were probably tougher than those to today (especially in terms of game), sterilizing the meat, and allowing the preparation of broth and sauces derived from the meat [19]. The preparations included many herbs and spices (the latter only for those who could afford them) to give the dishes strong and sweet-and-sour flavors, which was also achieved through the addition of wine and vinegar. Contrary to many reports, this was a precise need to suit taste and not a method of hiding possible ingredients in poor conditions [19]. Particularly for spices, in the High Middle Ages, the spices of Asian origin continued to circulate, traded by Venetian and Comacchio merchants (see, for example, the references to pepper in the Capitular of Liutprand in 715 CE), but the local spices (as defined by Braudel [21]) were much more widespread than Asian spices. The term local spices means all those aromatic herbs that were available in any garden (sage, anise, coriander, garlic, thyme, etc.) and were used at every social level. Only with the increased trade of the Late Middle Ages did large quantities of Asian spices arrive, which would become a necessity on the tables of the rich [20]. The wide use of boiling did not, however, prevent the meat from being directly used on the fire, with direct roasting, which produced different and stronger flavors (perhaps closer to the dietary preferences of the aristocracy) [19].

Our preliminary hypothesis will need to be supported by further analyses, such as studies of soil samples from Nogara, so that the results can be compared with those obtained for the encrustations and to check for possible traces of strontium, another bone marker [38], and animal-derived lipids. This is required because the complexity of soil chemistry needs to be considered, because the P and Ca (and, consequently, apatite) present in the soil can have multiple origins both human- and geological-related [26], and because the P is involved in complex chemical and biochemical dynamics, some of which are still not completely understood [25]. So, more data are needed to ascribe our traces to bone material with certainty.

5. Conclusions

Dario Monaco

The central finding of this study emerged from the SEM-EDS analysis: the presence of phosphorus and calcium. Our analyses, however, did not allow us to determine their origin, whether culinary (linked to traces of bone material) or postdepositional (linked to the presence of organic- or geologic-related phosphorus and apatite in the soil), with certainty. Future analyses will shed more light on the use of pietra ollare containers. Their use for the preparation of meat dishes remains probable given the thermal properties of pietra ollare [1], which are well-suited for the preparation of stews, braises, and boiled meats. This type of use for the preparation of stews and long-cooked meat dishes, if confirmed, would date as far back as the Middle Ages, demonstrating long continuity, reaching to the present day.

Regarding the pollen analysis, the scarcity of data did not allow a clear interpretation of the use of pietra ollare for the preparation of vegetable-based dishes. This scarcity of palynomorphs (with exceptions such as *Equisetum*, *Cruciferae*, and *Lamiacea*) can be explained by two factors: diagenetic and conservation factors or that pietra ollare was predominantly used for the preparation of meat dishes, with little contributions from vegetables and herbs. Future analyses, both on the pietra ollare and pottery, will help us to clarify the situation. If other samples and analyses were to confirm the use of pietra ollare for vegetable preparations, it would enrich the "recipe book" of foods prepared at the time with pietra ollare, such as soups or cereal porridge.

Future investigations may include the following:

- Analysis of ceramic materials from the same contexts to understand if the use of the containers was differentiated and specific based on the manufacture material: ceramic or pietra ollare.
- Isotopic analysis of samples from pietra ollare to add detail to the findings.
- Analysis of the soil near the excavation site.
- An experimental archaeology study using a pietra ollare container used for the preparation of meat dishes that must be analyzed after a certain period of burial to identify the validity of the hypothesis and possible influential diagenetic factors.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/heritage6040178/s1, Data S1: Encrustations SEM-EDS data; Data S2: Encrustations vs. pietra ollare SEM-EDS data; Data S3: Pollen extraction method.

Author Contributions: Conceptualization, D.M. and F.S.; methodology, D.M., F.S., C.V., E.M. and M.M.; validation, D.M., F.S., C.V., E.M. and M.M.; formal analysis, D.M. and E.M.; investigation, D.M., E.M. and M.M..; resources, F.S., C.V. and M.M.; data curation, D.M., E.M. and M.M.; writing—original draft preparation, D.M.; writing—review and editing, D.M., F.S., C.V., E.M. and M.M..; visualization, D.M.; supervision, F.S., C.V. and M.M.; project administration, F.S., C.V. and M.M.; All authors have read and agreed to the published version of the manuscript.

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Conflicts of Interest: The authors declare no conflict of interest.

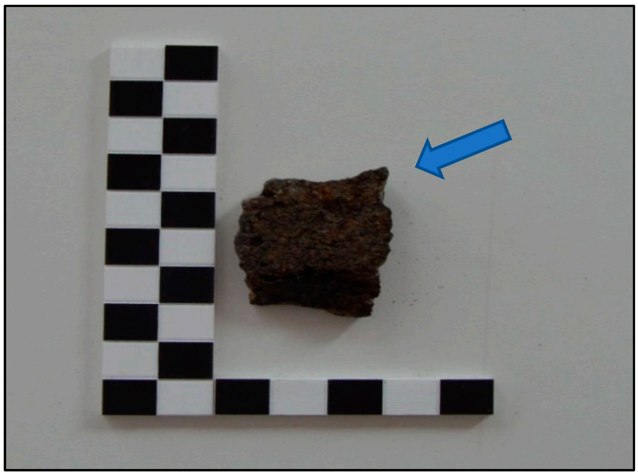
Appendix A

(**a**)

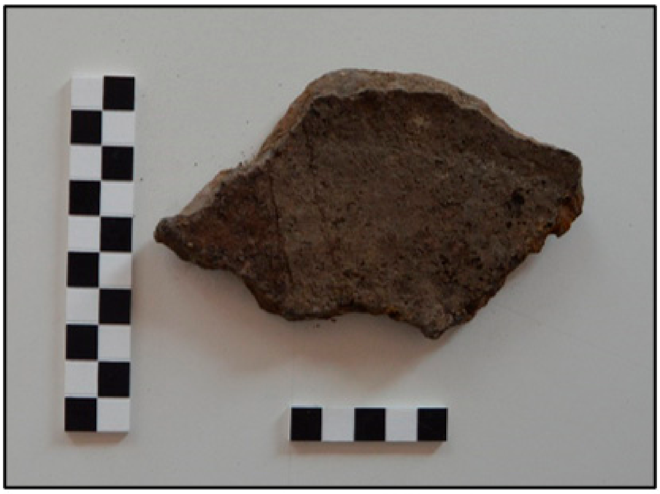
(**b**)

Figure A1. *Cont.*

(**c**)



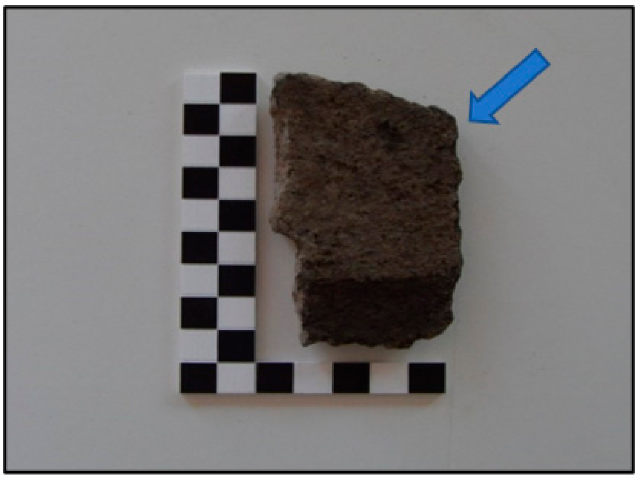
(**d**)



(**e**)

(**f**)

(**g**)



(**h**)

Figure A1. *Cont*.

(i)

(j)

Figure A1. Pictures of sampled fragments. Blue arrows on samples 2, 4, 6, and 8 indicate where we removed samples for comparation of the chemical compositions of the stone and encrustations. The pictures were taken from the sampled side: (**a**) Sample 1, inner face; (**b**) Sample 2, outer face; (**c**) Sample 3, outer face; (**d**) Sample 4, outer face; (**e**) Sample 5, inner face; (**f**) Sample 6, outer face; (**g**) Sample 7, inner face; (**h**) Sample 8, inner face; (**i**) Sample 9, outer face; (**j**) Sample 10, inner face.

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