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A New Filtered Alcoholic Beverage: Residues Evidence From the Qingtai Site (*ca*. 5,500–4,750 cal. BP) in Henan Province, Central China

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Recent studies have provided evidence of alcohol production and consumption in 16 sites in northern China during the Neolithic period, focusing on the Yangshao Culture (*ca*. 7,000–5,000 cal. BP). Yet, the comparison of similarities and differences in brewing technology and drinking patterns within the Yangshao Culture still needs more supporting information from case studies in different regions. In this paper, 17 pottery samples excavated from the Yangshao Culture site of Qingtai (*ca*. 5,500–4,750 cal. BP) in the central part of Henan Province were analyzed for microfossils (starch grains, phytoliths, fungi) and organic acids, on the basis of the theoretical model constructed from our simulation experiments. The results revealed a mixed filtered alcoholic beverage, likely to be fermented by fruit and/or honey. The ingredients were mainly foxtail millet, rice, Job's tears, Triticeae, snake gourd roots, lotus roots, legumes, nuts, fruits, and/or honey. What's more, we found that the *jiandiping* amphora from Qingtai was not likely used for brewing or drinking. In terms of prehistoric drinking habits, in the large-scale settlement of the late Yangshao Culture in China, it is possible that people drank filtered alcohol alone or that a few people drank filtered alcohol poured from the painted bottle, indicating a switch from communal drinking to individual drinking. This study sheds light on the similarities and differences in brewing techniques, fermentation ingredients, and drinking patterns among different regions of the late Neolithic Yangshao Culture, and deepens our understanding of alcoholic beverages in the early Chinese civilized societies.

Keywords: prehistoric alcoholic beverages, qingtai site, yangshao culture, microfossil and organic acid analyses, brewing technology, drinking pattern

1 INTRODUCTION

Alcoholic beverages have always been given special status because of their miraculous medical, religious, social, and political value (McGovern et al., 2004). With the prevalence of religious ceremonies and feasting activities, as well as the expansion of the population and the progress of agriculture, the production and consumption of alcoholic beverages became more and more common in the Neolithic period (Hayden, 2003; Liu, 2021a). Since the late Neolithic period,

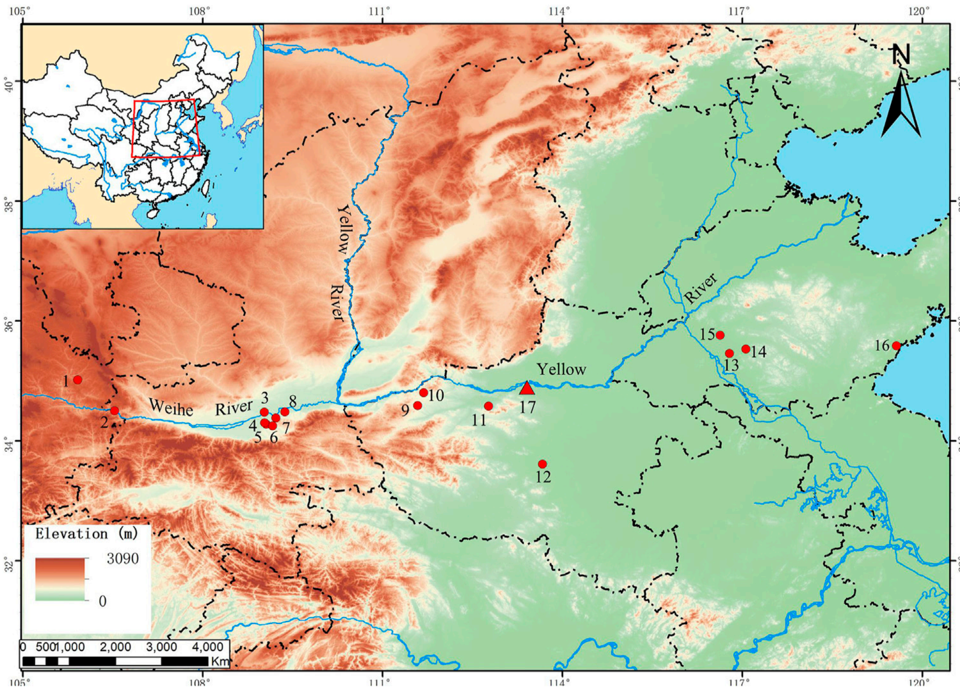

FIGURE 1 | Location of the Qingtai site and other related archaeological sites in north China. 1) Dadiwan; 2) Guantaoyuan; 3) Yangguanzhai; 4) Mijiaya; 5) Banpo; 6) Xinjie; 7) Jiangzhai; 8) Lingkou; 9) Xipo; 10) Dingcun; 11) Huizui; 12) Jiahu; 13) Wangyin; 14) Xixiahou; 15) Dongjiabai; 16) Liangchengzhen; 17) Qingtai.

China gradually entered an early civilized society, and the ritual system was about to emerge (Wang, 2008; Gao, 2019; Wang, 2020). At that time, although the pottery vessels associated with alcohol had not completely lost their practical function, some were in the transformation stage into special ritual vessels (Xu, 2004). In the historical period, alcohol became an important part of the ritual system, laying the foundation of Chinese ritual and music civilization (Huang, 2002; Huang, 2008). Therefore, as a unique carrier of civilization, the evolution of alcoholic beverages, to a certain extent, reflected the origin of Chinese civilization and the process of social complexity.

Recently, considerable archaeological evidence about prehistoric alcohol brewing in China has been reported based on the chemical and microfossil (starches, phytoliths, and fungi) analyses on pottery vessels, almost spanning the entire Neolithic period (**Figure 1**; McGovern et al., 2004; Wang et al., 2016; Liu et al., 2017a; Liu et al., 2018a; Liu et al., 2019a; Liu et al., 2019b; Liu et al., 2020a; Liu et al., 2020b; Liu et al., 2020c; Liu et al., 2020d; Feng et al., 2021; Zhao and Liu, 2021; Liu et al., 2021b). In the early Neolithic of central China, the analyses of residues from Jiahu, Guantaoyuan, and Lingkou sites have shown that globular jars were used to make cereal-based fermented beverages, and two brewing methods, including the use of malted cereal and *qu* starter, had already been developed and used throughout the Neolithic period (McGovern et al., 2004; Liu et al., 2019b; Liu, 2021a). By the middle and late Neolithic, several archaeological studies proved that the brewing and drinking vessels in the Yangshao Culture had evolved from globular jars to flat-based jars (pingdiqi), then to conical-based jars (*jiandiping*) in the Weihe River valley and the western Henan, central China (Wang et al., 2016; Liu et al., 2017a; Liu et al., 2018a; Liu et al., 2019a; Liu et al., 2020a; Liu et al., 2020b; Liu et al., 2020c), while in Beixin culture in eastern China, the globular jars were still be used (Liu et al., 2020d). During the late and end Neolithic period, various pottery, including goblets and cups, were related to alcohol drinking in the Haidai region, eastern China (McGovern et al., 2005; Liu et al., 2021b). These two types of fermentation and drinking patterns in central and eastern China reflected different development trends of alcoholic culture. However, the brewing materials in the above sites were similar, containing a mixture of cereals (foxtail millet, common millet, Job's tears, rice, Triticeae), roots, tubers, nuts, and honey or fruits. Comparing Paleoethnobotanical research of these sites, it has been proved that the fermentation ingredients were the same as daily food (Liu, 2021a).

Previous studies have made significant achievements on regional variation in fermentation techniques, drinking rituals, and socio-political developments in northern China during the Neolithic period, with a focus on the Yangshao Culture. In the middle and late stages of Yangshao Culture, the central Henan region became the most representative and influential political center, and the large-scale regional center settlements such as Qingtai, Shuanghuaishu, and Xishan sites entered the early civilized society (Han, 2019; Wang, 2020; Wei, 2021). However, the alcoholic culture in this core region is still unclear. What's more, most of the published data were on the results of microfossil residues analysis or only conducted chemical analysis; only a few studies combined both two approaches for experiments. To obtain more information on brewing materials and techniques, it is necessary to employ multi-disciplinary research.

FIGURE 2 | Pottery samples from the Qingtai site (scale bar: 5 cm). S1, *Jiandipng*; S2, *jiandipng*; S3, funnel (a hole in the bottom); S4, lip; S5, jar; S6, jar; S7, jar; S8, jar; S9, *jiandipng*; S10, *jiandiping*; S11, jar; S12, cup; S13, *jiandipng*; S14, *jiandipng*; S15, lip; S16, *jiandipng*; S17, painted bottle.

Thus, microfossils and chemical analyses of the pottery unearthed from the Qingtai site in central Henan were conducted in this study. The aim of this paper is to provide more evidence for a better understanding of the production and consumption of alcoholic beverages in the early civilized societies at the core region of the Late Neolithic period, as well as the similarities and differences in brewing technology and drinking patterns among different regions within the Yangshao Culture.

2 MATERIALS AND METHODS

2.1 Materials

The Qingtai site is located on the mound of Qingtai Village, Xingyang City, Henan Province, central China (**Figure 1**). In 1981, Zhengzhou Municipal Museum and Xingyang County Cultural Center excavated the Qingtai site, and ^{14}C dates placed the time period between *ca.* 5,500–4,750 cal. BP, a large-scale settlement site in the political hinterland of the late Yangshao culture (Zhang and Zhao, 1987). In 2015, to explore the origin of Chinese silk, the Zhengzhou Municipal Institute of Cultural Relics and Archaeology conducted a systematic investigation, exploration, and excavation at this site again (Fang, 2018). The excavation uncovered significant relics, such as three-fold ring trenches, adobe houses, tombs, and astronomical sacrifice areas, representing the emergence of civilization in central China. In addition, *jiandiping*, jars, cups, and funnels, suspected to be related to alcoholic beverages, were also discovered. It was worth noting that a painted bottle was found in a tomb with niches, which was also the only complete painted pottery unearthed from Qingtai during this excavation period.

In this study, we selected 17 pottery samples from the Qingtai site for starches, phytoliths, fungi, and organic acids analyses, including seven *jiandiping* amphorae, one funnel, two lids, five flat-based jars, one cup, and one painted bottle (**Figure 2**).

2.2 Methods

Residue sampling of the pottery was completed in the field laboratory at the Qingtai site. First, each surface of the sample was washed separately with distilled water. Then, an ultrasonic tooth cleaner was used to clean the pottery inside; the ultrasonic water samples were then transferred to the 50 ml centrifugal tube as the experimental samples. To test potential contamination, we also collected the control samples by gathering dust on shelves in the field laboratory and soil on each pottery surface. Further extraction was conducted at the Bio-archaeology laboratory, University of Science and Technology of China.

2.1.1 Extraction of Starches, Phytoliths, and Fungi

The liquid samples were treated with 5% $(NaPO_3)_6$, 10% HCl, and 30% H_2O_2 to disperse carbonates and minerals. After that, two kinds of heavy liquid (CsCl at a specific gravity of 1.89 and $ZnBr_2$ at a specific gravity of 2.35) were used for the centrifuge procedure, the former to extract starch grains and fungi, and the latter to extract phytoliths. In addition, to prevent contamination from the experimental environment, instruments, or reagents, a blank control sample was also set up and treated using the same protocol. Extractions obtained from residue samples were examined under the Leica DM4500P polarizing microscope. Starch and phytolith identifications were based on published studies (Madella et al., 2005; Wei et al., 2008; Lu et al., 2009; Yang et al., 2009; Ge et al., 2010; Yang et al., 2010;

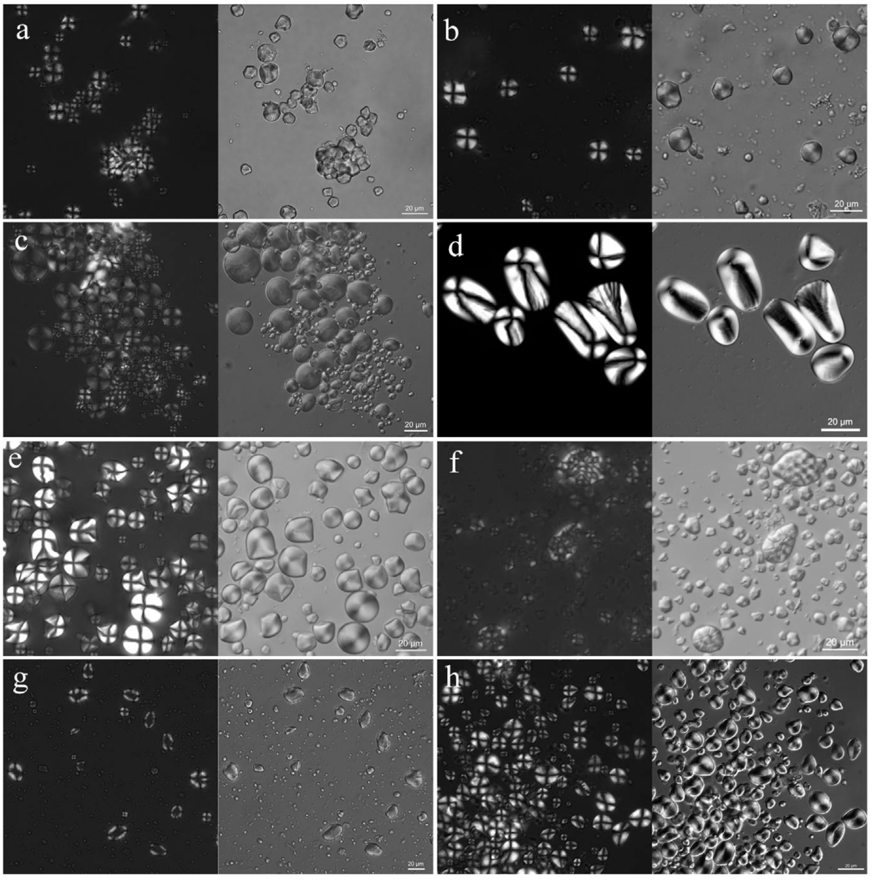

FIGURE 3 | Examples of starch grains morphology from the modern reference (scale bar: 20 μm). **(A)**: *Setaria italica*; **(B)**: *Coix lacryma-jobi;* **(C)**: Wheat; **(D)**: *Nelumbo nucifera*; **(E)**: *Trichosanthes kirilowii;* **(F)**: *Oryza sativa*; **(G)**: Leguminosae; **(H)**: *Quercus* sp.

Wan et al., 2011; Wang et al., 2013; Yang and Perry, 2013; Neumann et al., 2019; Henry, 2020) and our lab modern reference collection of common plant species (**Figure 3**). Fungi identification was based on the published book (St-Germain and Summerbell, 2011).

2.1.2 Extraction of Organic Acid

First, all the samples were centrifuged at 3,000 r/min for 15 min, then transferred to new 15 ml centrifuge tubes. Subsequently, samples were filtered by 0.45 μm microfiltration membrane to 5 ml sample bottles. Next, a vacuum centrifugal concentrator was used to centrifuge at 1,000 r/min and concentrate to 100 μl at 55°C. Finally, the samples were sent to the Center for Science and Chemical Science Experiments of the University of Science and Technology of China for liquid chromatography-mass spectrometry (LC-MS) testing.

2.1.3 Simulation Experiments of Brewing

Previous simulation experiments have proved that starch grains can be damaged by saccharification and fermentation, so the evidence of alcohol residues would be found by observing the morphology of starch grains (Henry et al., 2009; Wang et al., 2017). This discovery has been applied to the analysis of the archaeological context in recent years, and experimental evidence for the brewing of *qu* wine, malted wine, and *koujiao* wine has been reported in 14 prehistoric sites in China (Liu, 2021a). To further understand the fermentation technology, scholars have established an analysis method: based on the residues of microbotanical and microbial remains to determine the brewing function and methods (Liu et al., 2019b; Liu et al., 2020a; Liu et al., 2020b; Liu et al., 2020d; Liu et al., 2021b; Feng et al., 2021; Zhao and Liu, 2021). However, this method has not been demonstrated by simulation experiments.

Therefore, a simulation experiment was designed to verify the different combinations of microfossils in three kinds of alcohol residues. Six common grain alcohol ingredients, including rice, foxtail millet, wheat, yam, lotus root, and mung bean, were selected and brewed into malted alcohol, *qu* alcohol, and *koujiao* alcohol separately under the same experimental conditions in our laboratory. Given the turbid state of the fermented liquor, the fermentation samples were divided into filtered and unfiltered residues to observe starch grains, phytoliths, and fungi under a microscope, respectively.

The results showed that starch grains do unique damage during saccharification and fermentation (**Figure 4**). However, different brewing methods have similar damage to the same kind

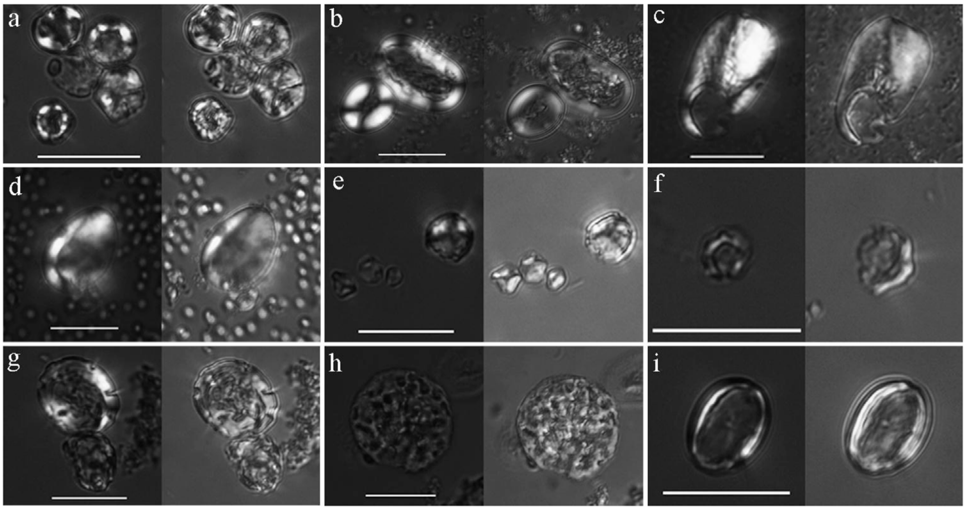

FIGURE 4 | Damaged starch grains in the three alcohol (scale bar: 20 μm). **(A)** foxtail millet in *koujiao* alcohol; **(B)** mung bean in *qu* alcohol; **(C)** lotus root in *qu* alcohol; **(D)** yam in *koujiao* alcohol; **(E,F)** rice in malted alcohol; **(G–I)** wheat in malted alcohol.

of starch grains, making it difficult to distinguish brewing methods by the different morphological changes of starch grains. Large amounts of husk phytoliths were found in all unfiltered malted and *qu* alcohol, small amounts were found in some unfiltered *koujiao* liquors, and none or minute amounts were found in all filtered *qu* alcohol, malted alcohol, and *koujiao* alcohol. The results indicated that the presence of husk phytoliths remains is not only related to the brewing method but also the filtration behavior. Fungi are present in all filtered and unfiltered liquor after fermentation. In sum, the microbotanical and microbial remains can be used as a basis for judging whether pottery was exposed to alcohol; however, it is hard to accurately speculate on the brewing method.

3 RESULTS

Among the 17 experiment samples of pottery, 218 starch grains were extracted from the painted bottle S17, the funnel S3, and the lid S4. No starch grain was found in all the control samples, and only one starch grain was yielded from the unused surface of the jar S8. As the amounts of starch grains from the experiment samples were much higher than the control samples and unused surfaces, we believe that starch grains recovered from the three potteries are associated with human behavior in processing foods. Therefore, this study focused on these three pottery pieces in statistical analysis. Among them, organic acids were also detected in these three pottery pieces, but not fungal remains. In addition, 32 phytoliths were only found on the funnel.

3.1 Starch Remains

Among the 218 starch grains, 19 starch grains could not be identified due to the damage or lack of typical characteristics. The remaining 199 starch grains were classified into nine broad categories based on their morphology and size (**Table 1**; **Figure 5**).

Type A: starch grains (n = 48, 8.72–20.41 μm) are mostly faceted, hilum is centric with a "−" or "+" or "Y" or star-shaped fissures, some parts of starch have depressions (**Figure 5A**). The extinction arms are crossed and vertical under polarizing light, and lamellae are invisible. This type of starch grains is mostly from Panicoideae plants (Ge et al., 2010; Yang et al., 2010), such as foxtail millet (*Setaria italica*), common millet (*Panicum miliaceum*), as well as Job's tears (*Coix lacryma-jobi*). However, the size of a common millet is relatively small, while the size of Job's tears is relatively large, and the end of the extinction arm of Job's tears starch grains is mostly similar to a "Z" shaped curve. The size range and morphological structure of this type of starch granules are consistent with those of foxtail millet, so it is identified as *Setaria italica*.

Type B: starch grains (n = 27, 12.18–26.03 μm) are polygonal and nearly circular. Its characterized by a centric hilum, linear fissures, and invisible lamellae. The extinction arms are crossed and vertical under polarizing light, and the end of the extinction arms presents a "Z" shaped curve (**Figure 5B**). In modern plants, the starch grains of Panicoideae plants generally have a polyhedral structure, and the extinction arms cross vertically. According to our lab modern sample database (**Figure 3B**), the size of foxtail millet and common millet starch grains are relatively small, and the end of the cross-extinction arm of Job's tears has a unique "Z" shaped curve (Ge et al., 2010). Thus, type B starch granules come from *Coix lacryma-jobi*.

Type C: starch grains (n = 92, 5.37–39.65 μm) are nearly round or convex lens-shaped, the hilum is centric and closed, the extinction arm is "Z" shaped; if turning over the starch after tapping the glass slide, a long "—" shaped fissure appeared. This type can observe two kinds of starch grains of different sizes. The larger starch grains (11.23–39.65 μm) have clear lamellae (**Figure 5C**), while the smaller ones (5.37–9.4 μm) are not obvious. Combined with related (Yang and Perry, 2013) research on the morphology of ancient and modern starch grains in Triticeae. We judged that this kind of starch grains come from the Triticeae plants.

TABLE 1 | Starches from the Qingtai site.

Sample no	Artifact no	Name of pottery	Type A	Type B	Type C	Type D	Type E	Type F	Type G	Type H	Type I	Unknown	Total	Brewing damage
S3	H183②	funnel	28	9	27	5	8	1		1	5	16	100	37
S4	H183②	lip			1	3						3	7	6
S17	M145①:2	Painted bottle	20	18	64	2	3	2	2				111	57
		Total	48	27	92	10	11	3	2	1	5	19	218	100

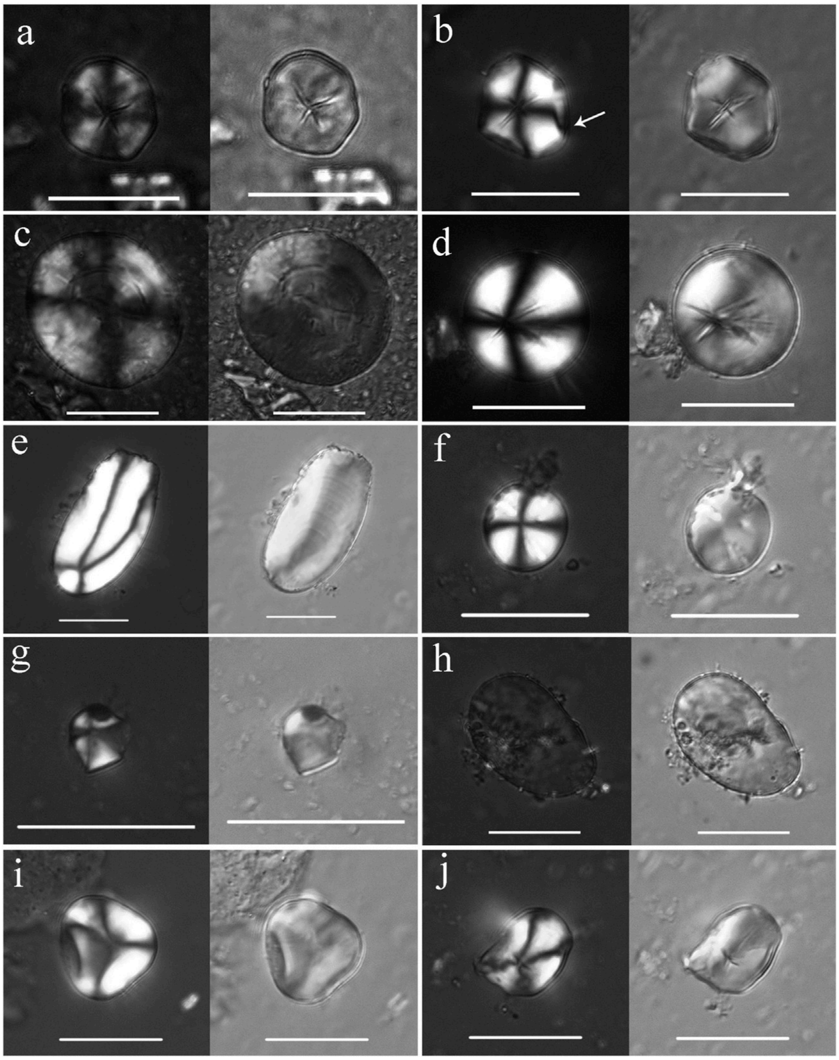

FIGURE 5 | Types of starch grains at the Qingtai site (scale bar: 20 μm). **(A)** *Setaria italica*; **(B)** *Coix lacryma-jobi*; **(C)** Triticeae; **(D,E)** *Nelumbo nucifera*; **(F)** *Trichosanthes kirilowii;* **(G)** *Oryza sativa*; **(H)** Leguminosae; **(I)** *Quercus* sp.; **(J)** tubers.

Type D: starch grains (n = 10, 11.46–47.24 μm) are the circle (**Figure 5D**) and long oval (**Figure 5E**), which have a large size distribution range. Short "-" shaped or "X" shaped fissures can be observed at the hilum, and the extinction arms under polarizing light are cross. The lamellae of this kind of starch grains gradually spread outward around the hilum is obvious, and the hilum of the long oval starch grains is eccentric. Comparing our laboratory's modern database (**Figure 3D**) and related analysis (Wan et al., 2011) of the starch grains in roots and tubers in modern southern China, this type of starch grains should come from lotus root (*Nelumbo nucifera*).

Type E: starch grains (n = 11, 17.35–23.18 μm) are round, semi-circular, and bell-shaped with a smooth surface and no fissure, the hilum is centric or eccentric, and the lamellae are invisible. Extinction arms are crossed vertically or curved under polarizing light (**Figure 5F**). Compared with the modern sample database of our laboratory (**Figure 3E**), the shape and length of this type of starch granules are similar to those of the root of snake gourd (*Trichosanthes kirilowii*), so this type of starch granule is identified as the *Trichosanthes kirilowii*.

Type F: starch grains (n = 3, 5.26–8.63 μm) are polyhedral structures, with the centric hilum and invisible lamellae and the cross-extinction arm is "X" shaped (**Figure 5G**). All these grains have small sizes of less than 10 μm, and most of them are closely arranged. Based on the morphological characteristics and the microscopic observation of starch grains of modern rice by Wei et al. (2008), we infer that Type F starch grains originate from rice (*Oryza sativa*).

Type G: starch grains (n = 2, 9.62–32.52 μm) are kidney-shaped and oval, and the hilum is invisible. One of them has a fissure through the long axis, and the other has no fissure (**Figure 5H**). According to our laboratory database and related study on legumes starch grains (Wang et al., 2013), this type of starch granules should come from Leguminosae.

Type H: starch grain (n = 1, 19.36 μm) is triangular oval, the hilum is closed and centric, the lamellae are invisible, and the cross-extinction arm is "X" shaped (**Figure 5I**). The starch grains of nut plants are mostly triangular oval and drop-shaped, such as *Castanea* sp. of the Fagaceae tribe and *Quercus* sp. However, the hilum of the *Castanea* sp. starch grains is mostly eccentric, and the *Castanea* sp. starch grains with a long axis greater than 10 μm can be observed with lamellae, while the *Quercus* sp. starch grains basically have no lamellae (Yang et al., 2009). Thus, these starch grains can be identified as *Quercus* sp.

Type I: starch grains (n = 5, 16.43–27.79 μm) are mainly oval-shaped, lamellae are unclear, cross-extinction arms are "X" shaped, hilum is eccentric, and the part of them have "-" shaped fissures (**Figure 5J**). According to the database of our laboratory, one of the typical characteristics of starch grains in roots and tubers is the eccentric hilum. These five starch grains extracted lacked further species characteristics and cannot be further distinguished, so this type can be classified as a roots or tubers plant.

Compared with the results of our simulation experiments, nearly half of the starches show signs of morphological alterations to some extent and were related to brewing behavior (n = 100, 45.9% of the total). These damage characteristics (n = 58) included small pits and cracks, missing edges, hazy extinction cross, and weakened birefringence which was the direct result of enzymatic hydrolysis of starch grains (**Figure 6A,B**). Simultaneously, there are also some other damage characteristics (n = 42) caused by fermentation and gelatinization, such as enlarged fissures radiating outward from the hilum, further expansion of the central depression, swelling, and melting (**Figure 6C–H**). Some starch grains only have the edge, and the central area almost disappears, forming a ring structure (**Figure 6G**). As the starch grains continue to decompose, the extinction cross arm gradually disappears until the crystal structure is lost (**Figure 6G,H**).

3.2 Phytolith Remains

Of the three pottery samples (S3, S4, S17) yielding brewing damaged starch grains, 32 phytoliths were found only on the funnel S3, and most of which were from Poaceae plants (**Table 2**). Two double-peak phytoliths (**Figure 7**: g) from rice husk and dumbbell with scooped ends paralleled arrangement (**Figure 7A**) phytoliths from rice stem or leaf were present, corresponding to the presence of rice starch grains on the funnel. One Ω-type phytolith (**Figure 7H**) of foxtail millet husks was also found, but no η-type phytolith typical or starch of common millet was recovered. Other Poaceae families include two fan-shaped (**Figure 7E**), three cross (**Figure 7F**), 14 bilobate (**Figure 7D**), and two square saddle (**Figure 7B**) phytoliths, also found under the microscope. Further, hair cells (n = 1, **Figure 7C**) were found, mainly in the stem or leaf of eudicots.

3.3 Organic Acid Remains

Through the LC-MS analysis, 11 kinds of organic acids, including lactic acid, acetic acid, amber acid, fumaric acid, propanoic acid, butyric acid, citric acid, 3-hydroxybutyric acid, malic acid, pyruvic acid, and oxalic acid were detected from the funnel, lid, and painted bottle (The metrical data for organic acids remains is listed in **Supplementary Table S1**). Among them, eight kinds of organic acids were found in the funnel except for citric acid, 3-hydroxybutyric acid, and malic acid. Eight kinds of organic acids were found in the lid except for lactic acid, fumaric acid, and malic acid. Nine kinds of organic acids were found in the pottery bottle except for pyruvic acid and oxalic acid.

4 DISCUSSION

As mentioned in the previous article, some scholars believed that the combination of microbotanical and microbial can determine the fermentation methods based on experimental research and experience in the analysis of archaeological materials (Wang et al., 2017; Liu et al., 2019b; Liu et al., 2020a; Liu et al., 2020b; Liu et al., 2020d; Liu et al., 2021b; Feng et al., 2021; Zhao and Liu, 2021): 1) In the case of malted alcohol, the husk of the cereals and the starch grains with fermentation characteristics (saccharification and gelatinization) might be preserved on the brewer. 2) If it is *qu* alcohol, fungi related to *qu* and starch grains with fermentation characteristics might be detected by microscopy. 3) The production of *koujiao* alcohol does not require the malted grains or *qu*, so the residue might mainly contain starch grains with fermentation characteristics. Our simulation results revealed that these data need to be interpreted with caution, as husk phytolith residues are also associated with filtration behavior.

4.1 Fermentation Methods and Ingredients

Among the 17 pottery samples selected from the Qingtai site, three pottery samples (funnel, lid, and painted bottle) with brewing damaged starch demonstrated that they were used as alcoholic vessels. The brewing materials at Qingtai included foxtail millet, rice, Triticeae, Job's tear, legumes, lotus root, and Quercus, which correspond to the daily food sources as

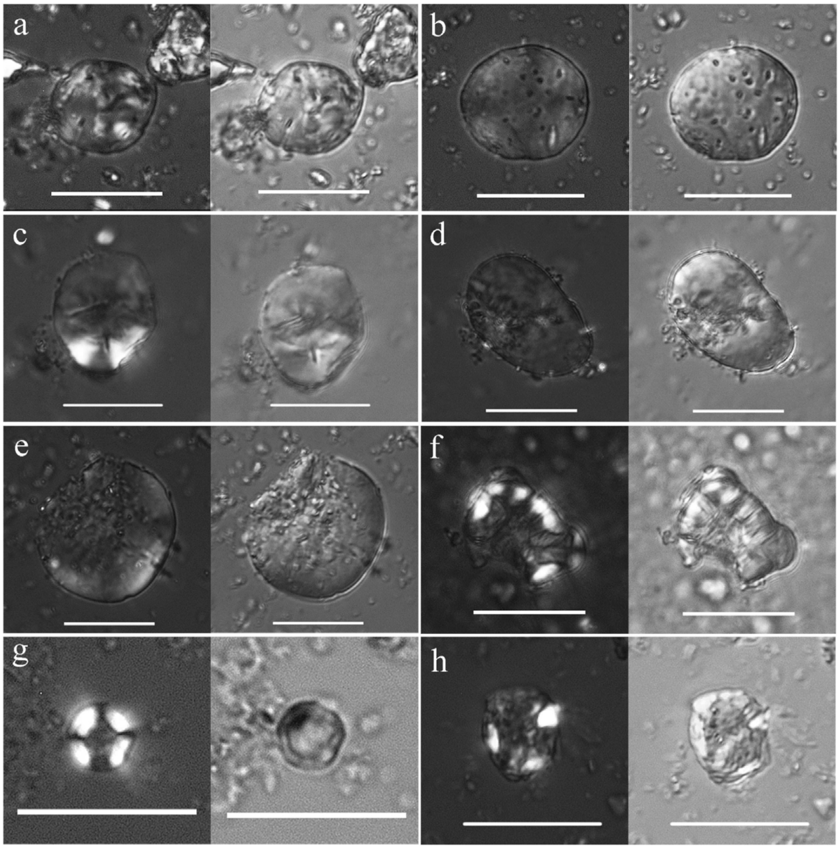

FIGURE 6 | Damaged starch grains from the Qingtai site (scale bar: 20 μm). **(A,B)**: showing small pits and cracks, hazy extinction cross; **(C)**: showing swelling, melting, and hazy extinction cross; **(D)**: showing pits, melting, and hazy extinction cross; **(E)**: showing missing edges; **(F–H)**: showing central depression and swelling.

TABLE 2 | Phytoliths from the Qingtai site funnel.

Phytolith morphotype	Taxonomic attribution	funnel
Scooped ends paralleled arrangement	Oryza stem/leaf	1
Double-peak	Oryza husk	2
Square saddle	Poaceae	2
Silicified cells		6
Hair cells		1
Fan-shaped	Poaceae	2
Cross	Poaceae	3
Bilobate	Poaceae	14
Ω-type	Foxtail millet husk	1
Total		32

indicated by the microbotanical remains from Qingtai (Sun, 2018). This phenomenon also accords with the selection of fermentation ingredients in other Yangshao sites (Liu, 2021a).

The types of starch grains and phytoliths extracted from the funnel, lip, and painted bottle can match each other. The species of starch grains were mainly foxtail millet (22.02% of the total) and Triticeae (42.20% of the total). Correspondingly, Ω-type phytoliths from foxtail millet husks were found, and the total number of Poaceae phytoliths accounted for the highest proportion, up to 62.50%. Besides, small amounts of starch grain (n = 3) and phytoliths (n = 3) of rice were present. Although husk phytoliths were found in the funnel, it is hard to define whether the sprouting or chewing, or *qu* method was used, because simulation experiments showed that the husk phytoliths existed in these three saccharification methods of alcohol. What is surprising is that no fungi remain was seen in any of the three alcoholic vessels. This result is likely attributable to the preservation environment of the microorganisms. Studies have shown that the perishable nature of fungi makes it more difficult to preserve archaeological records than other plant or animal remains (Dugan, 2008; Berihuete-Azorin et al., 2018).

From the result of LC-MS analysis, four common alcoholic organic acids, including lactic acid, acetic acid, amber acid, and fumaric acid (Li, 2017; Coelho et al., 2018) were found in three pottery. Lactic acid and fumaric acid are produced by the fermentation of sugar contained in starchy raw materials such as rice and wheat owing to the action of lactic acid bacteria (Hao et al., 2021). Acetic acid is commonly found in various types of alcohol, and it is converted from different organic matters by *Acetobacter* through fermentation (Barata et al., 2012). Lactic acid is the most common organic acid in grain wine, followed by amber acid (Zhao et al., 2020). These results are consistent with data obtained in starch grains and phytoliths analyses, suggesting

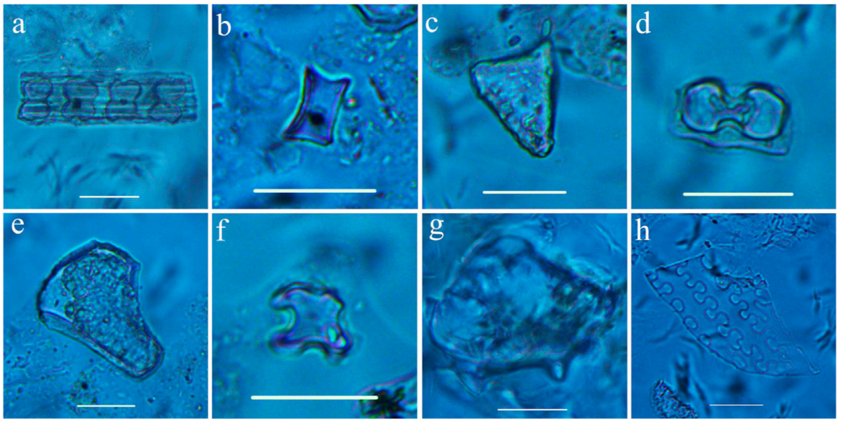

FIGURE 7 | Phytoliths from the Qingtai site (scale bar: 20 μm). **(A)**: dumbbell with scooped ends paralleled arrangement; **(B)**: square saddle; **(C)**: hair cell; **(D)**: bilobate; **(E)**: fan-shape; **(F)**: cross; **(G)**: double-peak; **(H)**: Ω-type.

the three potteries were related to the cereal-based beverages. However lactic acid and amber acid are also present in fruit and honey wines (He, 2017; Zeng et al., 2018). Meanwhile, malic acid, citric acid, oxalic acid, and pyruvic acid are the main organic acids in fruit and honey wine; citric acid is also commonly found in honey wine (He, 2017; Li, 2017; Zeng et al., 2018). The macro-botanical remains of fruit such as jujube, grape, and hawthorn were recovered from the Qingtai site (data from Miaomiao Yang's result, unpublished). Due to the absence of tartaric acid, which is the strongest biomarker of grape wine (Cheng et al., 2013), the addition of grapes might be ruled out. As the surfaces of fruits and honey contain yeast which can convert sugars to ethanol and carbon dioxide (McGovern et al., 2005), it can be seen that the Qingtai people were likely to add fruits and/or honey as fermentation agents.

Based on multiple lines of evidence in the current data, the wine from Qingtai was likely a mixed alcoholic beverage made of various cereals as main ingredients, fruit and/or honey as a starter, as well as supplemented by roots, tubers, beans, and nuts.

4.2 Brewing Vessels

First, phytoliths were detected only on the funnel among the three wine vessels of the Qingtai site. Our simulation experiments show that filtration will affect the amount of phytoliths residues in wine. Given that silk relics have been unearthed from the Qingtai site, it is believable that people at the site were able to separate the dregs from the wine (Zhang and Gao, 1999). Combining the shapes of the three vessels, the combination of residues, and the brewing simulation experiment results, we speculated that the unhulled cereals were indeed used in the production of alcoholic beverages, and then the funnel was used to filter the dregs. Therefore, starch grains, phytoliths of husk, stems, and leaves, as well as organic acids were left on the surface of the funnel. The painted bottle was likely used to store filtered alcohol, so no phytolith was found in it. Because the sample size of the lid residue was too tiny to make a clear judgment, it might be covered on the wine storage container to prevent the evaporation of alcohol. What's more, three pottery strainers were unearthed from the layers of the late Yangshao Culture in Dahecun, Huizui, and Yangshaocun sites in central and western Henan, and alcohol residues were found on one of the strainers (Liu et al., 2019a). It can be said that the filtering behavior had appeared in the political center of late Yangshao Culture, which represents the progress of brewing technology and people's higher pursuit for the taste of alcoholic beverages.

Second, throughout the Yangshao period, the shape of fermentation and storage vessels gradually evolved from globular jars to *pingdiqi*, then to *jiandiping* and vats (Liu, 2021a; Feng et al., 2021). In our experiment, it is a remarkable fact that no starch grain was observed in seven *jiandiping* and five flat-based jars collected at the Qingtai site, suggesting that the functions of these vessels were probably not related to alcoholic beverages. The existing statistics data show that the Yangshao sites where *jiandiping* and *pingdiqi* were used as wine vessels were distributed in the Weihe River valley (**Figure 1**: Lingkou, Jiangzhai, Banpo, Yangguanzhai, Mijiaya, Xinjie) and the western Henan (**Figure 1**: Dingcun), so the findings at the Qingtai site might have reflected the inconsistency among different regions. In addition, no alcohol residue was found in 10 *jiandiping* or flat-based jars collected from the Shuanghuaishu site in central Henan (mid-late Yangshao Culture), but alcohol residues were detected in one *jiandiping* and one vat from Chengyan site in western Henan (early Yangshao Culture) base on residue analysis of other sites in our laboratory (data from Jingwen Liao's master thesis, unpublished). These data further confirmed that the fermentation vessels in Yangshao Culture were probably not a single linear evolutionary model, but a more complex multi-mode between different regions and stages.

4.3 Drinking Patterns

Yangshao Culture is famous for its painted images. This 36 cm-high painted bottle was painted with black patterns of zigzag, octagonal, and circular electric fans on its surface. The leader of the Qingtai excavation team believed the images were symbolic of the Sun and reproductive worship, and partly reflected the religious beliefs (Gu, 2018). Speculated that the geometric patterns on the Yangshao amphorae were likely to be the earliest symbol of alcoholic beverages in prehistoric China, which expressed a functional significance Liu (2021a). Whether as a religious or functional expression, such an exquisite wine vessel was a funerary object and carefully buried in a niche (the only niche in the Qingtai), highlighting the significance of alcoholic beverages in the late Neolithic.

Previous studies have pointed out that the drinking patterns in the Yangshao Culture were likely to communal siphoning drinking with group dancing (Liu, 2017b; Liu et al., 2018b; Liu et al., 2020a; Liu et al., 2020c). In the early Yangshao period, this kind of communal feast was mainly to maintain community solidarity. While in the late period, it was the competitive feasting for gaining and maintaining personal status (Feng et al., 2021). However, the phenomenon of siphoning drinking has not been observed in Qingtai. Funnel for filtering and small painted bottle for storage from Qingtai indicated a new way of drinking pattern, which might have evolved from communal siphoning drinking to drinking alone, or a few people using cups to drink the clear liquid poured from the bottle. Although no evidence of wine cups was found in this study, which may be related to the small sample size, scientific evidence has been provided for the use of wine cups at the Shuanghuaishu, the same period and area site as the Qingtai site (data from Jingwen Liao's master thesis, unpublished). In general, the appearance of these new wine vessel types reflected the changes in drinking methods of prehistoric humans in the early civilized society of the late Yangshao culture. But it is unclear whether this change in drinking patterns implied a new form of social organization in the late Neolithic period.

5 CONCLUSION

This paper provides a scientific case study of the production and consumption of alcoholic beverages in the early civilized Chinese society by analyzing microfossils and organic acids on 17 pieces of late Neolithic pottery from the Qingtai site. Multiple shreds of evidence suggest that the painted bottle, funnel, and lid at the Qingtai site, a large-scale settlement of the late Yangshao culture, were associated with brewing and serving mixed filtered alcohol beverages, which were probably fermented by fruits and/or honey. The ingredients were mainly foxtail millet, rice, Job's tears, Triticeae, snake gourd root, lotus root, legumes, nuts, fruits, and/or honey. What's more, this research has also shown that the *jiandiping* amphora or flat-based jars at the Qingtai site were probably not used for brewing or drinking. Another major finding is that people in Qingtai preferred to drink filtered alcohol alone, or a few people drink the filtered alcohol poured from the painted bottle.

As a pilot study, our simulation experiments propose a more cautious model for the interpretation of alcohol residues, and offer the first comprehensive archaeobotanical and organic chemical analyses of Chinese prehistoric alcoholic vessels, highlighting the regional differences in the Yangshao Culture alcoholic vessels, brewing techniques, and drinking patterns. Unfortunately, although a variety of artifacts potentially associated with the brewing process were sampled, the fermenter and wine cup were not found in Qingtai yet, probably because of the limited sample size. Moreover, the links between the consumption of fermented beverages and social changes at a critical time in the origin of Chinese civilization were not sufficiently discussed in our paper. Thus, a further expansion of the sample size and the integration of cultural context and archaeological data are expected in future work to enhance our understanding on the role of prehistoric alcoholic beverages in the origins of world civilization.

DATA AVAILABILITY STATEMENT

The original contributions presented in the study are included in the article/**Supplementary Material**, further inquiries can be directed to the corresponding author.

AUTHOR CONTRIBUTIONS

YY, JZ, and JL designed the research. JL, YY, JZ, and YG completed the writing. WG, QW, and LD completed the excavation of the Qingtai Site. JL, WL, LY, YG, and CG completed sampling in the field and experiments in the laboratory.

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SUPPLEMENTARY MATERIAL

The Supplementary Material for this article can be found online at: https://www.frontiersin.org/articles/10.3389/feart.2022.884630/full#supplementary-material

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