**Millets and Cereal Meals from the Early Iron Age Underwater Settlement of “Gran Carro” (Bolsena Lake, Central Italy)**

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**Abstract:** Archeobotanical materials recovered from pottery vessels originating from the underwater archeological site of “Gran Carro”, located in Central Italy on the shore of Bolsena Lake, were analyzed to obtain new insight into the agricultural habits present in this Iron Age settlement. The archeobotanical study of cereal remains was combined with analytical data obtained from an amorphous organic residue using optical microscopy, SEM-EDS, ATR/FT-IR and Py-GC/MS. The cereal remains of emmer wheat (*Triticum dicoccum*), barley (*Hordeum vulgare*), broomcorn millet (*Panicum miliaceum*), and foxtail millet (*Setaria italica*) were identified as the preferred crops used for food and/or fodder at the site. The presence of charred millets, which have been directly dated by AMS, confirms consumption at the site and adds to the little-known background of millet use in central Italy. The find of millets in a perilacustrine pile-dwelling during a period when the water level of the Bolsena Lake was several meters lower than at present, attesting to a general dry period, suggests that the cultivation of millets, complementing more productive crops of wheat and barley, may have been favored by the availability of a large seasonally dry coastal plain, characterized by poor and sandy soils unsuitable for more demanding cereals.

**Keywords:** archeobotany; chemical analysis; villanovan pile-dwelling; Latium; foodstuff; organic residue; Panicum; Setaria

1. **Introduction**

In Italy, the transition from the 2nd to the 1st millennium BC reflects cultural and technical changes, while at the same time still strongly relying on the previously established traditions. Even though the Iron Age brought new economic and political values, transforming the structure of the society, most of the commonly exploited food sources, including cereal crops, were introduced to the Italian Peninsula in earlier periods. However, food preferences reveal distinct regional variations in consumption trends that reflect different exchange and cultural networks. The societies of Central Italy, exploiting the fertile volcanic soils, depended on plant sources for multiple purposes, incorporating cereals as both food and animal fodder. To better understand crop selection and farming, storage, processing, and consumption choices, which reflect the interplay between the environment and culture, a rich new archeobotanical record from Central Italy, recovered from the “Gran Carro” underwater archeological site, was compounded into the mosaic of existing knowledge.
The complex of the “Gran Carro” is a large site located on the eastern shallow flat shore at S. Antonio of the Bolsena Lake (42.591 N, 11.995 E), in the Lazio region of Central Italy (Figure 1). It was founded starting from the Middle Bronze Age (15th century BC), but the most substantial remains are framed at the beginning of the first Iron Age between the 10th and 9th centuries BC, being distinctive for the Villanovan culture in Central Italy. Currently, the site is submerged, and is considered to be the first underwater archeological site in inland waters discovered in Central Italy [1]. “Gran Carro” is unique because it is the only Villanovan site to be submerged since the Iron Age without being reoccupied in successive phases, as well as for the abundance of materials found and for the excellent state of preservation of this archeological site.

Figure 1. Location and underwater photographs of the “Gran Carro” pile-dwelling: (a) Location of Bolsena Lake; (b) Bathymetry (meters a.s.l.) of Bolsena Lake (in brown, the area emerged at the time of the “Gran Carro” settlement); (c) Google Earth © 2019 image of the underwater “Gran Carro” excavation area. The yellow circle and the red square approx. correspond to the extension of the “Aiola” and the village, respectively; the orange circle indicates the location of the Middle Bronze Age (MBA) materials; (d) Planimetry of the excavation (grid 2 × 2 m; numbers correspond to vessels of Table 1); (e) Underwater excavation uncovering Iron Age materials (Vessel 38).
It was possible to ascertain that the “Gran Carro” complex is divided into several subsystems and functioning as a link between the coast and the hinterland in the resource management system. The “Gran Carro” settlement was discovered in 1959 by the mining engineer Alessandro Ferretti. The “Gran Carro” settlement was discovered in 1959 by the mining engineer Alessandro Ferretti in collaboration with underwater archaeologists and specialists merged today.

Both sedimentological and archaeological evidence support that the “Gran Carro” settlement was located in a broad coastal plain, much larger than the current one, gradually down to a depth of 7.5 m, around 100 m from the current coastline, indicating that the settlement was part of the natural landscape from the Middle Bronze Age, which has been identified on the basis of the geomorphology of the lakebed and the sandy/rocky poles of the “Gran Carro” pile-dwelling supports a construction technique indicating dry stilt house construction [6]. Two other extensive underwater settlements coeval to “Gran Meridionale,” documented the availability of now submerged land around the lake.

Below the isobath 297 m (approximately 7.5 m water depth), where an ancient coastline (Figure 1) has been identified on the basis of the geomorphology of the lakebed and the sandy/rocky poles of the “Gran Carro” pile-dwelling supports a construction technique indicating dry stilt house construction [6]. Two other extensive underwater settlements coeval to “Gran Meridionale,” documented the availability of now submerged land around the lake.

Table 1. List of vessels containing the cereal remains that were analyzed. Scale bar = 5 cm.

<table>
<thead>
<tr>
<th>Number</th>
<th>Photograph</th>
<th>Form</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vessel 16</td>
<td><img src="image1.jpg" alt="Image" /></td>
<td>globular “olletta” with four protrusions</td>
</tr>
<tr>
<td>Vessel 21</td>
<td><img src="image2.jpg" alt="Image" /></td>
<td>small, rounded bowl with one perforated handle, on raised leg</td>
</tr>
<tr>
<td>Vessel 23A</td>
<td><img src="image3.jpg" alt="Image" /></td>
<td>conical bowl on four legs</td>
</tr>
<tr>
<td>Vessel 23B</td>
<td><img src="image4.jpg" alt="Image" /></td>
<td>biconical jar with encrusted geometric decorations</td>
</tr>
<tr>
<td>Vessel 25</td>
<td><img src="image5.jpg" alt="Image" /></td>
<td>beaker with one handle</td>
</tr>
<tr>
<td>Vessel 26</td>
<td><img src="image6.jpg" alt="Image" /></td>
<td>small pot with two handles and impressed decoration</td>
</tr>
<tr>
<td>Vessel 38</td>
<td><img src="image7.jpg" alt="Image" /></td>
<td>ovoid vessel with corded decoration</td>
</tr>
<tr>
<td>Vessel 42</td>
<td><img src="image8.jpg" alt="Image" /></td>
<td>beaker with one ribbon handle</td>
</tr>
<tr>
<td>Vessel 58</td>
<td><img src="image9.jpg" alt="Image" /></td>
<td>conical bowl on four legs</td>
</tr>
</tbody>
</table>
The “Gran Carro” settlement was discovered in 1959 by the mining engineer Alessandro Fioravanti [1], and was excavated from the 1960s until the late 1980s in agreement with the Superintendence, also in collaboration with volunteer divers. The excavations mainly focused on the surface finds, but always strived to incorporate a multi-disciplinary approach and environmental information to obtain a well-rounded overview of the archeological site [2]. After a hiatus, research in the area restarted in 2012, under the supervision of the Soprintendenza Archeologia Belle arti e Paesaggio per la provincia di Viterbo e per l’Etruria meridionale, in collaboration with underwater archeologists and specialists merged today in the Centro Ricerche Archeologia Subacquea.

It was possible to ascertain that the “Gran Carro” complex is divided into several functionally distinct sectors (Figure 1c) spread over ca. 1.5 hectares [3,4]. The material analyzed was excavated from the currently submerged area, occupied by the remains of pile-dwelling structures mainly attributable to the Early Iron Age (late 10th–9th century BC), built at the time on lands emerged on the edge of the lake. Adjacent is the so-called Aiola, an elliptical structure formed by unworked stones, first investigated in 2021 and preliminarily interpreted as an open-air ritual place dating from at least the Late Bronze Age (11th century BC), where rites were held that included the lighting of fires in the upper part and contributing food offerings in pots in the lateral parts. The third area identified is on land near the current shore, in topographical continuity with respect to the submerged part, where materials from the beginning of the Middle Bronze Age (15th century BC) were found.

The remnants of the Iron Age settlement were found on a low flat lakebed that slopes gradually down to a depth of 7.5 m, around 100 m from the current coastline, indicating that the settlement was located in a broad coastal plain, much larger than the current one (Figure 1). Both sedimentological and archeological evidence support that the “Gran Carro” village was at least periodically on dry land. No archeological evidence is found below the isobath 297 m (approximately 7.5 m water depth), where an ancient coastline has been identified on the basis of the geomorphology of the lakebed and the sandy/rocky substrate [5]. Besides this, the presence of foundation holes filled with sand to hold the poles of the “Gran Carro” pile-dwelling supports a construction technique indicating dry stilt house construction [6]. Two other extensive underwater settlements coeval to “Gran Carro” (Bisenzio and Tempietto; Figure 1b) have been found on the shores of Bolsena Lake [3,4], documenting the availability of now submerged land around the lake.

The settlement area of pile-dwellings with stilts is remarkable for its state of conservation, with more than 450 preserved wooden poles arranged in parallel bands set three meters apart, with structures oriented NE/SW, comparable to pile-dwellings in northern Italy. At the time of its occupation, in the Early Iron Age, this part of the settlement was located in the middle of a vast coastal plain, exploiting the various resources of the lake system and functioning as a link between the coast and the hinterland in the resource exchange system. Regionally, it is a part of the Early Iron Age Bolsena Lake network, which includes settlements and a necropolis on, and connected to, the waterfront [3].

The rise of lake water levels influenced, in part, the gradual displacement of the houses to higher inland levels, and eventually led to the settlement’s abandonment. In the lifecycle of the settlement, at least five phases of leveling have been recorded, alternating with stages of fire, resulting in cultural levels with a thickness of up to 160 cm. Among the submerged heritage, in addition to wooden structures, other settlement remains have been discovered, including parts of walls and roofing, bronze objects, remains of ceramic hearths, ceramic remains of looms, wooden artifacts, faunal remains, as well as ceramic vessels and pots that contained remains of stored cereals [3].

Despite the importance of this underwater archeological site, which has the potential to provide new significant information on the subsistence economy of the Iron Age communities of Central Italy, only two preliminary papers on carpological remains have been published in the sixty years after the site was discovered (excavation 1974 [7] and excavation 1980 [8]).
The aim of this work is to study the vegetal contents of the ceramic vessels recently recovered from the occupation layers of the settlement through archeobotanical and chemical analyses. Even though these vessels were recovered from underwater conditions in organic sediment, their archeobotanical contents show no evidence of having been reworked, as they are in an excellent state of preservation [9] (Figures 1d and 2b,c). The selected vessels were found in occupation layers in locations that were abandoned after fires and soon after preserved in waterlogged conditions, as suggested by the preservation state of waterlogged plant macroremains [9]. Thus, the organic content of the vessels attests to the local consumption of food in everyday life. Moreover, the study of these vessels may, indirectly, provide new information on the agricultural practices of this ancient community, during a period when the lake level was much lower than at present, being a testament to environmental and climate conditions different from the present.

Figure 2. Carpological remains from the “Gran Carro” settlement: (a) agglomeration of Panicum miliacea from the bottom of Vessel 38; (b) caryopsis with lemma and palea of Panicum miliacea (Vessel 21); (c) caryopsis with lemma and palea of Setaria italica (Vessel 42). Scale bar = 1 mm.

2. Materials and Methods

The material analyzed in this work was recovered during the excavation campaigns of 2016–2017 directed by Dr. Patrizia Petitti. The content of the vessels was entrusted by Dr. Barbara Barbaro, who has been directing excavations since 2019, to the Laboratory of Palaeobotany and Palynology, Department of Environmental Biology, Sapienza University of Rome. Analysis was carried out exclusively on the plant remains recovered from inside ceramic vessels. Traces of burning were observed on the vessels, probably as a result of settlement fires after the pots had already been discarded. The cultural layers from which the vessels have been retrieved correspond to collapsed segments of the dwelling, evidenced by burned wooden structures that were identified as parts of degraded flooring and roofing. Most of the vessels were discovered in an inclined position (Figure 1d), and cannot be considered in place since they were abandoned and collapsed through the floors of deteriorated stilt units. The cereal remains recovered from eight vessels were studied, along with a food residue recovered from Vessel 26 (Table 1), which did not contain any cereal grains. The vessels containing cereals include different forms—open conical bowls, beakers, rounded bowls, and bigger storage containers (Figure 2). Their typology indicates their possible use for the storage of solid or liquid contents, especially since no evidence of charring specific to cooking has been observed, and the evidence of exposure to high temperature is in line with the destruction of the occupational levels. All the vessels that contained cereals can be typologically attributed to the end of the 10th century BC until the 9th century BC, belonging to the Early Iron Age 1A, representative of the Villanovan culture in the Lazio region.
After the sampling of vessel contents at the archeological site, plant remains were recovered by wet-sieving and kept in waterlogged conditions prior to and post analysis [10]. A subsample of mixed organic sediment from each vessel was analyzed, totaling 3.3 dm$^3$ wet volume of material. The “water separation” technique [11–13] was adopted in order to separate cereal remains from the rest of the clayish and organic sediment, using 2.0 mm and 0.5 mm mesh diameter sieves. Charred remains of cereal spikelets and entire caryopses were picked from the 2.0 mm sieve, as they were clearly visible and distinct from the remaining sediment. A stereomicroscope (Zeiss Stemi 508, Carl Zeiss) was used to pick the cereal fragments isolated during the sieving operation with a 0.5 mm sieve, to carry out morpho-biometric analyses and to take photographs of the macroremains. The reference collection of Sapienza University of Rome and carpological atlases [14–16] were used for the identification of the cereal grains.

Pollen analysis of the organic residue of Vessel 26 was carried out following the standard chemical treatment with HCl (37%), HF (40%) and NaOH (10%), and storage in glycerol [17]. Phytolith extraction followed modified Kooyman’s method with 37% HCl [18].

The content of Vessel 38 was dated by Accelerator Mass Spectrometry (AMS) and calibrated using OxCal v3.10 software [19] and the IntCal 20 curve [20] at the Centro di Datazione e Diagnostica (CEDAD) of the University of Salento.

Vessel 26 contained an amorphous residue, visually distinct from the lacustrine sediment filling the vessel. In total, 3.6 g of wet residue was subsampled by the archeologists immediately after the recovery and kept at $\leq 0^\circ$C to preserve organic material if present. Since the material seemed homogenous, chemical analysis was conducted to identify the natural source of the residue and examine the possibility of it being a cereal-based product. It was examined and photographed under a stereoscopic microscope, while a scanning electron microscope coupled with energy dispersive X-ray spectrometry (SEM-EDS) was used to obtain high-resolution images and elemental analysis. Attenuated total reflectance/Fourier-transform infrared spectroscopy (ATR/FT-IR) and pyrolysis–gas chromatography/mass spectrometry (Py-GC/MS) were employed for the chemical characterization of the amorphous material.

Variable-pressure SEM-EDS analysis was carried out using a Hitachi S3700N SEM coupled to a Bruker Xflash 5010 SDD EDS Detector. The analysis was done using a low vacuum of 40 Pa and an accelerating voltage of 20 kV.

FT-IR spectra were obtained using a Bruker ALPHA spectrometer equipped with a universal ATR attachment. Spectra were acquired over the range of 4000–400 cm$^{-1}$ at a resolution of 4 cm$^{-1}$, and 182 accumulated scans were coadded to produce a spectrum. The instrument was controlled by the Bruker OPUS software. Spectra were normalized and averaged using the SpectraGryph software (Version 1.2.14).

For Py-GC/MS analysis, four micro-samples were collected and derivatized with 3 µL of tetramethylammonium hydroxide (TMAH, 2.5% (v/v) in methanol) in a 50 µL Eco-cup capsule. The samples were pyrolyzed using a single-shot method at 500 °C. Analysis was performed with a Frontier Lab PY-3030D single-shot pyrolyzer, coupled to a Shimadzu GC2010 gas chromatographer and a Shimadzu GCMS-QP2010 Plus mass spectrometer. A capillary column Phenomenex Zebron-ZB-5HT was used for separation, with helium as the carrier gas, adjusted to a flow rate of 1.50 mL min$^{-1}$. The split/splitless injector was operated at a temperature of 250 °C in the splitless mode. The gas chromatography temperature program started at 35 °C for 1 min, ramped at 60 °C min$^{-1}$ until 110 °C, then to 240 °C at 14 °C min$^{-1}$, and finally increased to 280 °C at 6 °C min$^{-1}$, at which point it was held for 10 min. The source temperature was placed at 240 °C, and the interface temperature was maintained at 280 °C. The mass spectrometer was programmed to acquire data between 40 and 850 m/z.

Compound identification was performed using AMDIS software integrated with the NIST-Wiley database. The obtained results were compared to modern reference samples of hand-ground cereals, flour, cereal paste and baked cereal products of *Triticum* sp., *Hordeum* sp.
vulgare and Panicum miliaceum. To identify possible botanical origin, a comparison was made with reference samples based on retention time and $m/z$ values, as well as available published data [21–24]. Selected Ion Monitoring (SIM) was employed on specific targeted compounds ($m/z$ 189, $m/z$ 204, $m/z$ 231, $m/z$ 425 and $m/z$ 440 reported for miliacin [21]; $m/z$ 268 reported for alkylresorcinols) [23,24].

3. Results

The analyzed material yielded cereal carpological remains found in eight distinct vessels (Table 2). Emmer (Triticum dicoccum) was discovered unthreshed, with a total of 19 caryopses, 15 intact spikelets, and one spikelet fork detected in six vessels. Eleven grains of hulled barley (Hordeum vulgare) were identified in three vessels, as well as three spikelet forks. In six vessels, a total of 14 broomcorn millet (Panicum miliaceum) caryopses were found in addition to a charred lump of ears (Figure 2a). Setaria italica was present in all the eight vessels (Table 2). Cultivated cereals were concurrent in most of the vessels, without separation. Two vessels (16 and 58) contained the four cereal taxa. Vessel 23A contained only caryopses of Panicum and Setaria.

Table 2. List and abundance of identified cereal carpological remains.

<table>
<thead>
<tr>
<th>Wet Volume of Processed Sediment (dm$^3$)</th>
<th>Type of Remain</th>
<th>Triticum dicoccum</th>
<th>Hordeum vulgare</th>
<th>Panicum miliaceum</th>
<th>Setaria italica</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vessel 16 0.3</td>
<td>caryopsis</td>
<td>4</td>
<td>1</td>
<td>7</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>spikelet</td>
<td>4</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Vessel 21 0.13</td>
<td>caryopsis</td>
<td>3</td>
<td>-</td>
<td>1</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td>spikelet</td>
<td>2</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Vessel 23A 0.45</td>
<td>caryopsis</td>
<td>-</td>
<td>-</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td>spikelet</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Vessel 23B 0.5</td>
<td>caryopsis</td>
<td>9</td>
<td>-</td>
<td>-</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>spikelet</td>
<td>4</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Vessel 25 0.5</td>
<td>caryopsis</td>
<td>1</td>
<td>-</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>spikelet</td>
<td>1</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Vessel 26 0.045</td>
<td>organic residue</td>
<td>-</td>
<td>6</td>
<td>2</td>
<td>agglomeration 4</td>
</tr>
<tr>
<td>Vessel 38 0.45</td>
<td>caryopsis</td>
<td>-</td>
<td>2</td>
<td>4</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>fork</td>
<td>-</td>
<td>-</td>
<td>agglomeration</td>
<td>9</td>
</tr>
<tr>
<td>Vessel 42 0.4</td>
<td>caryopsis</td>
<td>4</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>spikelet</td>
<td>1</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Vessel 58 0.6</td>
<td>caryopsis</td>
<td>2</td>
<td>4</td>
<td>1</td>
<td>8</td>
</tr>
<tr>
<td></td>
<td>fork</td>
<td>-</td>
<td>1</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Total number of remains</td>
<td></td>
<td>35</td>
<td>14</td>
<td>14</td>
<td>8</td>
</tr>
</tbody>
</table>

Vessel 38 contained aggregated carbonized ears of Panicum (Figure 2a), shaped like the bottom of the container from which they were recovered. Charred cereal remains were fused together, forming an agglomeration, but identifiable fragments, between 0.5 and 1 mm in size, were still clearly visible and distinct. This charred lump of millet was directly radiocarbon dated to between 1195 and 899 cal BC (2 $\sigma$), which is within the timeframe of the occupation of the site (sample LTL21223, radiocarbon age BP: 2847 ± 45).

Furthermore, Vessel 26 contained visually distinct amorphous residue (Figure 3a). The remains examined under SEM showed a fine layered structure consisting of thin sheets and voids (Figure 3b,c). The diameters of voids ranged from 15 µm to 50 µm. The analytical study of microremains did not reveal identifiable plant tissues, pollen grains or phytoliths.
Since it was not certain that the foodstuff was cereal-based, it was necessary to conduct chemical residue analysis.

Elemental mapping and point analysis performed by SEM-EDS revealed a carbon-rich matrix, covered in fine-grained arsenic and sulfur-rich particles (Figure 3c,d). These particles were also visible under optical microscopy, presenting a yellow hue. Given their composition, they are likely the As-sulfide orpiment (As$_2$S$_3$), which is known to precipitate through the reaction of aqueous As (III) (H$_3$AsO$_3$) and sulfide (H$_2$S or HS$^-$), and is commonly found in low-temperature hydrothermal veins, hot springs and fumaroles [25]. The high levels of arsenic detected in the lakes of the Viterbo area [26] and the hydrothermal activity that still occurs in the Bolsena Lake [27] can therefore explain the formation of As-sulfide precipitates present on the surface of the amorphous residue in Vessel 26.

The initial ATR/FT-IR analysis of the amorphous residue in Vessel 26 confirmed the organic origin of the substance (Figure 4a). The absorbance spectra present a characteristic...
The initial ATR/FT-IR analysis of the amorphous residue in Vessel 26 confirmed the presence of plant material [37]. Long chain fatty acids, docosanoic (behenic) and tetracosanoic (lignoceric) acid, together with sitosterol, along with the absence of cholesterol, confirm the presence of plant material. The ratio between C16:0 and C18:0 is between 1.48 and 2.00, pointing to plant source material. The most prevalent fatty acid is palmitic acid, followed by stearic acid. The ratio between C16:0 and C18:0 is between 1.48 and 2.00, pointing to plant source material. Long chain fatty acids, docosanoic (behenic) and tetracosanoic (lignoceric) acid, together with sitosterol, along with the absence of cholesterol, confirm the presence of plant material [37].

Figure 4. (a) ATR/FT-IR spectra (4000–400 cm$^{-1}$) of an archaeological sample from the Vessel 26; (b) Comparative ATR/FT-IR spectra (4000–1200 cm$^{-1}$) of an archaeological sample and modern reference of a cereal paste.

Py-GC/MS analysis revealed that the organic residue was a predominantly protein-based substance, characterized by the presence of nitrogen-containing components including N-heterocyclic compounds, pyrroles, pyridines, nitriles, and amines/amides, likely deriving from a plant source. The most abundant molecules detected in the sample are amino acids. Methyl pyroglutamate and methyl ester of L-Proline, 1-methyl-5-oxo, characteristic of the pyrolysis of proline and glutamic acid [31], were identified along with other protein biomarkers (Table 3). The high content of proline and glutamic acid is typical for the amino acid composition of gluten, a cereal protein [32–34]. Furthermore, cellulose biomarkers, pyrans and furans were also detected [35]. These compounds, including levoglucosan, maltol and 5-methylfurfural, are abundant pyrolysis products of cereal grains [36,37]. The most prevalent fatty acid is palmitic acid, followed by stearic acid. The ratio between C16:0 and C18:0 is between 1.48 and 2.00, pointing to plant source material. Long chain fatty acids, docosanoic (behenic) and tetracosanoic (lignoceric) acid, together with sitosterol, along with the absence of cholesterol, confirm the presence of plant material [37].
### Table 3. List of identified compounds of the organic residue from Vessel 26 by Py-GC/MS.

<table>
<thead>
<tr>
<th>Compounds</th>
<th>RT (min)</th>
<th>Compounds</th>
<th>RT (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>PROTEIN MARKERS</strong></td>
<td></td>
<td><strong>CELLULOSE MARKERS</strong></td>
<td></td>
</tr>
<tr>
<td>1H-Pyrrole, 1-methyl-</td>
<td>2.6508</td>
<td>Cyclopentanone</td>
<td>2.9187</td>
</tr>
<tr>
<td>Pyridine</td>
<td>2.7017</td>
<td>Furfural</td>
<td>3.2517</td>
</tr>
<tr>
<td>Pyrrole</td>
<td>2.7408</td>
<td>Benzenes, 1,3-dimethyl-</td>
<td>3.5175</td>
</tr>
<tr>
<td>Toluene</td>
<td>2.8358</td>
<td>2-Cyclopenten-1-one, 2-methyl-</td>
<td>3.7592</td>
</tr>
<tr>
<td>1H-Pyrrole, 3-methyl-</td>
<td>3.3367</td>
<td>2(5H)-Furaneone</td>
<td>3.8092</td>
</tr>
<tr>
<td>Acetamide, N,N-dimethyl-</td>
<td>3.5083</td>
<td>Cyclohexanone</td>
<td>3.8792</td>
</tr>
<tr>
<td>Phenol</td>
<td>4.2442</td>
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</tr>
<tr>
<td>Benzene, 1-methoxy-4-methyl-</td>
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<td>1,2-Cyclopentanediol, 3-methyl-</td>
<td>4.6608</td>
</tr>
<tr>
<td>Phenol, 2-methyl-</td>
<td>4.8325</td>
<td>Malt</td>
<td>5.3933</td>
</tr>
<tr>
<td>Phenol, 3-methyl-</td>
<td>4.9817</td>
<td>Levoglucosan</td>
<td>8.7942</td>
</tr>
<tr>
<td>2,5-Pyrrolidinedione, 1-methyl-</td>
<td>5.1400</td>
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<tr>
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<td>Hexadecanoic acid, methyl ester</td>
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<tr>
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<tr>
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<tr>
<td>L-Proline, 5-oxo-, methyl ester</td>
<td>7.7017</td>
<td>Hexacosanoic acid, methyl ester</td>
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<tr>
<td>1H-Isoidole, 1,3(2H)-dione, 2-methyl-</td>
<td>8.2900</td>
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<td>Pyrrolo[1,2-alpyrazine,1,4-dione, hexahydro-9H-Pyridero[3,4-b]indole, 1-methyl-</td>
<td>11.1192</td>
<td>Sitosterol</td>
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<td></td>
<td>13.0367</td>
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</tr>
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</table>

### 4. Discussion

#### 4.1. Cereal Meals

Cereal food products include cereal fragments, agglomerations and amorphous masses that originate from food preparation procedures [38]. The processing of cereals involves the intentional removal or breaking down of the plant tissues in the grains to varying degrees, which leads to improved palatability and digestibility. This includes actions such as crushing/grinding/milling, sieving, soaking, boiling, fermenting, or baking/roasting [39]. These products have been classified based on the processing of cereals and the final product as follows: ground cereals used as such, ground pre-cooked cereals, ground malt and malt products, porridge and bread remains [38]. The agglomeration of *Panicum miliaceum* caryopses, found at the bottom of Vessel 38, could have been the product of the fusing of grain fragments due to charring conditions, since small grains tend to aggregate, or the result of intentional partial processing that was charred post-deposition. Grain agglomerations have at times been interpreted as porridge, a fine meal with coarse inclusions, or a coarse meal, generated through charring, but it has been pointed out that, based on morphological features, it is not possible to differentiate between accidentally formed lumps and prepared meals [38]. Since Vessel 38 likely served as a storage container, based on its size and shape, it is more like that these joined remains result from the intentional and selective gathering of millet grains. Cereals may have been stored unprocessed to make the grains more resistant to insect and fungal attacks [40].

At Roca in Southern Italy, a lump of broomcorn millet with glumes, retrieved together with other cereal grains from the sediments of Recent Bronze Age levels, was intentionally charred as part of a ritual offering [41]. The similar assemblage of unprocessed charred millet at “Gran Carro” might suggest a ritual meaning, also given the vicinity of the settlement to the ritual structure of the “Aiola”.

For the amorphous remains, such as those recovered from Vessel 26, the terms “cereal preparation” or “cereal product” have been suggested [39]. Intensive studies [38,39,42–44] have been employed to identify and characterize cereal-based products relying on macroscopic/microscopic structure analysis and an archeobotanical approach, offering new in-
sights into food preparation practices. However, when the structure analysis for uncharred material is inconclusive, other methods of investigation become necessary.

Chemical analyses of amorphous food products provide an insight into the compositions of substances that have been altered by degradation processes but were preserved due to specific environmental conditions. At “Gran Carro”, a dual mode of preservation occurs—carbonization and waterlogging. Carbonized cereal remains were fossilized through charring under oxygen-poor conditions, irreversibly altering the structure and the chemical composition of the remains, therefore limiting the results of potential chemical analyses [45]. On the other hand, the amorphous food residue in Vessel 26 was preserved by waterlogging, due to anaerobic conditions and still water. In waterlogged conditions, organic materials are preserved as a result of the abundance of static water and the chemical balance of this water’s composition, pH and oxidation-reduction potential. Water that excludes air creates reduced oxygen levels and prevents most microorganisms from thriving. Since organic materials get saturated with water, their form is mostly retained. In an anoxic environment, however, some breakdown might occur due to the presence of anaerobic microorganisms such as sulfur-reducing bacteria [46]. Altering stable conditions and exposure to air, by removing the material from its original archeological context, can cause the further deterioration of organic remains.

The preservation of cereals and cereal foods, composed of polysaccharides (starch, cellulose, hemicellulose) and lignin, cereal protein and fats, is affected by their molecular structure. For example, long-chain lipids are more resistant than carbohydrates and proteins as they are insoluble and less vulnerable to water leaching and biodegradation. However, starch decomposes preferentially over cellulose, while cellulose is more easily broken down than lignin and other polyphenols. The degradation of glucose-based products such as starch and cellulose leads to the breaking of the carbohydrate chain, resulting in smaller saccharides more prone to hydrolysis and removal from the residue. A good example is waterlogged wood; sometimes, there is almost no cellulose remaining in the wood and the material can be identified through lignin content [47,48]. The preservation of fats and protein has been reported in carbonized cereal remains even after thermolysis [49], while in waterlogged conditions, lipids and proteinaceous components can be reasonably well preserved [50,51]. The decay of archeological materials is caused by a complicated interplay between the environment and the matter itself. The key to the good conservation of cereals, as shown at “Gran Carro”, is stable environmental conditions with limited oxygen access and water circulation. This allows the preservation of not only carpological, but also amorphous, food remains.

In this case, chemical analysis confirmed the organic origin of the amorphous residue and allowed its identification as a substance based on carbohydrates and protein. Elemental analysis showed a carbon-rich matrix, and the presence of arsenic particles. Since arsenic has the ability to bind to proteins [52], its presence in the lake environment affected the organic protein-rich archeological sample. Analysis of the IR spectra demonstrated absorption bands that can be mostly assigned to starch, water, and proteins, while the comparison with modern reference samples indicated that the archeological material is similar to a simple cereal paste composed of a mixture of grounded cereals and water. The spectra results have certainly been affected by waterlogged conditions and the aging of the material [53], but band assignments could indicate β-sheet content that has been associated with the working and processing of gluten protein products [29,30,54], forming a melded and palatable meal. Ground cereals, when mixed with water, exhibit viscoelasticity that is increased by working, attributed to interactions between the aligned β-sheet structures of gluten. During mixing, disulfide bonds break and increase the opportunities for all the gluten proteins to interact and restructure, resulting in a decrease in α-helices and β-turns, and an increase in β-sheets [30].

Even though specific biomarkers do not allow for the identification of cereal species, the chemical profile, which is in agreement with reference samples, as well as the abundance of other cereals at the site, suggest the processing and use of cereals at “Gran Carro”. The
challenge of identifying cereals in an archeological context through organic residue analysis lays in the relatively low content of chemically stable compounds, the susceptibility to degradation, and the lack of distinguishable biomarkers (except for specific cases such as miliacin for millet). Still, advancements have been made showing positive results, even on archeological material [23,24], focusing on the presence and ratios of alkylresorcinols. These compounds that consist of an odd-numbered alkyl chain (C$_{15}$ to C$_{25}$) have been reported in fresh samples of wheat and rye at higher levels, and in low amounts in barley, millet, and maize [55]. However, the analyzed residue from Vessel 26 did not show the preservation of alkylresorcinols. Since these compounds are mainly found in the outer layers of cereal grains [56], and are susceptible to decay and affected by processing, they are not detectable in cereal flour and cereal products [55].

The possibility of a C4 plant source, or a mixture of C3 and C4 plants in the residue from Vessel 26, was considered. However, targeted GC-MS analysis did not present a biomarker for broomcorn millet, miliacin. Miliacin, the principal pentacyclic triterpene methyl ether, was present in only a small number of the C4 grasses of the Panicoideae subfamily. Selected Ion Monitoring (SIM), which allows the mass spectrometer to detect specific compounds with very high sensitivity, using specific ions (m/z 189, m/z 204, m/z 231, m/z 425, m/z 440) reported for miliacin [21] and detected in contemporary millet reference samples, did not demonstrate its presence in the archeological sample.

As such, the residue from Vessel 26 could be interpreted as cereal preparation or porridge remains, and the cereals present at the site imply the use of emmer, barley or millet as the botanical origin of this foodstuff, even if these could not be confirmed by chemical analysis. The absence of phytoliths further suggests that the cereals used to produce the porridge were without glumes, which indicates extreme attention in processing the grains, or the usage of naked grains.

4.2. Millets: Food Choices, Environmental and Socio-Cultural Dynamics

The representation of emmer wheat and barley recovered from the site is not surprising, since both were prevalent, and a staple of plant-based human nutrition, in Italy during the Late Bronze Age and Iron Age [57,58]. On the other hand, millets are scarcely found, and the higher representation of this cereal from the “Gran Carro” site is noteworthy.

Broomcorn millet may have arrived in the Italian Peninsula via northern Italy, but the exact path and timing of its arrival are unknown [59]. Neolithic finds are uncertain [60], and while this region did not take an active part in the domestication of the species, the discovery of remains in Copper Age sites [61] indicates its potential use and the knowledge of this species, if not intentional cultivation. However, none of these finds have been directly radiocarbon dated, which is necessary to establish the age of millet remains, as small grains may move downwards through stratigraphic sequences [62–65].

Intentional cultivation most likely occurred during the Early Bronze Age through connections with the Eastern Alpine region and Danube–Carpathian agricultural sites [60,64,66]. During the Middle Bronze Age, abundant findings of broomcorn millet grains are connected to the Po Plain and the sites of the Terramare Culture [64,67–70]. These findings are supported by isotopic evidence demonstrating the direct consumption of millets, as well as their use for animal feed [59,71,72]. The first isotopic results from Central Italy suggest that the introduction of C4 plants in the human diet occurred in the Bronze Age, revealing that millets might have been consumed by certain individuals [73]. These data are supported by plant macroremains from Pienza [74], while the Middle Bronze Age findings of Panicum grains at Grotta Misa [75] do not appear sufficiently well documented.

In southern Italy during the Bronze Age, isotopic analysis of human bone collagen shows a lack [71], or limited evidence [76], of C4 plant consumption, in opposition to the reconstructed diet trends for the populations of northern Italy, which demonstrate the direct and possible indirect consumption of C4 plants such as millets [69]. However, archeobotanical occurrences of Panicum have been reported from Campania at the Bronze Age sites of Nola–Croce di Papa [77], Capua, Strepparo, Cento Moggie [78] and Oliva
Torricella [79], and at Apulia, at Roca, where abundant unprocessed grains of *Panicum* were aggregated in a charred lump [41].

During the Late Bronze Age and Iron Age, in northern Italy, the incorporation of millets into the regular diet continued, and was clearly established [66,80–84], while the archeobotanical evidence for its consumption in central and southern Italy remains very limited [85]. In pre-Roman levels, *Panicum* was detected as a grain imprint in the Early Iron Age Grave T of Forum Romanum in Rome [86], in Archaic period structures at the Forum and Palatine Hill in Rome [87], and in the Faliscan settlement of Narce [88]. In these sites, millet was never found in substantial quantities.

Due to the rarity of these discoveries in central and southern Italy, the findings of *Panicum* in multiple vessels in the “Gran Carro” village take on added significance, which is further increased by the findings of *Setaria* (foxtail millet), which is extremely rare in the Italian Peninsula. In many European records, *Panicum* and *Setaria* have been found in the same assemblages [66,89–95]. In northern Italy, *Setaria* has been recorded together with *Panicum* in Bronze Age and Iron Age settlements [58,60,66,70,84], as well as in several sites of the Roman Age [96,97]. In Central and Southern Italy, carpological remains of foxtail millet are very rare, being documented in the archeobotanical assemblage from Insula VI.I of Pompeii, but in smaller quantities than *Panicum* [98], and in Medieval layers [99,100].

While information about the wider incorporation of millets in the human diet seems to be lacking, which might be in part due to the limited analysis and the difficult preservation of small grains, the evident dichotomy between the agricultural practices of northern and central–southern Italy is indisputable. In fact, evidence of the cultivation, exploitation and use of millets in the settlement context of “Gran Carro” goes against the established pattern of cereal preference in Central Italy. Even though previous archeobotanical research reported only the presence of *Triticum dicoccum* (four caryopses from the 1974 excavations [7], and one ear fragment of emmer wheat excavated in 1980 [8]), the current research detected the presence of broomcorn millet in six out of eight vessels containing caryopses, including the agglomeration in Vessel 38, accompanied by foxtail millet in all the analyzed vessels. This indicates the value that millet had in the community, and suggests that it was intentionally grown and utilized. Carpological analysis attests to cereal cultivation based on polyculture, combining annual (*Hordeum vulgare, Triticum dicoccum*) and single short season (*Panicum* and *Setaria*) crops. These species were staple crops in the human diet for the population of the “Gran Carro” settlement, and might have also been utilized as animal fodder. However, the vicinity of the settlement to the ritual structure of “Aiola”, which is currently being excavated and researched, might infuse a new meaning into the significance of cereals in Iron Age ceremonial rites.

Plant food resources were obviously very important for the subsistence of the inhabitants of the “Gran Carro” site, and therefore cereals played a significant part in human diet and the agricultural economy. Even though nowadays the reports on millets in the central Italian Iron Age suggest that it was not a preferred crop, and it was either sporadically or accidentally cultivated, the cereal findings from “Gran Carro” shine a different light on the dispersion and value of this small grain crop. Millets were without a doubt present, utilized, and bore importance in the diets of central Italian ancient communities. The discord in distribution compared to northern Italy is undeniable, and this separation might be attributed to ecological or cultural barriers. Interestingly, similar contrasting geographical patterns have been found in the Balkans and the Iberian Peninsula.

In Greece, *Panicum* was more common and abundant in the northern regions of the country, where it has been recorded since the Early Bronze Age, than in the south, where only a few grains were identified from the Late Bronze Age levels [101]. According to Valamoti [101], climate differences between different sections of the country are unlikely to have caused this geographical pattern in millet distribution in prehistoric Greece, which may be better explained by a north-to-south introduction of the crop. Another environmental factor that might have hindered larger millet use is the limiting long-term storage in warm conditions, without affecting the flavor and making it develop a rancid taste [102].
In the Iberian Peninsula, sporadic Middle Bronze Age finds have been recorded in the north [94,103]. However, broomcorn millet only became common during the Late Bronze Age in northern Portugal and northwestern Spain [104,105]; in Valencia or in Andalusia, there is no evidence of millet cultivation until the first millennium BC, despite there being rich archeobotanical assemblages recorded [106]. In the Iron Age and during the Roman period, millets spread throughout Iberia, but were still most abundant in the northwest [107].

One hypothesis that has not been thoroughly explored is that millets were introduced late in central Italy, as a complement to the more productive and demanding crops of wheat and barley, in relation to a climatic and environmental change. At the time of the “Gran Carro” village, the vegetation of the central Mediterranean showed a response to decreases in water availability [108,109], which is confirmed by the low water level of the Bolsena Lake and by the similarly low lake level at Lago dell’Accesa in Southern Tuscany [110]. This aridity might have favored the complementary cultivation of millets, which, as C4 plants, can thrive under even more arid conditions. In addition, the lowering of the Bolsena Lake resulted in the formation of a vast sandy coastal plain around the lake (Figure 1), which could be exploited profitably for summer crops, such as millets requiring a short growing period of between 40 and 90 days. According to ancient sources, millet was grown in areas not suitable for wheat, in sandy or wet soil [111], which could also explain the abundance of *Panicum* in the Terramaras, Bronze Age villages located in the central alluvial plain of the Po Valley characterized by shallow water habitats and seasonal water-level oscillations [69], and in the lake-dwelling site of Lavagnone in the Lake Garda area of northern Italy [70]. The presence of millets in these Bronze Age sites suggests that *Panicum* and *Setaria*, which are typically dry-adapted species, may have found favorable pedological and edaphic conditions in summer-desiccated sandy soils in alluvial areas.

Still, it does not seem plausible that the wider utilization in central Italy of this fast-growing and adaptable crop was restricted by the changing climate conditions in the later periods for a whole millennium, up to the Middle Ages. Keeping in mind the current state of research and the preservation of small grain cereals in the archeological context of the Mediterranean, one might look to food preferences, taste, and cultural identities as reflected in culinary choices as possible causes for the limited evidence of millet consumption.

5. Conclusions

The study of cereal grains and food remains from the vessels of the underwater “Gran Carro” settlement provides evidence of agricultural and dietary variability in Italy during the Early Iron Age. The analyzed archeological residue suggests the possibility of the processing of cereals and the consumption of cereal meals at the site. Cultural preferences and taste might have played a role in crop selection during the Iron Age, but the agricultural practices from northern Italy, active exchange networks, as well as the occurrence of broomcorn millet throughout the Peninsula, even if limited, demonstrate that knowledge existed regarding the successful cultivation and incorporation of this small grain cereal into the human diet. Crop selection at the “Gran Carro” settlement attests to higher levels of millet production and its economic significance compared to the current known distribution of broomcorn millet in central Italy. Millet could have been cultivated on sandy soils, in the large coastal plain (100 m width) created by the lowering of the lake level, attesting to a general dry period. This land could be dry, and available in summer for the fast cultivation of millet, without disrupting the cultivation of wheat and barley in the fertile soils around the lake. Even though millet was not grown as a main crop in the region, these new findings demonstrate its use and value in society, offering additional harvests and enriching the diet of the local population. Its possible use as an offer in ritual ceremonies could be confirmed by future excavations at the “Aiola” structure. Still, further research is necessary to better understand how social dynamics influenced the selection of plant food sources, and if they mirror the values of a specific population on a local level.

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