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Ancient bread recipes: Archaeometric data on charred findings☆

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ABSTRACT

This study examines charred bread-like samples found in several archaeological sites across northern Italy and dating from the Early Bronze Age to the Early Middle Ages, some of which are included amongst the UNESCO World Heritage Sites. The aim is to investigate differences and homogeneities in bread production processes in different eras and cultures. Bread was a staple food in many ancient societies, but has rarely been found amongst the materials that survive in archaeological sites. When it is found, it is usually because the bread was charred by accidental combustion (falling into the oven during baking) or deliberate combustion (for ritual purposes). The literature on the issue is not abundant, but has been growing over the past decade. There is, therefore, room to propose new study methodologies at this time.

We studied eight samples of charred bread-like products and we used optical and scanning electron microscopy to identify plant tissue remains attributable to cereal caryopses, partly modified by bread-making processes. Energy dispersive X-ray spectroscopy and, for the first time, infrared spectroscopy in attenuated total reflectance mode (FTIR-ATR) were also used to investigate the composition and preparation methods of the different types of bread-like products. In particular, FTIR-ATR analysis can give indications about the presence of starch, gluten and lignin in the sample under investigation and it can, therefore, be used as a screening to guide subsequent SEM analysis in the search for specific cereal residues in the dough.

In some cases, the different techniques used also revealed the presence of minerals such as silicates and carbonates, probably due to grinding residues or poor sample cleaning. During SEM observations, phytoliths, diatoms and framboids were also found in some of the samples.

1. Introduction

Food is one of the fundamental aspects of human life and a key aspect of archaeological studies, as it can indirectly provide much information about past cultures, technological knowledge, relationships between different civilisations and social stratifications within the same community.

Analyses of the dietary habits of our ancestors can be conducted directly on ancient human remains (e.g., bones, teeth, dental calculus), by searching for markers of particular diets, or on food remains stored over time [1–14].

Of all foodstuffs, bread and cereal-based products have been amongst the most widespread since ancient times, having also taken on ritual significance as part of the grave goods. The ingredients, processing and shapes can vary widely and give information about the past populations.

Although a staple foodstuff since ancient times, bread is not frequently found amongst the materials that survive in archaeological records because it is difficult to identify [15]. Ancient bread remnants may persist if dried or, even better, charred: this is the situation that occurs in most archaeological findings [9,15]. More rarely, desiccation can occur in exceptional situations in an archaeological deposit. When dried, bread often retains many of its original features, which can be observed under the microscope or identified

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with chemical analyses. Bread samples may also be accidentally conserved due to combustion, for example, bread offered during a ceremony of cremation, or that fell in an oven during cooking [15].

In the mid-19th century, several cases of archaeological finds of combusted bread were reported and analysed in Europe [16–19]. Descriptions and observations of macroscopic morphology were generally conducted, supported by optical microscopy, to identify remains of structures typical of the raw materials used, for example whole grains [20–25]. The later introduction of scanning electron microscopy also made it possible to observe the micromorphology of archaeological bread remains to identify, for example, cell structures, starch granules, phytoliths and minerals from milling residues [9,10,15,26–32].

In Italy, samples of archaeological bread or farinaceous products, dating to different epochs, have been found in many sites, both from Northern (for example, in Castelletto Ticino (Novara) [33,34], Lazise (Verona) [35], Morano sul Po (Alessandria) [36,37] and Bande di Cavriana (Mantova) [38]) and from Southern Italy (for example, in Pompeii (Napoli) [39], Roca-Melendugno (Lecce) (XII sec. BCE) [40], Monte Papalucio-Oria (Brindisi) (Hellenistic Age) [11,40]). Studies have also been carried out on 'crusts' that have remained attached to the walls of ceramic vessels such as at Ponzone d'Acqui (Alessandria) [33,41] and of soapstone artefacts such as at Castelseprio (Varese) and Monte Barro (Lecco) [42] (all of these sites are located in Northern Italy).

This study focuses on archaeological bread-like products and exploits optical and electronic microscopy to identify the raw materials and techniques used in its preparation. Since microscopic observations are not always able to identify microstructures in case of alteration for cooking, carbonization or fragmentation of the samples we decided to evaluate the potential of another analytical technique which is able to give an indication of the chemical composition of the sample and that could be used as a screening to direct and complement the subsequent microscopic observation. Given the versatility, speed, and the small amount of sample required for the analysis (few micrograms), we chose Fourier transform infrared spectroscopy in attenuated total reflectance mode (FTIR-ATR), which requires no sample preparation other than grinding the micro-fragment if necessary [43]. Infrared spectroscopy is commonly used in archaeometry as a diagnostic and screening tool to direct further analysis for a wide variety of materials, although has never been not focused on the direct analysis of bread-like remains and on the detailed interpretation of the characteristics of individual spectra [44,45]. The technique is established and extensively chosen for the investigation of archaeological findings and works of art because it can detect a wide range of compounds present even in small amounts in the samples analysed, both inorganic and organic, and in some cases it is possible to recognize the mineralogical form too [46]. The characterization of samples can be enhanced with information on the matrix and conservation environment and with relative dating within the site, by comparison with databases of aged samples or with similar samples dated by other techniques, all very important aspects in the case of the study of archaeological finds [13,47–50]. The technique is inexpensive and common in laboratories in the more traditional set up too. Nevertheless, there are still unexplored fields of application in which infrared spectroscopy could be used. To the best of our knowledge, this is the first time that FTIR-ATR has been used to investigate archaeological bread-like samples. In this specific type of sample, this technique can provide indications of the presence of starch, gluten and lignin. This information can then be used either as a screening to guide subsequent SEM analyses in the search for specific cereal residues in the dough, or as support in the interpretation of the observed structures.

Image analysis was carried out on all the remains, to determine the pore size of samples. The traditional classification system [28], which takes into account the height of the bread-like products to determine whether it is a leavened or unleavened one, cannot be applied in cases where the entire loaf is not found, but only fragments. According to this classification, a product whose thickness is lower than 25 mm is called 'galette' or 'flat bread', unleavened. On the other hand, a product whose thickness exceeds 45 mm is defined as 'bread', leavened. Even the criterion of observing whether there is a distinction between a compact crust and a porous inner part may not be easily applicable in the case of crumbs. An alternative approach, which has been gaining ground in recent years, is to determine the size of the pores by means of image analysis [9,30]. By observing their size distribution, it is possible to formulate alternative hypotheses on the leavening of the product.

The method was applied to eight case studies from seven sites in northern Italy (Fig. 1), and was performed on different types of bread-like products spanning from the Early Bronze Age (2200–1600 BCE) to Early Middle Ages (6th-7th century CE). This wide variety of materials allowed us to test the versatility of the method and to describe the breadmaking process in different periods and in different cultures.

2. Research aim

Our aim was to obtain information on the raw materials and techniques used in ancient times for the preparation of bread, which is a very common staple food that has rarely been studied in archaeology.

We propose an analytical method for archaeological bread-like samples, which involves microscopic techniques and Fourier transform infrared spectroscopy in attenuated total reflectance mode (FTIR-ATR). We believe this is the first study to use FTIR-ATR analysis directly to investigate archaeological bread-like remains without any pre-treatment. This means the analysis can be carried out quickly and even on extremely small samples. FTIR-ATR analysis was also used to support more traditional optical and scanning electron microscopy techniques. This technique offers insight into the chemical composition of the sample, such as the presence of starch, gluten, and lignin. It can serve as a screening method to guide and supplement subsequent microscopic observations.

The method was then applied to samples from seven different archaeological sites in northern Italy, ranging from the Early Bronze Age to the Early Middle Ages, in order to highlight similarities and differences in ingredients and preparation methods.

3. Materials and methods

3.1. Sampling

The studied samples came from archaeological sites located in northern Italy (Fig. 1) and are from different ages (Table 1); two of these, Bande di Cavriana and Lucone di Polpenazze del Garda, were listed by UNESCO as 'World Heritage' in the database of 'Prehistoric Pile Dwellings around the Alps'. The sites and context of the findings (tomb and US-stratigraphic unit) are briefly described. Images of whole samples are shown in Supplementary Material S1.

The oldest sites from which our bread-like remains come are located in the Garda moraine amphitheatre; these are the pile-dwelling settlements of Lucone di Polpenazze, Bande di Cavriana and Lazise la Quercia, all dated to Bronze Age (Fig. 1, Table 1).

In the case of Lucone it is a large basin, now largely reclaimed, once occupied by a small lake. Since the 1960s the site has been the subject of numerous excavation campaigns, defining at least five areas of outcrops of archaeological materials. Since 2007, excavations have focused on the so-called 'area D' with the discovery of ceramic finds, wooden tools, portions of fabric, seeds, fruits, and wood charcoal. Particularly numerous are the charred remains of

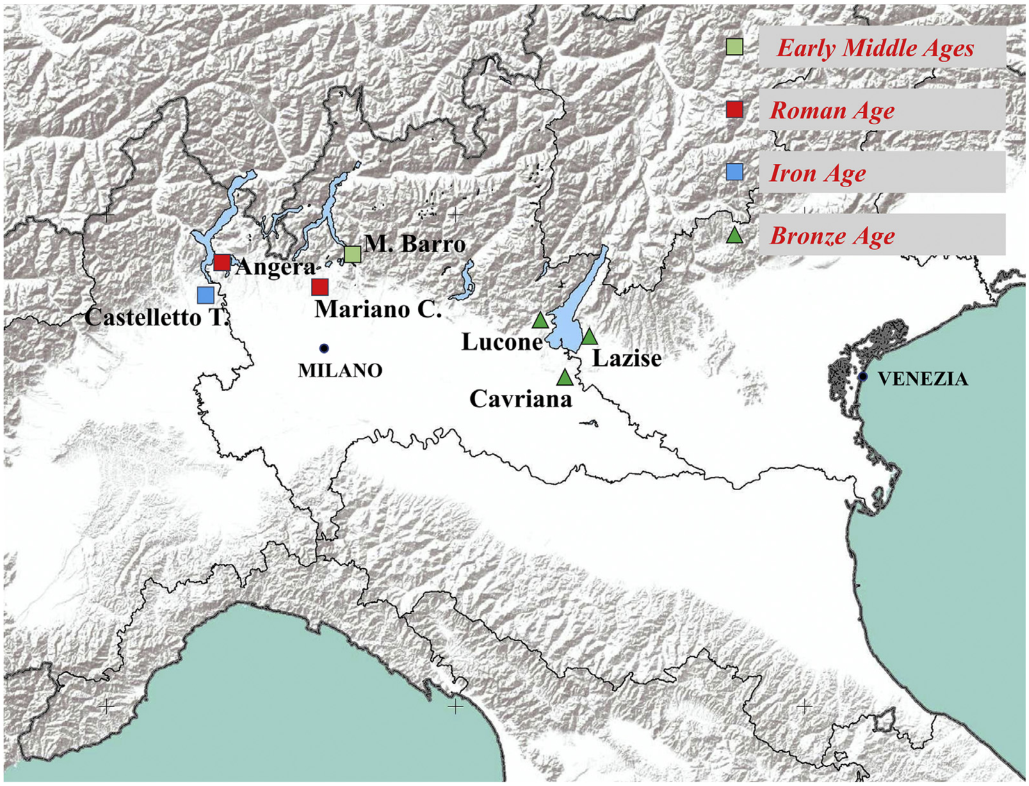

Fig. 1. Map of Northern Italy with the studied sites.

Table 1
Sites from which the analysed samples were collected, listed according to their chronology, from the oldest to the newest.

	site	context	chronology	type of finding examined
Bronze Age	Lucone di Polpenazze del Garda (Brescia)	pile-dwelling settlement	2035 cal BCE to 1969 cal BCE ±10yrs	loaf of bread
	Bande di Cavriana (Mantova)	pile-dwelling settlement	2200–1600 BCE	loaf of bread
	Lazise La Quercia (Verona)	pile-dwelling settlement	1600–1300 BCE	loaf of bread
Iron Age	Castelletto Ticino (Novara)	necropolis	10th-7th cent. BCE	crumbs
Roman Epoch	Angera (Varese)	necropolis	1st-3rd cent. CE	fragments
	Mariano Comense (Como)	necropolis	1st-3rd cent. CE	fragments
Early Middle Ages	Monte Barro, Galbiate (Lecco)	settlement	6th cent. CE	fragments

planks, beams and poles that constituted the dwelling structures, which were destroyed by fire. Two charred loaves were found in this same ‘area D’ (Figures S1a, S1b, S1c, S1d) [51–54]. The first, found in US 422 (US=stratigraphic unit), has a length and width of 5.5 and 3 cm respectively and a thickness varying from 1.4 to 2 cm; the second, in US 457, has a diameter of almost 6.5 cm and an average thickness of 2 cm. Stratigraphic units 422 and 457 refer to lake sediments, not to those within the huts.

A loaf of bread was found both at the sites of Bande di Cavriana and Lazise La Quercia.

Bande di Cavriana in particular was a complex pile system with numerous piles driven into the bottom of the lake basin; they supported a raised deck on which huts were placed.

The sample from Bande di Cavriana, consists of a charred bread, with a diameter of 10 cm and a thickness higher than 5 cm (Figures S1e, S1f) [38,55,56].

The Lazise La Quercia site consists of a pile-dwelling settlement covering a vast area with numerous piles. These piles, although outcropping only a few centimetres from the bottom, stand out without interruption.

The sample from Lazise La Quercia consists of flattened bread that is almost perfectly intact, rounded, and with a slightly concave base, with a diameter of about 9.2 cm and thickness ranging from 1 to 1.2 cm (Figures S1g, S1h) [35,38].

The stratigraphic units of occurrence of these two breads (Cavriana and Lazise) are not known.

At Castelletto Ticino, in the remains of burial pyres numerous bread-like remains have been found, which were offerings for incineration rites or funeral banquets. They consist only of 1–4 mm crumbs, found either inside or outside the cinerary urns, mixed with bone remains and wood charcoal (Figure S1i) [34]. Grave goods allowed to date the tomb in which the crumbs were found to the culture of Golasecca IB.

Whole loaves have been found in the incineration necropolis in Angera, in the Roman Cemetery, along with fragments of bread-like products (Figure S1j), used as votive offerings in 57 graves [57].

In Tomb 65 of the cremation Roman necropolis in Mariano Comense fragments of charred bread-like remains were found, with a total weight of approximately 56 g, and a diameter of up to 7–10 cm (Figure S1k) [58].

In the Monte Barro settlement, a fragment of charred bread-like product (max. length 4 cm) (Figure S1l) was found inside the larder (compartment f) of the so-called 'Great Building', a noble mansion. The 'Great Building', whose walls were divided into three bodies (North, East, West) with two floors, facing a large inner courtyard, occupied an area of approximately 1500 m^2. The compartment f was located in the north body of the building, the so-called 'noble wing', which housed a larder with a considerable amount of cereals and chestnuts, all burnt together in an intentional fire set to the area by its own inhabitants about 540 CE [59].

In almost all cases, the bread-like samples analysed consist of small fragments, of around 3–4 mm, extracted without damaging the finding. Preliminary observations with optical microscope selected the most significant samples for analysis with scanning electron microscopy and Fourier transform infrared spectroscopy.

3.2. Optical microscopy (OM)

Optical microscopy has been used for an initial observation of the remains of the grain structures and to acquire some of the images used to calculate the size of the pores.

A Nikon Optiphot episcopic optical microscope in reflected light was used. 'Focus stacking' (assemblage of multiple pictures focused on different depths) was used when necessary.

A Leica MZ 125 stereomicroscope was also used.

3.3. Scanning electron microscopy and energy dispersive X-ray spectroscopy (SEM-EDX)

The micromorphology of the samples was observed with a FEI/Philips XL30 ESEM. The elemental analyses were carried out using an X-ray energy dispersive spectrometer EDX Quantax 400 coupled to SEM. Every sample was analysed 'as is' in low vacuum mode (1 torr) at 20 kV, by using GSE, BSE and X-Ray detectors.

3.4. Fourier transform infrared spectroscopy (FTIR)

FTIR spectroscopy has been employed for assessing the chemical composition of the samples, including the detection of starch, gluten, and lignin.

FTIR spectra were recorded in attenuated total reflectance (ATR) mode, by a Thermo Scientific Nicolet iS10 instrument. Spectra were acquired in the 4000–600cm^{-1} range, with a resolution of 4cm^{-1}, 32 scans. The technique requires only a few micrograms of sample, which can generally be analysed 'as is' or, if necessary, after grinding in an agate mortar.

3.5. Image analysis

The charred samples were photographed and the images, calibrated with the appropriate scale and cropped to obtain a reasonably flat area, were subjected to image analysis using ImageJ software [9,30,60]. Black and white images were thresholded with the automatic 'Otsu' method and then 'analyze particles' was used [61,62].

Area and Feret equivalent diameters were calculated for each pore.

The distributions of Feret equivalent diameters of the identified pores were displayed in histograms representing the number of counts per size class (in 100 µm intervals) (Figure S2).

4. Results

4.1. SEM-EDX and FTIR analysis

Optical and SEM images of cereal microstructures were acquired, and their interpretation was compared with literature data [9–11,30,63–75]. For the purposes of diagnosis to distinguish one species from another within cereals, it is essential to be able to correctly describe the characteristics of certain tissues that form the caryopsis. For example, in the outer coating of the grain, it is essential to observe the crossing between the two layers of cells, the longitudinal ones and the underlying, transverse ones. Under the bran, the diagnostic element is the set of aleurone cells, which may form one or more layers.

Regarding FTIR spectroscopy, the lack of specific references in the literature for the interpretation of infrared spectra of archaeological bread-like samples led us to conduct band assignment mainly on the basis of articles concerning modern, non-charred, flour, dough or bread [76–78]. This is definitely an approximation, but the signals in the spectra of the analysed samples coincide fairly well with those found in the literature. This statement is also partly supported by a study highlighting the fact that the spectra of extracts in organic solvents of modern, non-charred cereals appear to be identical to those of the same cereals charred at low-temperature [79]. The same study also shows that, in most cases, there is a good agreement between the extracts of modern and ancient cereals of the same species. A close accordance between the infrared spectra of bread (made with flour, yeast and water) and those of its flour was also observed [80]. Experimental studies on how chemical characteristics change in cereals that had been carbonized, which also involved the use of FTIR, were also considered [67,81]. During heating, the weakening or broadening of certain bands was reported, due to condensation reactions between proteins and starch and an increase in the aromaticity of the compounds present [81]. This conversion is believed to be responsible for the preservation of charred grains over time [67]. After prolonged heating, there were new absorption peaks. Based on these evidences, the presence and abundance of gluten and starch were mainly assessed.

4.1.1. Lucone di Polpenazze del Garda

The loaf of bread from US 422 shows, on macroscopic examination of the surface, some fragments of caryopses of *Panicum miliaceum*/*Setaria italica* (millet/foxtail millet) and some portions of tegument, most likely belonging to the same taxon, in a rather coarse mixture (Figures S1a, S1b). When observed by SEM, this sample contained shreds of rolled cross cell tissue, fused starch granules, rolled monostratified aleurone (Fig. 2a) and, at higher magnification in the Figure S3a, surrounded by fused amyliferous parenchyma.

A shred of longitudinal cells (Figure S3b) and individual as well as groups of yeast cells (*Saccharomyces cerevisiae*) (Fig. 2b and S3d) were also identified by comparison with those found in an ancient beer residue from Pombia (Novara) [33,82].

There were phytoliths with different shapes (Figures S3c,d, S4b) [83] and diatoms [84] (Figures S3d, S4a,b,c) in several places in the sample.

With regard to diatoms, the genera *Synedra* (*Ulnaria*) (Figure S4a), *Alaucoseira* and *Gomphonema* (Figure S4b), *Ulnaria* (Figure S4c) were classified.

FTIR pattern (Fig. 3a) revealed that the sample seemed to be well preserved. In fact, the intense peaks are due to gluten. The peaks at 1626 and 1521cm^{-1} are due to C=O stretching in amide I and to N–H bending in amide II, respectively [78,81]. There are other peaks are possibly due to gluten at 3277cm^{-1} (N–H or O–H stretching modes), 2929cm^{-1} (C–H stretching mode) and 1447cm^{-1} (other amide-related mode) [78]. Starch was also present, as indicated by its peaks linked to the presence of C–O alcohol groups (1152, 1076, 1026cm^{-1}) [76–78,81]. There are also signals at 1558 and 1398cm^{-1}, which may be linked to the presence of carboxylates [81]. A signal at 1279cm^{-1}, likely due to lignin, may indicate the presence of bran [85,86].

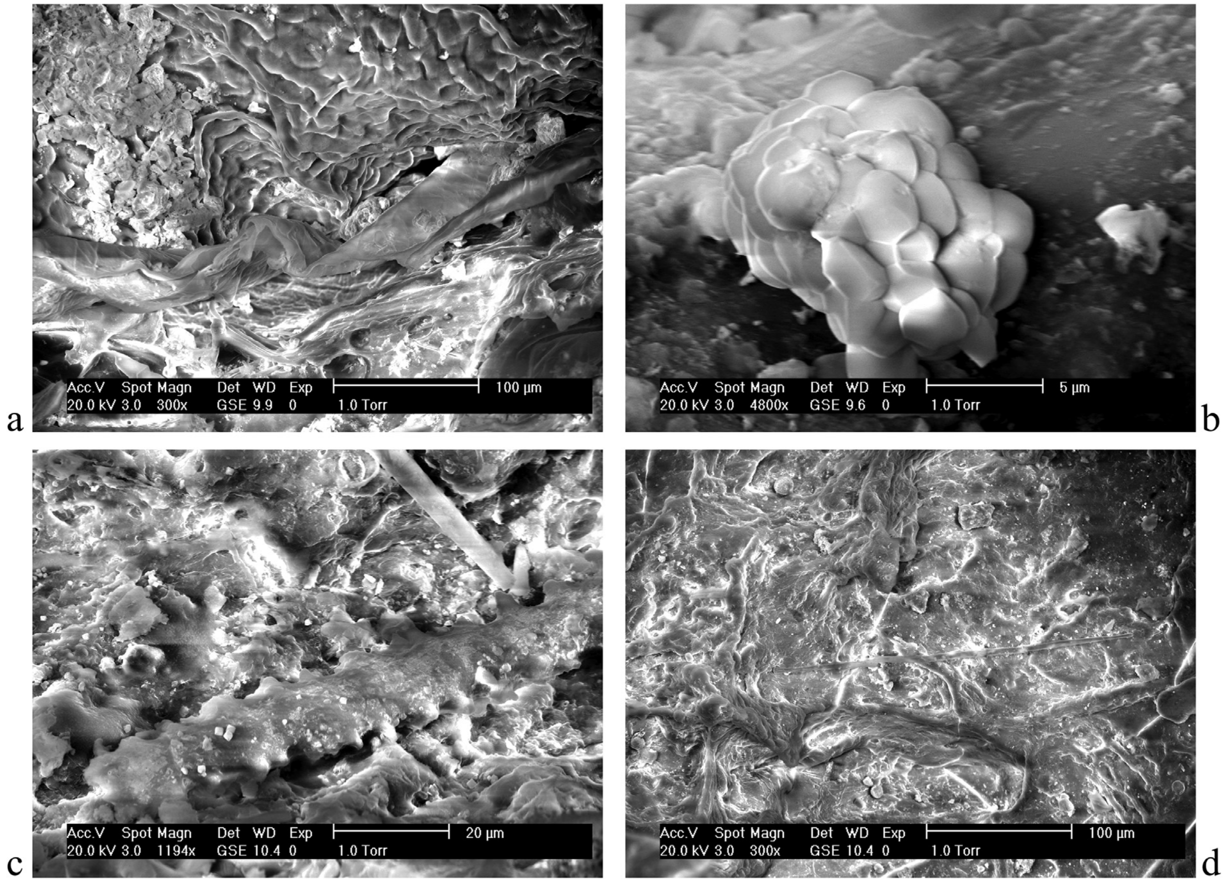

Fig. 2. SEM images – Lucone US 422 a) shreds of rolled cross cell tissue and fused starch granules, rolled monostratified aleurone b) groups of yeast (*Saccharomyces cerevisiae*) cells (h = 2.857 µm, l = 2.143 µm); Lucone US 457 c) tabular phytolith with clavate margin; d) diatom (in the centre of the image).

As for the loaf coming from US 457, SEM analysis revealed traces of cross cells (Figure S5a), molten endosperm (Figure S5b), and leavening bubbles. Some starch granules with a small size (on average under 10 µm in diameter) were observed.

There are also some phytoliths: a tabular phytolith with clavate margin (Fig. 2c), a hypodermal phytolith from woody plants (*Pinaceae*) (Figure S5c) and a subepidermal dendritic phytolith (Fig. 4a). In addition, the analysis revealed some diatoms (Fig. 2d): fragment of *Fragilaria* (Figure S5d), *Achnanthes* and *Gomphonema* (Figure S5e).

There were groups of framboids in many places in the sample (Figures S5f,g,h,i).

EDX analysis was performed on some structures which highlighted, for example, that phytolith is composed of silicon and oxygen (Fig. 4a,b), and that framboids are composed of iron and sulphur (Fig. 4c,d,).

4.1.2. Bande di Cavriana

The charring of the find did not alter the shape of bread. The crust was thick on the bottom, but much less at the top. During analyses conducted in the past, it was possible to observe on the surface of the bottom part of the loaf a fragment of a glume (length about 8 mm), ascribable to a hulled cereal, probably einkorn (*Triticum* cf. *monococcum*) [55]. Bran was widespread in the bread of Bande di Cavriana, throughout the dough, in the form of small flakes (about 1 mm).

The sample showed, at SEM observation, several small fragments of clavate phytoliths, a leaf lamina phytolith and a papillae phytolith from lamina tissue (cf. *Triticum* sp.) (Fig. 5a), monostratified aleurone (Figure S6a), along with transverse cells with thickened walls ascribable to *Triticum* sp. (Figure S6b), amyliferous parenchyma with rounded rondel and keeled rondel short cell (Figure S6c), longitudinal cell patches and amyliferous parenchyma (Figure S6d), protein filaments (Figure S6e) and diatoms (Figs. 5a, S6d). The presence of barley (*Hordeum vulgare* L.) is deduced from the presence of the spongy parenchyma, typical of this species, adhering to the inner epidermis of the seed (Figure S6f) [74,87]. Starch was very rare and showed a bimodal distribution. Its shape also appeared to be modified from baking, becoming oval and flattened with a relief stretched in the middle.

The FTIR analysis showed very weak signals, probably due to the poor preservation of the charred remains (Fig. 3a). There are few clear peaks, of which the signal at 1570cm^{-1} is linked to the presence of carboxylates [81], at 1695cm^{-1} possibly due to the stretching of C=O groups in carboxylic acids or ketones [81], and at 1104cm^{-1}, probably attributable to the C–O alcohol groups of starch [76,77,81]. The weak peaks at 875 (O–C–O out-of-plane bending) and 1417cm^{-1} (CO_3^{2-} asymmetric stretching) suggest the presence of carbonates [88,89], perhaps residues from grinding.

4.1.3. Lazise La Quercia

The surface is strongly granular, due to the abundant fragments of caryopses and some portions of glumes. Initial analyses, conducted in the 1990s, had allowed a spikelet of *Triticum monococcum* L. (einkorn) to be found in a fracture [35].

The sample, observed by SEM, showed fragments of multilayered aleurone, compatible with barley (*Hordeum vulgare* L.) (Fig. 5b) and of cross cells with amyliferous parenchyma containing starch granules (Figures S7a,b,c) sometimes in excellent state of preservation. There are also tracheary annulate/helical tree phy-

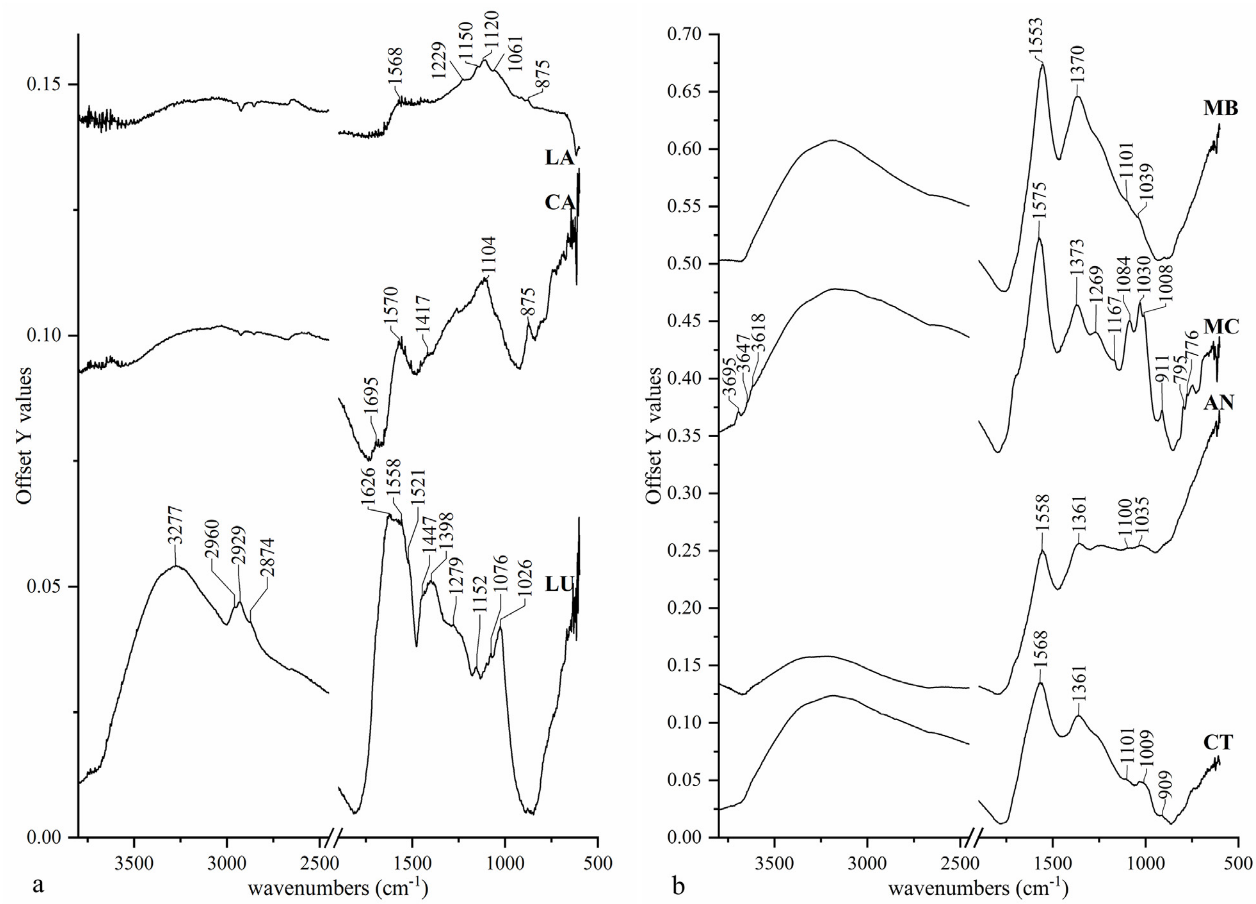

Fig. 3. FTIR-ATR spectra of samples. The names of the sites are summarized as follows: CT: Castelletto Ticino, AN: Angera, MC: Mariano Comense, MB: Monte Barro, CA: Cavriana, LA: Lazise, LU: Lucone US 422.

toliths (Figure S7d). The presence of sharp-edged fragments of broken millimetric caryopses and small bran flakes was also observed.

Very weak signals were observed in the FTIR spectrum (Fig. 3a), which could be ascribed to C–O and C–C stretching of starch (1150 and 1061cm^{-1}) [76–78,81]. The peak at 1568cm^{-1} could either be related to the presence of carboxylates or gluten (N–H bending of amide II) [81]. The weak signal at 1229cm^{-1} could also be related to an amide III group (N–H bending and C–H stretching) [76,77].

A weak peak at 875cm^{-1} indicates the presence of some calcite (O–C–O out-of-plane bending) [88,89], present either as dirt or grinding residue.

4.1.4. Castelletto Ticino

SEM observations were conducted on a crumb found in the filling (US 286a) of Tomb 20/2001 (750-675 BCE) [90]. A portion of aleurone can be noted in Fig. 6a, and additional observations revealed the presence of unistratified aleurone (Figure S8a) and phytoliths (Figure S8b).

FTIR-ATR analysis (Fig. 3b) showed an intense band at 1568cm^{-1} which could be related to the presence of carboxylates or gluten (N–H bending of amide II) [13,81,91]. Another signal at 1361cm^{-1} probably also originated from ionized carboxylates groups [91]. Signals of starch were observed at 1101 and 1009cm^{-1} (C–O alcohol groups) [76,77,81]. The peak at 909cm^{-1} was perhaps due to silicate residues [88].

4.1.5. Angera

A fragment of a bread-like product from Tomb III 27 was examined and transversal cells with thickened/punctate walls typical of *Triticum* sp. were observed (Fig. 6b). Elsewhere in the sample, remains of aleurone and clusters of transversal cells with punctate walls were observed in the dough (Figure S9a), collapsed and fused aleurone (Fig. 6c) and cells of tissue probably belonging to bran or chaff (Figure S9b) were found.

In terms of the FTIR-ATR analysis, signals at 1558 and 1361cm^{-1}, due to the stretching of the carboxylate group or of C=C aromatic bonds [13,81,91], were observed (Fig. 3b). The peaks generally related to starch were very weak, with a shoulder-like shape, around 1110 and 1035cm^{-1} (C–O and C–C stretching) [13,76–78,81].

4.1.6. Mariano Comense

The fragment analysed came from Tomb 65/98 and showed the presence of a lot of bran and even almost whole grains. A piece of caryopsis with cross cells was found: the transverse cells showed punctuated walls referable to *Triticum* sp. (Fig. 7a), and monostratified aleurone (Fig. 7b), together with patches of transverse cells and molten endosperm (Figure S10) could also be seen.

The FTIR-ATR signals (Fig. 3b) could be attributable to carboxylates or aromatic C=C (1575 and 1373cm^{-1}) [13,81,91]. The particular peaks of silicates, such as quartz (1167, 1084, 795 and 776cm^{-1}) and kaolinite (3695, 3647, 3618, 1030, 1008, 911cm^{-1}) were also visible [88]. Unfortunately, many of these signals coincided with those of starch (in particular, those at 1008 and 1084cm^{-1}) [76–78,81], and thus it is not possible to assess the state of preservation of the latter. Finally, in the same spectrum there is a moderately intense peak at 1269cm^{-1}, which could be due to the presence of lignin, contained in the bran [13,85,86].

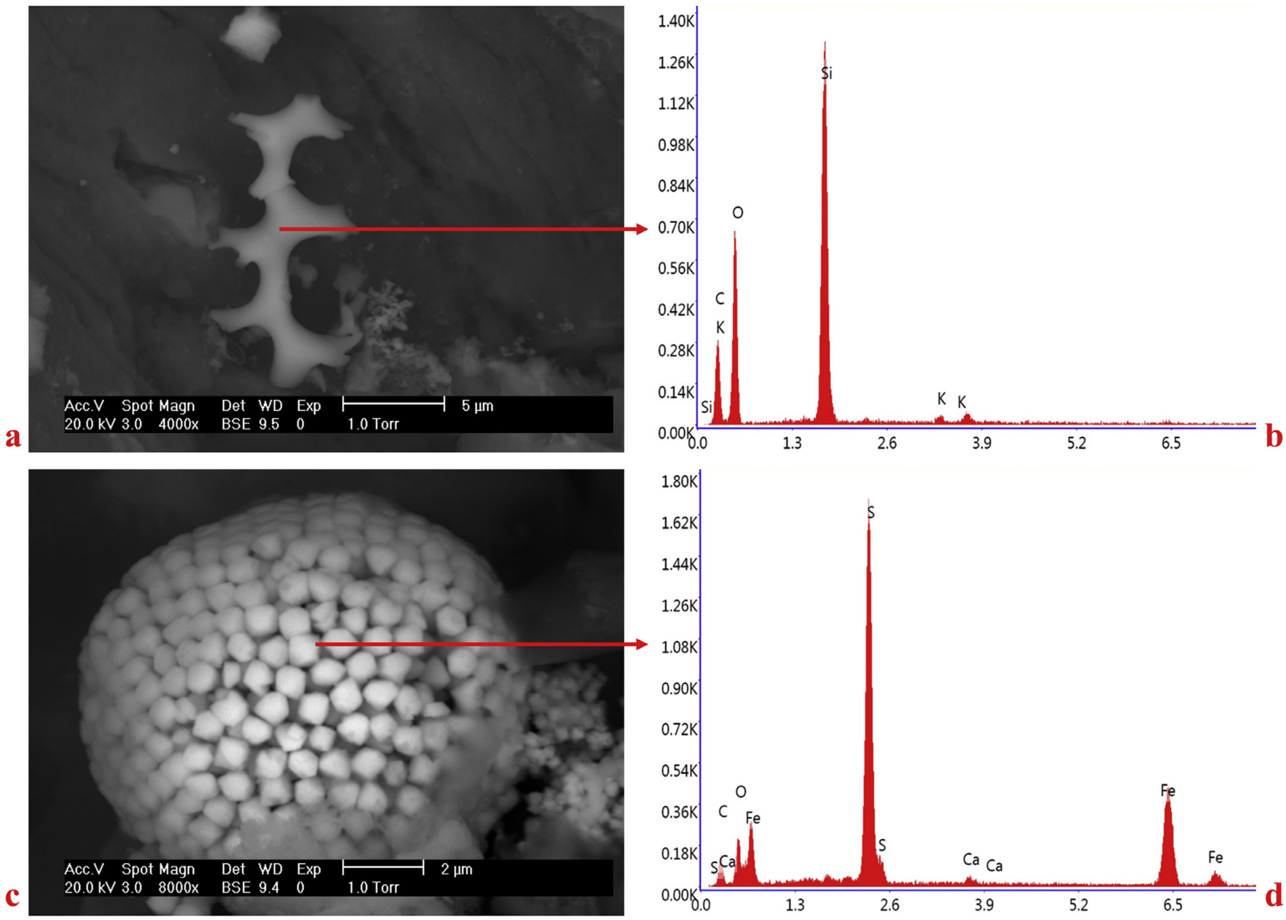

Fig. 4. EDX analyses on structures found in sample Lucone US 457. a,b) image and elemental analysis of a phytolith, evidencing the presence of silicon and oxygen c,d) image and elemental analysis of a framboid, evidencing the presence of iron and sulphur.

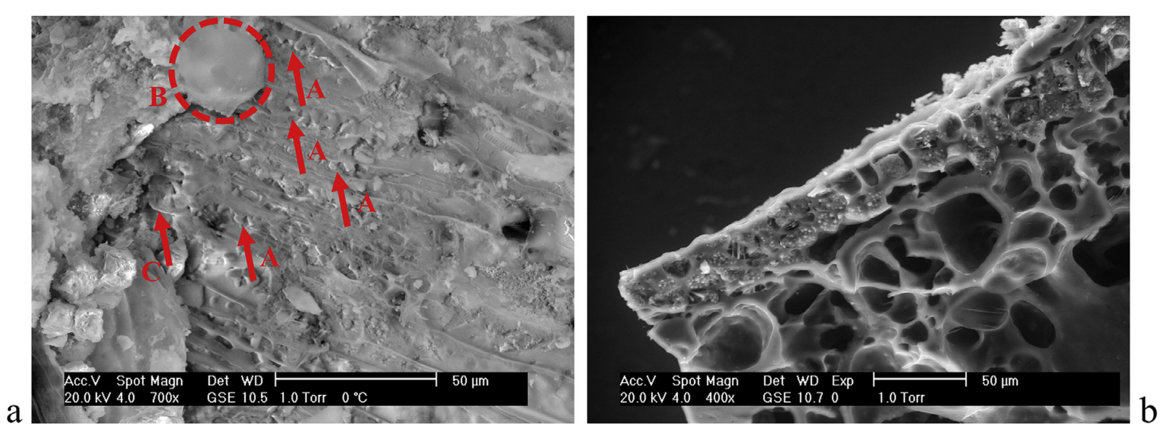

Fig. 5. SEM images a) Cavriana, small fragments of clavate phytoliths (A), a leaf lamina phytolith (B) and a papillae phytolith from lamina tissue (C) (cf. *Triticum* sp.); b) Lazise, fragments of multi-layered aleurone, compatible with barley (*Hordeum vulgare* L.).

4.1.7. Monte Barro

Tubular cells and monostratified aleurone (Fig. 7c) were clearly visible in the sample. Bimodal starch was visible in many areas (Fig. 7d), together with protein filaments throughout the dough (Figure S11).

Signals at 1553 and 1370cm^{-1}, due to the stretching of the carboxylate group or of C=C aromatic bonds [13,81,91], were observed in the FTIR spectrum (Fig. 3b). The very weak peaks of starch (C–O and C–C stretching) were visible at 1101 and 1039cm^{-1} [13,76–78,81].

4.2. Image analysis

In the case of our samples, the traditional classification system that measures the height of the bread to determine whether it is a leavened product or not [28] could only be applied to the samples from Lucone US 422 (thickness between 14 and 20 mm), Lucone US 457 (average thickness 20 mm), Bande di Cavriana (thickness 50 mm) and Lazise (thickness between 10 and 12 mm). In all these cases one should therefore speak of ‘flat bread’, except for Cavriana which can be classified as a real leavened bread. To try to

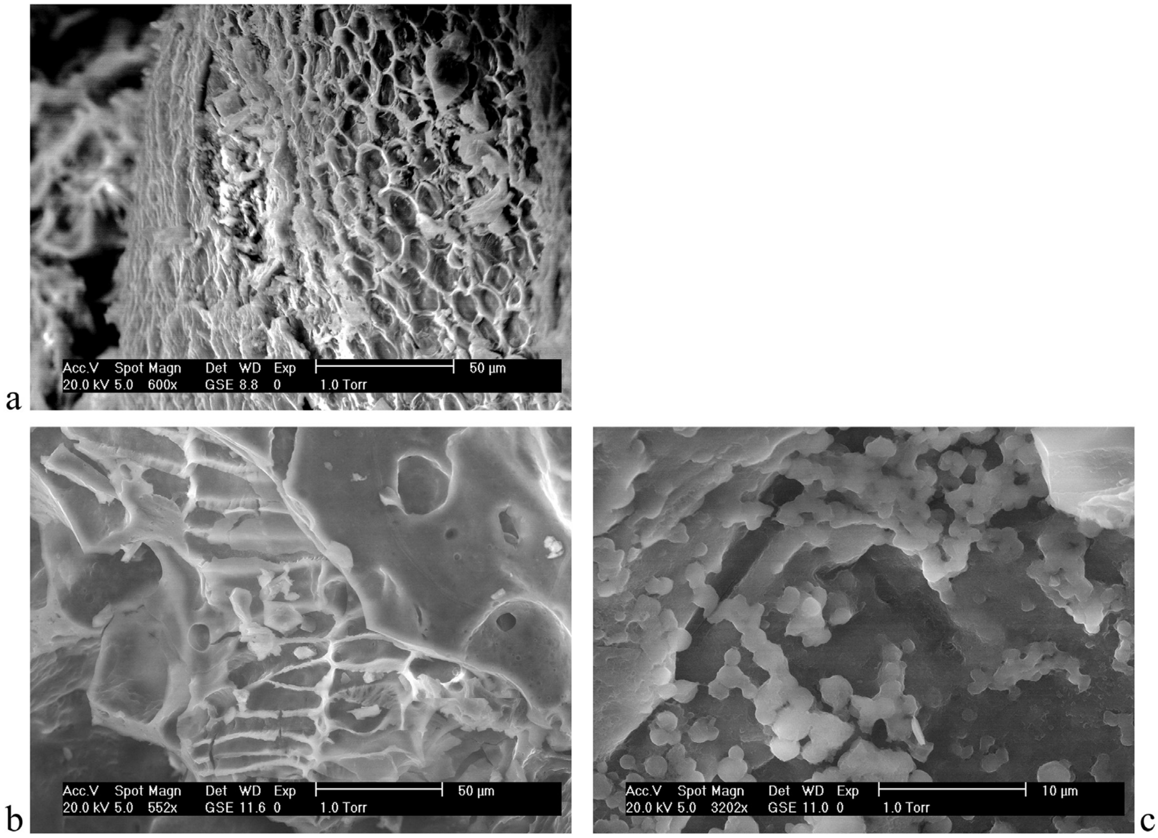

Fig. 6. SEM images – a) Castelletto Ticino, aleurone b) Angera, cross cell tissue of *Triticum* sp. c) Angera, collapsed and fused aleurone.

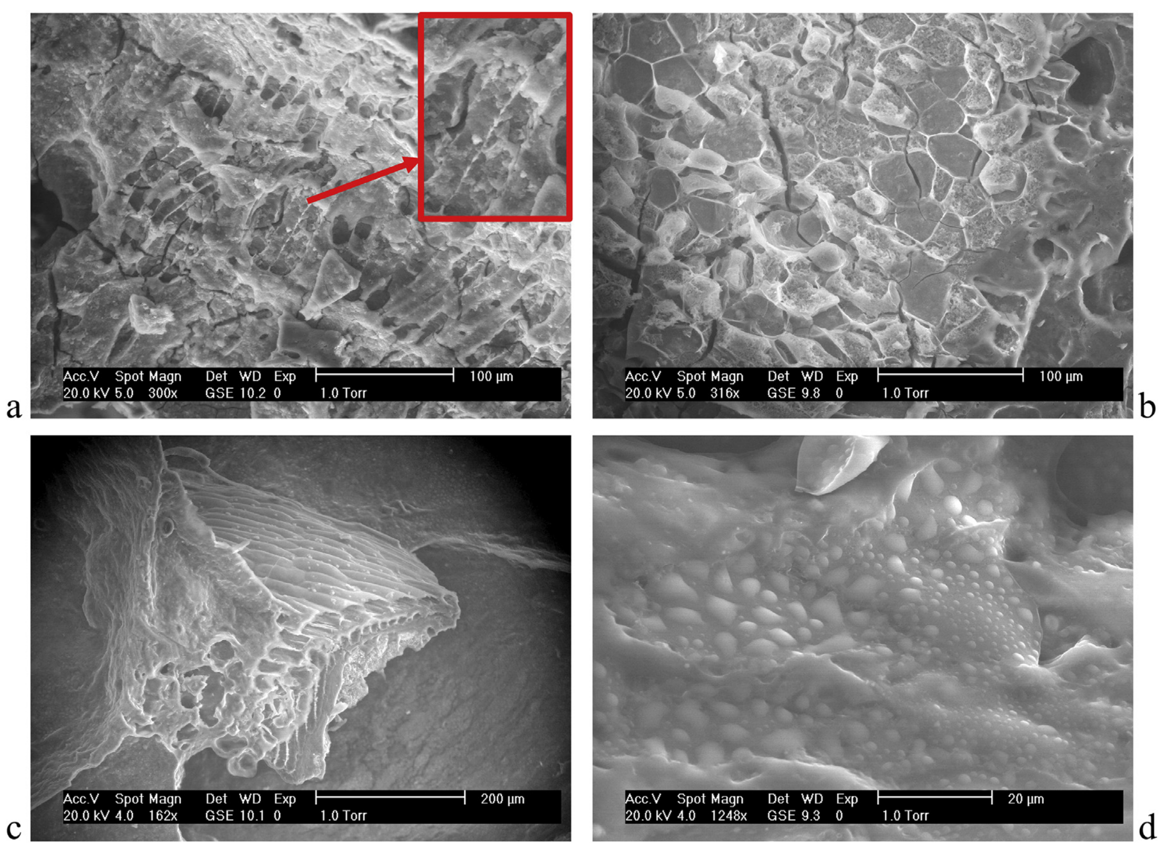

Fig. 7. SEM images – Mariano Comense a) punctuated walls referable to *Triticum* sp. (see also zoom in the box) b) monostratified aleurone; Monte Barro c) tubular cells and monostratified aleurone; d) bimodal starch.

obtain information on the leavening of the samples, an alternative approach involving the measurement of pores by image analysis was then applied [9,30].

The technique was applied to all case studies, selecting sufficiently large portions of the images to be able to include as many pores as possible and obtain distributions that were reasonably representative of the whole sample.

The graphs obtained, representing the Feret equivalent diameter distributions of the identified pores, are shown as histograms representing the number of counts per size class (in 100 μm intervals) (Figure S2). For clarity of representation, pores with equivalent diameters up to 5 mm have been included in the histograms.

It can be seen that of the two samples from the Lucone site, the one with generally larger pores is that of US 422, where the presence of yeast (*Saccharomyces* sp.) was observed by SEM.

The Cavriana bread is the one with the largest amount of relatively large pores, consistent with its thickness and the presence of a crust distinct from the inner part. All these clues lead to the hypothesis that this is a real leavened bread. The Lazise sample also shows a distribution that appears to be very similar, despite the fact that it is classified as a ‘flat bread’ on the basis of its thickness.

The ‘crumbs’ from Castelletto Ticino show the smallest pores, all below 0.6 mm in agreement with its uncertain identification as a real bread.

In the Angera sample, few pores were identified by this method. In contrast, the remains from Mariano Comense and Monte Barro show similar distributions, with a slight prevalence of larger pores in the former one.

5. Discussion

SEM analyses performed on the eight samples showed heterogeneity in the preparation of the doughs: in some cases, combinations of different cereal species were observed, in others the components used were less definable due to a lack of sufficiently diagnostic structures at a systematic level. The efficacy of the FTIR-ATR examination is confirmed, which specifies, supports and/or confirms the SEM findings and can also be used as a preliminary screening to direct subsequent microscopic observations.

The bread found in **US 422** of the **Lucone** site presents a rather coarse dough, based on minor cereals such as millet and foxtail millet (*Panicum miliaceum*/*Setaria italica*) of which fragments of caryopses are clearly visible on its surface. SEM analysis revealed the presence of starch granules and at least one other cereal, thanks to the identification of monostratified aleurone shreds (compatible with most cereals except barley). This is confirmed by the intense peaks of gluten, of which millet and foxtail millet are devoid, observed by FTIR-ATR. In addition, the insertion of bran is visible by SEM through the finding of cross cell fragments. Also peculiar to this find are the cells of brewer’s yeast, as well as numerous diatoms belonging to at least three taxa.

The composition of the dough of the sample found in **US 457** of the **Lucone** site is less defined. There are traces of cross cells (bran) and starch granules, the only clues that generally indicate the presence of cereals, without being able to better define them taxonomically. In addition to different types of diatoms, phytoliths and framboids are characteristic of this find. Phytoliths are difficult to relate to the species they belong to: in this particular case, one of them is attributed to the *Pinaceae* group. As for framboids, these are spherical aggregates of pyrite microcrystals constructed by anaerobic bacteria, which reduce sulphates to sulphides; the sulphides then react with the iron present in the aqueous environment, crystallising into cubes or icosahedra [92]. The image analysis revealed the presence of smaller pores compared to the sample from US 422, in which yeast had, in fact, been observed.

Only in the bread from **Cavriana** could an outer crust be observed, in which a glume fragment belonging to a dressed cereal, most likely einkorn (*Triticum* cf. *monococcum*), was inserted. The use of a type of wheat (*Triticum* sp.) is confirmed by SEM observation of shreds of a tissue in which the transverse cells show their typical punctuation. The presence of barley (*Hordeum vulgare* L.) is evidenced by the spongy parenchyma typical of this species. The FTIR-ATR spectrum of Cavriana bread does not show particularly intense and recognizable peaks, except for weak carbonate signals, perhaps milling residues. Diatoms and phytoliths are also present in the dough of this bread. Of all the samples analysed, this is the one that shows the largest pores and, given also its thickness and the presence of an observable crust, can be identified as a leavened bread.

The sample from **Lazise** contains einkorn (*Triticum monococcum* L.), as evidenced by the finding of a spikelet base attributed to this species, and barley (*Hordeum vulgare* L.), recognised by SEM detection of the typical multi-layered aleurone. The numerous sharp-edged fragments of broken caryopses, visible under the optical microscope, could suggest a process of grain fragmentation and roasting, which allowed these fragments to retain their shape. Phytoliths, cross cell shreds (bran) and ‘fresh’ looking starch granules were also observed in the SEM. These last ones were in excellent condition in the cells of the amyliferous parenchyma, possibly compatible with a low-temperature cooking process. Signals of starch, although weak, are also detectable in the FTIR-ATR spectrum, along with those of calcite, a probable milling residue. The pores present a distribution thar is similar to that of the Cavriana bread, although the Lazise sample has a lower thickness, making it classifiable as ‘flat bread’.

It was not possible to determine whether the crumbs from **Castelletto Ticino** refer to some sort of bread or other food preparation. SEM analysis was rather difficult, allowing the identification of only a few phytoliths and a very small portion of aleurone, which could not be better identified. The FTIR-ATR technique showed, in addition to residual silicates, starch and, most likely, gluten, confirming that the analysed finding is cereal-based, excluding millet and foxtail millet. However, further evidence about the presence of aleurone comes from optical microscope observation, which shows it monostratified. Image analysis also indicates the presence of very small pores, all smaller than 0.6 mm.

In the **Angera** sample, a collapsed and fused aleurone and frequent bran fragments are observed by SEM analysis. These fragments consist of cross cells showing the punctate walls typical of the genus *Triticum*. In the FTIR-ATR spectrum, the starch signals are very weak, and the image analysis can identify a very low number of pores.

In the **Mariano Comense** sample, remnants of cross cells tissue are very abundant. In this case too, the cross cells show the typical punctuation of the genus *Triticum*. The presence of bran is indicated not only by SEM, but also by the lignin-related signals highlighted by FTIR-ATR analysis together with those pertaining to starch and silicates, in particular quartz.

SEM analysis of the **Monte Barro** sample shows tubular cells, adhering to monostratified aleurone, and bimodal starch. The evident presence of numerous protein filaments suggests the hypothesis that the dough was exposed to the fire that destroyed the site, preventing it from being cooked. FTIR-ATR examination reveals weak starch peaks, which are not exhaustive for a better understanding of the composition of this sample; however, the similarity of the spectrum of this finding with those of the Angera and Mariano Comense samples is noted. The pore size distribution is very similar to that of the Mariano Comense sample, with a slight prevalence of larger pores in the Roman sample.

6. Conclusions

The use of optical and scanning electron microscopy for the detection of plant tissue remains in bread or bread-like samples has proved effective. FTIR-ATR analysis, which has never been applied to archaeological samples of this type without any pre-treatment, confirmed and extended the results obtained from microscopic investigations. The possibility of using FTIR-ATR analysis as preliminary screening also emerged. This applies in particular in the case of samples so small that they are not immediately identifiable as bread or similar products (as in the case of the 'crumbs' from Castelletto Ticino). In particular, the most interesting information obtained from infrared spectroscopy concerned the possible content of gluten, a component that excludes the presence of minor cereals in favour of other cereal species, and of mineral residues due to milling. The results obtained by this technique alone are certainly not exhaustive, but its speed of execution and the possibility of combining it with other analytical techniques make it useful for extracting maximum information even from archaeological samples from which it is not possible to take large portions, e.g. because they are destined for later musealisation. As also demonstrated in another paper we recently published, this could become a routine methodology for the characterisation of this type of artefact [13].

According to the results obtained, prehistoric bread production in areas that are geographically quite close appears to be on average heterogeneous in terms of the ingredients used. In fact, the investigation of Bronze Age bread remains found in some pile-dwelling sites located in the Garda morainic amphitheatre shows einkorn and barley at Cavriana and Lazise, millet/foxtail millet and another cereal containing gluten, but not identified, in sample US 422 from Lucone. The sample found in US 457 in the site of Lucone did not allow us to recognize any species in the dough, which appears to have been altered by the water used in its preparation and, perhaps, by its conservation in a humid environment, as evidenced by the presence of numerous diatoms and many framboids. Diatoms are also contained in the sample from US 422 and in that from Cavriana.

The four findings from the Bronze Age and the only one from the Iron Age (Castelletto Ticino) contain a large number of phytoliths, testifying to poorly refined flour doughs. As for the phytoliths, most likely to be attributed to cereals contained in the doughs, it is very difficult to precisely code them and assign them to the plant species they belong to or the part of the plant in which they were originally contained. The difficulty is aggravated by the fact that they are reduced to fragments and no longer placed in the tissues in which they were originally found.

Regarding bread consumption in settlements, we must distinguish between the group of prehistoric carbonized breads, preserved in a humid environment, and an early medieval bread, preserved thanks to the fire that caused the destruction of the site where the bread was discovered. The first ones, Lucone, Cavriana and Lazise, allow some considerations about the water used for their preparation, an unpurified water as evidenced by the finding of some types of diatoms and framboids, most likely derived from the small lakes where the piles were located. In contrast, the sample found at the Monte Barro site (Early Middle Age), made of unidentifiable cereals, shows a refined dough, totally devoid of phytoliths and bran; it is a bread intended for individuals of high social class, given its discovery in the Great Building. Moreover, the protein filaments in which the dough is rich would attest to its combustion during the burning of the site and its failure to bake before the fire itself.

Other considerations are possible with regard to breads or similar foods constituting funeral offerings burnt in the fire of funeral pyres: the evidence in this study concerns the Iron Age (Castelletto Ticino) and the Roman Age (Angera and Mariano Comense) but, as anticipated, some traces are also known from the Bronze Age (necropolis of Morano sul Po, Alessandria). As for the 'crumbs' from Castelletto Ticino, found in some graves even in the order of a few hundred, they are perhaps referable to a kind of gruel/flat bread of very modest thickness (as evidenced also by the small size of its pores, detected by image analysis). In the case of Angera and Mariano Comense, they are instead portions of loaves. Both reveal a greater care in the use of water, they are free of diatoms and framboids and, since they are also free of phytoliths, they would appear to be made from a rather purified, wheat-based flour (*Triticum* sp.). However, both contain bran: the Angera bread in modest quantities, the Mariano Comense bread in considerable quantities, a fact that seems to contrast with the high class of the deceased for whom it was intended. We have no information to know whether these were special breads intended for the funeral ritual or whether they were common breads.

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Supplementary materials

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