

THE RISE OF THE COSMETIC INDUSTRY IN ANCIENT CHINA: INSIGHTS FROM A 2700-YEAR-OLD FACE CREAM*

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Cosmetics have a long history in China, but their origins remain unclear. Cosmetic industry potentially originated in the Spring and Autumn Period (770–476 BCE), but little is known about the early manufacture and use of cosmetics. The Liujiawa site, located on the southern edge of the Loess Plateau in northern China, was the late capital of the ancient Rui state in the early to mid-Spring and Autumn Period. During the excavation, a sealed small and exquisite container with suspected cosmetic use was unearthed from tomb M49 belonging to a male associated with the aristocratic class. We report in this paper the multidisciplinary application of ATR-FTIR, XRD, SEM, stable isotope analysis, GC-MS and GC-C-IRMS analysis of the residue inside the container, demonstrating that the residue, which was made of ruminant adipose fat mixed with monohydrocalcite from cave moonmilk, was likely used as cosmetic face cream by the nobleman of the Rui state. This study provides an early example of cosmetic production in China, and, together with the prevalence of similar cosmetic containers during this period,

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it suggests the rise of an incipient cosmetics industry. Furthermore, the exploitation of moonmilk, a special stalactite in some limestone caves, reflects the link between early Taoist School and cosmetic production encouraged by the aristocratic class.

KEYWORDS: RUMINANT ADIPOSE FAT, MONOHYDROCALCITE, STALACTITE, FACE CREAM, TAOIST SCHOOL

INTRODUCTION

The global cosmetics industry (products designed to help people meet cultural norms of ‘beauty’) was valued at over US\$500 billion in 2017, and is expected to reach a market value of over US \$800 billion by 2023 (Orbis Research 2020). Today, cosmetics (which is derived from the Greek *kosmetikos*, to adorn) use is driven by ‘fashion’ and cultural values of appearance and economic expenditure in households worldwide. The origins of this industry, and the importance of cosmetics in human identities, has, however, remained remarkably under-studied in archaeology. While symbolic signalling using ochre, beads and other forms of bodily ornamentation is a focus for much Pleistocene and Holocene archaeology (Vanhaeren *et al.* 2013), here we focus on cosmetic use as a widespread economic and social industry supporting cultural and political values of grooming and appearance (Schafer 1956; Blanco-Dávila 2000). Early cosmetic use has long been proposed for ancient China, potentially dating to the pre-Qin period (before 221 BCE) (Schafer 1956). However, the study of the origins of cosmetics in ancient China has been based almost entirely on historical descriptions, some of which date to considerably later than suggestions of the origins of such products. Moreover, the nature of commercial secrets and the rhetoric surrounding beauty products in many of these sources have made it difficult to reconstruct the ingredients and production practices at any level of detail.

The physico-chemical analysis of residues from archaeological excavations has emerged as a potentially more direct alternative for determining the origins and nature of cosmetic practices (Ribechini *et al.* 2011; Nesměrāk *et al.* 2017). Fourier-transform infrared spectroscopy (FTIR) (Pérez-Arantegui *et al.* 1996; Cotte *et al.* 2005; Gamberini *et al.* 2008), X-ray diffraction (XRD) (Walter *et al.* 1999; Vidale *et al.* 2012), Raman spectroscopy (Huq *et al.* 2006; Baraldi *et al.* 2020) and chromatographic/mass spectrometric hyphenated methods (Buckley *et al.* 2004; Evershed *et al.* 2004; Giachi *et al.* 2013; Han *et al.* 2018) have been applied in multi-analytical approaches in order to attain the robust identification and full characterization of the molecular composition (Ribechini *et al.* 2011). However, these studies are to date primarily limited to North Africa (Walter *et al.* 1999; Buckley *et al.* 2004; Cotte *et al.* 2005) and Europe (Pérez-Arantegui *et al.* 1996; Evershed *et al.* 2004; Giachi *et al.* 2013), while the direct biomolecular analysis of ancient cosmetics residue in China has been limited, despite the crucial role that China has played in the economic emergence of the cosmetics industry both historically and more recently (Schafer 1956). Limited research is in part a fact that the discovery of hypothetical cosmetic residues, in a condition amenable for detailed analysis, has been rare due to frequent degradation and poor preservation. To our knowledge, there has been no scientific analysis of cosmetic residues from the pre-Qin period (before 221 BCE) in central China. The clue of cosmetic origin is important given that the origins of the widespread cosmetic industry and economy are to be found in this period of ancient China (Zhao *et al.* 1990).

Recently, in the course of the excavation at the Liujiawa site (c.700–640 BCE) (Fig. 1), a well-preserved bronze jar with a lid (Fig. 2) was unearthed in tomb M49. The jar (coded as M49:142) was found in the outer coffin, sitting north-west of the head of the occupant (a male of aristocratic class identified from the set of funerary bronze weapons) of the tomb (Fig. 1, c,

and see Fig. S1 in the additional supporting information) (Chong *et al.* 2019). The jar and the lid were found sealed together during excavation (Fig. 2, a). Upon opening under controlled conditions, the jar was found to be filled with an agglomeration of yellowish white lumps (Fig. 2, c, and see Fig. S2 in the additional supporting information) weighing approximately 6 g in total. These special types of bronze vessels that prevailed in contemporary tombs of early and mid-Spring and Autumn Period were speculated to be cosmetic containers (Li 2009). Nevertheless, to date the contents of such vessels have remained unclear. This discovered residue provided a rare opportunity to determine whether it was likely a cosmetic product by characterizing its ingredients. Ultimately, as a result, the residue study illustrates its cosmetic essence and reflects the cosmetic production and use in the Spring and Autumn Period (770–476 BCE).

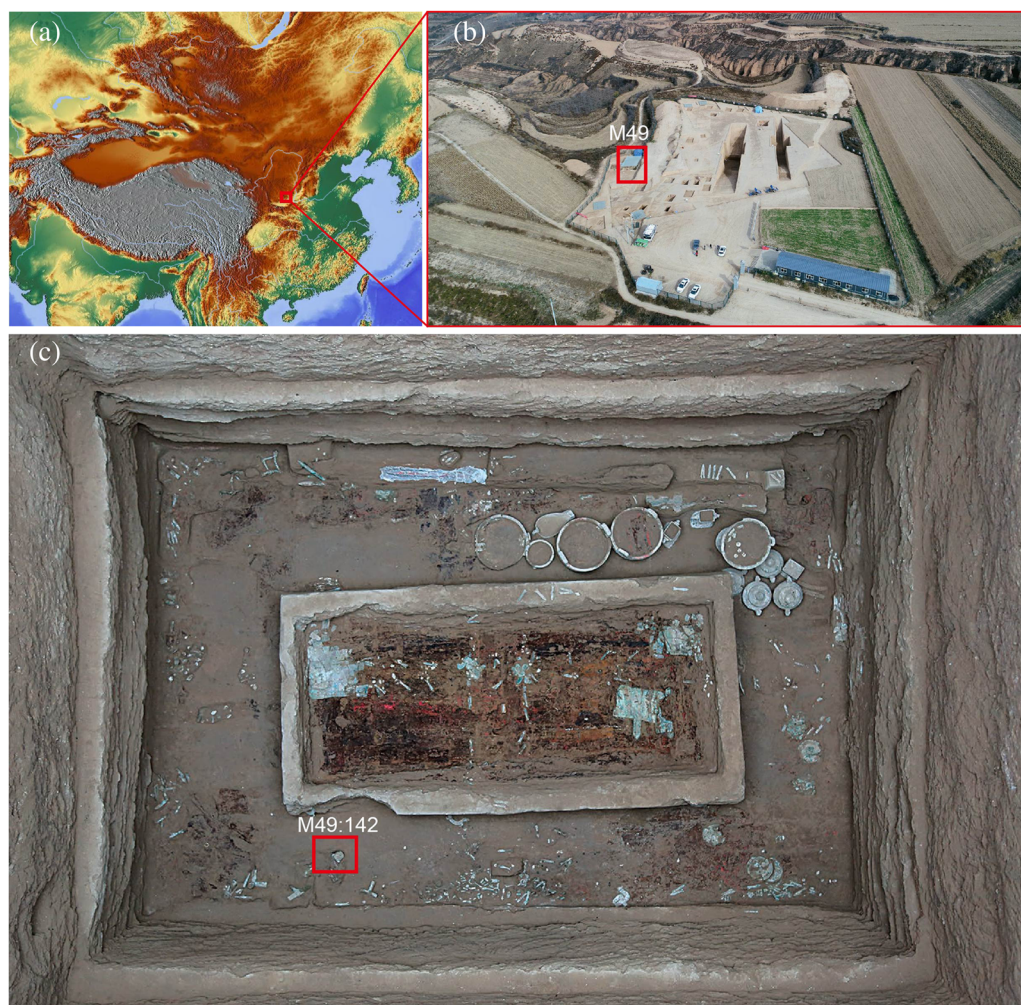


FIGURE 1 (a) Location of the Liujiawa site, indicated by the red square; (b) the landscape of the Liujiawa site and the location of tomb M49, indicated by the red rectangle; and (c) the buried artefacts within tomb M49 and the location of the bronze jar M49:142, indicated by the red rectangle. For the plane graph of artefacts in tomb M49, see Figure S1 in the additional supporting information.



FIGURE 2 (a) Bronze jar in situ; (b) decoration on the bronze jar after cleaning; and (c) a large quantity of agglomeration of yellowish white lumps inside the bronze jar.

MATERIALS AND METHODS

Site and sample background

The Liujiawa site is located in Liujiawa village, Chengcheng county, Shaanxi province, China (Fig. 1). It is comprised of both residence and cemetery areas, and it spans both sides of the Lujia River, a deep loess tableland with a total area of nearly 3 km². Relics of high-level buildings, casting copper and pottery handicraft industries, high-status tombs, massive rammed-earth walls and ditches have all been identified at the site. A preliminary study has revealed that it belongs to a principedom, Rui state, dating to the early stage of Spring and Autumn Period, more specifically from a time range of *c.* 700–640 BCE in terms of palaeography and style of bronze in the context.

Given the few historical records in relation to this enigmatic state, archaeological findings at the Liujiawa site have provided more insights into the subsistence, social organization and cultural practices in this part of China during this period (Chong *et al.* 2019).

During the course of the excavation, a bronze jar with a lid was unearthed in tomb M49 (Chong *et al.* 2019). It is small and exquisite with a 'U' shape and two handles (Fig. 2). The rim of the jar resembles an ellipse with a major axis of 5.5 cm and a minor axis of 4.3 cm. The height of the jar is 5.9 cm. Following removal of the outside soil, artistic decorative patterns became visible on the surface (Fig. 2, b). Following the discovery of the contents preserved inside the jar, a range of analytical methods was applied in order to reveal its ingredients and, accordingly, its function as well as usages in this specified archaeological background in the Liujiawa site.

FTIR analysis

The residue sample was analysed by a Nicolet 6700 (Thermo Scientific) FTIR spectrometer with an attenuated total reflectance (ATR) accessory. A tiny portion of the residue where the yellowish and white particle aggregated was removed separately and placed on the ATR testing platform using a cleaned dissecting needle. Spectra were acquired over the range of 4000–500 cm^{-1} using a resolution of 4 cm^{-1} , with 32 scans per spectrum. The software OMNIC 8.0 was used for data acquisition as well as data treatment.

XRD analysis

XRD analysis was applied to the residue sample using a Rigaku MiniFlex II Desktop X-ray diffractometer using $\text{Cu K}\alpha$ ($\lambda = 1.5406 \text{ \AA}$) radiation. A small amount of the mixture was ground into a fine powder and then dispersed evenly on a square silicon tablet ($1.5 \times 1.5 \text{ cm}$) using an ethanol solution. The sample was then left to dry. The analysis was conducted with the following parameters: voltage of 30 kV, current of 15 mA, divergence slit of 1.25° , anti-scattering slit of 1.25° and receiving slit width of 0.3 mm. Samples were scanned over an angular 2θ range from 10 to 75° with a scanning speed of 1° min^{-1} .

Scanning electron microscopy (SEM) analysis

SEM was conducted on a Phenom XL coupled with an energy-dispersive X-ray spectrometers (EDS) system. For this analysis, the powder specimens were sprinkled on carbon adhesive tape for SEM observation. The SEM observation was conducted at 15 kV and a spot size of 1.2 nA, and EDS analysis was conducted at 15 kV with a spot size of 8 nA in low-vacuum mode.

Inorganic C and O isotope analysis

A total of 8 mg of powder was collected in a 1.5 ml centrifuge tube. The sample was soaked in 1 M acetic acid for 10 min to remove diagenetic carbonates, followed by three rinses in distilled water and freeze-drying for 24 h. After reaction with 100% phosphoric acid, stable C and O isotopic measurements were performed on the gases evolved using a Thermo Gas Bench 2 connected to a Thermo Delta V Advantage Mass Spectrometer at the Department of Archaeology, Max Planck Institute for the Science of Human History. $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values were calibrated using International Standards (IAEA-603 ($\delta^{13}\text{C} = 2.5\text{‰}$; $\delta^{18}\text{O} = -2.4\text{‰}$); IAEA-CO-8 ($\delta^{13}\text{C} = -5.8\text{‰}$; $\delta^{18}\text{O} = -22.7\text{‰}$); USGS44 ($\delta^{13}\text{C} = -42.2\text{‰}$)) and an in-house standard (MERCK

($\delta^{13}\text{C} = -41.3\text{‰}$; $\delta^{18}\text{O} = -14.4\text{‰}$). Replicate analysis of MERCK standards suggests that machine measurement error is about $\pm 0.1\text{‰}$ for $\delta^{13}\text{C}$ and $\pm 0.2\text{‰}$ for $\delta^{18}\text{O}$.

Gas chromatography-mass spectrometry (GC-MS) analysis

Solvent extraction About 20 mg of residue powder were weighed out into a clean labelled vial and 2 ml of chloroform/methanol (2:1 v/v) were then added. The solution was sonicated for 15 min before centrifuging at 3000 rpm for 10 min. The solution was then carefully pipetted off into a clean, labelled vial. This extraction process was repeated twice, and the total extract was dried to 1 ml under a gentle stream of N_2 and then transferred into a reaction flask. A total of 1 ml of solution of chloroform/methanol (2:1 v/v) was added into the vial to wash it and was also transferred into the reaction flask and then dried under a gentle stream of N_2 . A total of 50 μl *n*-hexane and 100 μl BSTFA (*bis*(trimethylsilyl) trifluoroacetamide with 1% trimethylchlorosilane) were then added to the reaction flask for the derivatization process, undertaken at 70°C for 1 h. It was dried under a stream of N_2 and then processed with 500 μl *n*-hexane together with 10 μl *n*-tetratriacontane (1 μg μl^{-1}) as an internal standard in preparation for GC-MS analysis.

Acid extraction The extractions were following established methods (Craig *et al.* 2013). In brief, about 20 mg residue powder were transferred to a cleaned vial and 4 ml methanol were added before 15 min of ultrasonication. A total of 800 μl concentrated sulphuric acid was added and the vials were kept at 70°C for 4 h. The solution was then centrifuged at 3000 rpm for 5 min and the liquid extract was carefully pipetted off into a clean, labelled tube. A total of 4 ml *n*-hexane were added and the hexane layer (top layer) was separated out and pipetted off into a clean, labelled tube using a prepared Pasteur pipette. The separation of the hexane layer was repeated twice with the addition of hexane reduced to 2 ml. The sample was then dried under a very gentle stream of N_2 . A total of 90 μl *n*-hexane were added and transferred to a vial with addition of 10 μl *n*-tetratriacontane (1 μg μl^{-1}) as an internal standard. The solution was then ready for GC-MS and gas chromatography combustion isotope ratio mass spectrometry (GC-C-IRMS) analysis. To check for contamination, blank extraction and analysis were simultaneously carried out under the same experimental procedure.

The extracts were analysed using a 7890A GC and 5975C mass detector (Agilent Technologies, CA, USA) in 70 eV electron impact (EI) mode. Analytes were separated using an Agilent DB-5HT capillary column of 15 m \times 0.32 mm with a film thickness of 0.1 μm . A total of 1 μl volume of the sample was injected in a splitless mode. The oven temperature programme was as follows: initial temperature of 50°C for 1 min; ramped at 15°C per min to 100°C and maintained for 1 min, then ramped at 10°C per min to 375°C and isothermally maintained for 10 min. Helium was used as the carrier gas. The injector and auxiliary-heater temperatures were set at 300 and 350°C, respectively. Qualitative analysis was carried out under full-scan acquisition mode within the 50–800 u range. The tentative assignment of the compounds is based on their retention time, mass spectra and comparison with previous studies based on established fragmentations of lipids in the NIST08 Mass Spectral Library.

GC-C-IRMS analysis

Extracted fatty acid methyl esters (FAME) prepared using the acid extraction protocol were also analysed using a Thermo Trace Gas Chromatography Ultra coupled with an isotope ratio mass spectrometer (Thermo Fisher Scientific MAT 253) via a combustion furnace maintained at

1000°C. The GC system was equipped with an on-column injector and a DB-5 MS fused silica capillary column (30 m × 0.25 mm, 0.25 μm film thickness). A total of 2 μl of each sample was injected with the oven temperature held at 50°C (2 min) to 120°C at 15°C min⁻¹, then from 120 to 300°C at 5°C min⁻¹, and a final isotherm at 300°C for 16 min. Triplicate measurements of the standard were performed before the test to determine instrument precision (±0.24%) and accuracy (±0.30%) tested with an *n*-alkanoic acid ester standard of known isotopic value (Indiana standard F8-3). The stable C isotopic values of the methanol used for the extraction were measured. The isotopic shift due to the C introduced by the methylation was corrected by a mass balance equation (Regert 2011).

RESULTS

Source of inorganic mineral

Under the microscope, the yellowish lumps contain many grey-white particles (see Fig. S2 in the additional supporting information). The aggregate of these white particles was only observed in the residue inside the sealed jar, while it was not observed on the outside surface of the jar during archaeological excavation. The residue is generally mixed, while layers where the white particles were more aggregated can be observed in some lumps. The attenuated total reflectance Fourier-transform infrared (ATR-FTIR) analysis of the white particles as well as mixtures of yellowish lump powder suggest that the residue is composed of both carbonate and a lipid matrix

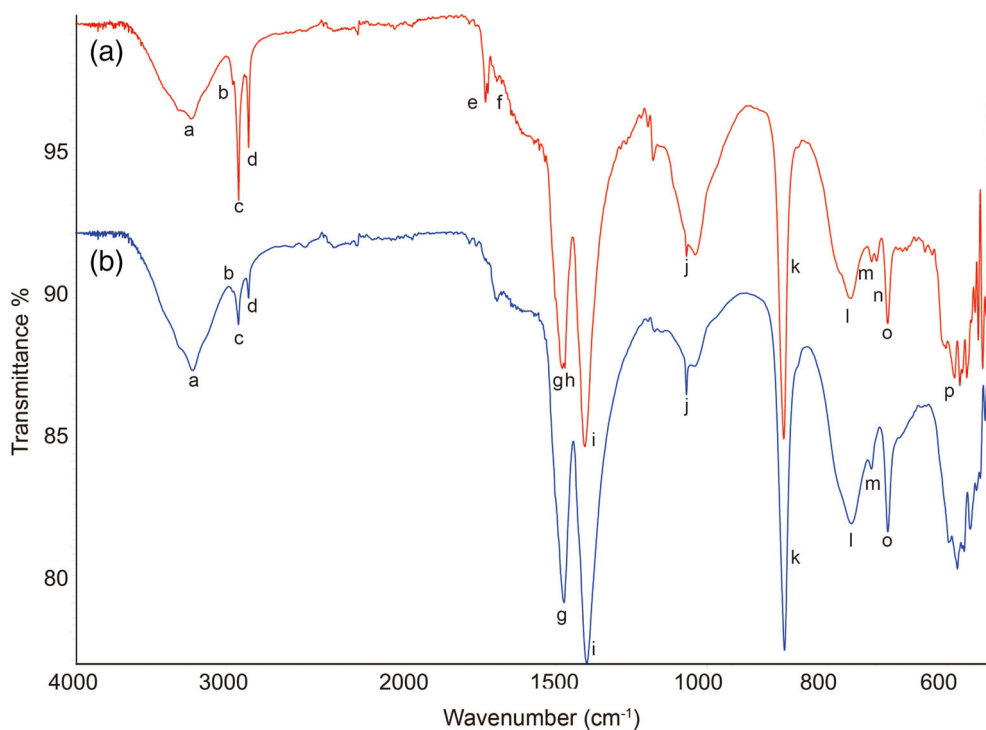


FIGURE 3 Attenuated total reflectance Fourier-transform infrared (ATR-FTIR) spectra of the residue sample: (values were calibrated) the spectrum collected from the yellowish powder; and (b) the spectrum collected from the white particles.

(Fig. 3). Asymmetric C-O stretching vibration is visible at 1408 and 1484 cm^{-1} (peaks g and i), an observed character of aragonite, vaterite or monohydrocalcite (MHC). The presence of a band at 872 cm^{-1} (peak k, indicative of CO_3^{2-}) serves as a distinguishable feature of MHC because of the different CO_3^{2-} bands of aragonite (860 cm^{-1}), calcite (876 cm^{-1}) and vaterite (877 cm^{-1}) (Neumann and Epple 2007; Jones and Jackson 2012). Other peaks were also in accordance well with identified IR features of the MHC (Coleyshaw *et al.* 2003; Rasmussen *et al.* 2012). The identification of MHC was further confirmed by XRD analysis in which almost all the peaks are attributable to those of MHC (see Fig. S3 in the additional supporting information). Besides the carbonate component of the residue, IR bonds between 3000 and 2800 cm^{-1} (peaks b–d correspond to C–H stretching vibrations) and around 1736 cm^{-1} (peaks e and f, corresponding to the ester groups) indicated the presence of animal lipid in the matrix (Gao *et al.* 2017). As a result, this residue from the sealed jar should be composed of animal lipid and MHC particles.

MHC is a metastable phase of Ca carbonate. Generally, the laboratory-produced MHC is unstable and easily transforms into calcite, especially in a heated environment, while the natural MHC is more stable and can last almost 10,000 years in proper storage conditions (Stoffers and Fischbeck 1974). Furthermore, MHC formation from other stable carbonates (e.g., calcite distributed within the loess) during the burial process is not plausible in a loess burial environment. As a result, the MHC within the residue should be formed in special geographical settings and microenvironments (Onac 1995; Rodriguez-Blanco *et al.* 2014) and purposefully collected.

MHC has been mainly found in lake deposits or cave speleothems (e.g., moonmilk) (Onac 1995). MHC crystals found in lake deposits are observed as trigonal-bipyramidal with spherules when certain algae or diatoms were involved in its formation (Stoffers and Fischbeck 1974; Li *et al.* 2008). However, SEM observation of the residue shows that the MHC particles in this study are mainly spherical (Fig. 4). The morphology of MHC can be varied

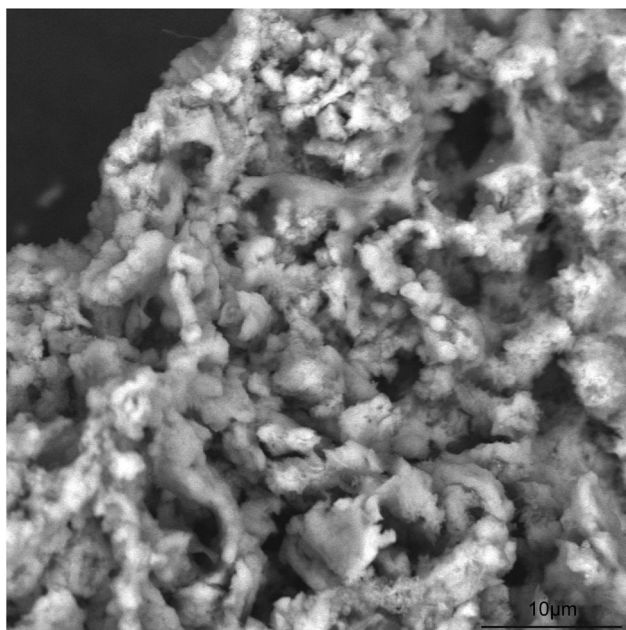


FIGURE 4 Scanning electron microscopy (SEM) observation of the residue.

in shape forms (Onac 1995; Cirigliano *et al.* 2018) that depend on its microenvironment while low Mg tends to form spherulite-like MHC (Rodriguez-Blanco *et al.* 2014). This is in accord with our EDS analysis which reveals the minor presence of Mg (see Fig. S4 in the additional supporting information). Moreover, the carbonate in the residue has a $\delta^{18}\text{O}$ of -9.0% and $\delta^{13}\text{C}$ of -8.6% . Given that $\delta^{18}\text{O}$ of carbonates are primarily determined by water in the environment in which they form, a $\delta^{18}\text{O} < -5\%$ is indicative of a deposit from a freshwater environment (Keith *et al.* 1964). The observed isotopic values are similar to those reported for cave speleothems of moonmilk (Lacelle *et al.* 2004), while the data may vary in other specific geographical settings. Furthermore, it is difficult to obtain pure, fine MHC particles from complex lake deposits. Also, other bizarre biological occurrences (e.g., otoliths of tiger shark) (Stoffers and Fischbeck 1974) were nearly inaccessible at that time and can be ruled out. Thus, the MHC in this residue should come from moonmilk, a kind of special stalactite from a limestone cave system (Onac 1995; Lacelle *et al.* 2004).

Origin of the fat matrix

The GC-MS analysis provides evidence for the origins of the fatty matters in the residue. The solvent extraction was employed to screen the total lipid profiles of the sample, which is mainly composed of mixtures of fatty acids, sterols, diacylglycerols and triacylglycerols (TAGs) (Fig. 5). The total ion current (TIC) chromatogram of the solvent extract documents a high proportion of saturated $\text{C}_{16:0}$ and $\text{C}_{18:0}$ *n*-alkanoic acids and the intact triacylglycerols are readily assessed by this solvent extraction, highlighting the preservation benefits afforded by the sealed bronze vessel. The distribution and ratio of fatty acids constituted preliminary information for the identification of lipid substances. Previous studies revealed that the non-ruminant fats usually have a higher palmitic acid/stearic acid (P/S) ratio (> 1.3) while ruminant fats have a lower P/S ratio (< 1.3) (Romanus *et al.* 2007). The P/S value of the analysed sample is 0.81, and together with the high $\text{C}_{18:0}$ saturated *n*-alkanoic acid content it can tentatively assign the lipid residues to ruminant animal fat (Evershed *et al.* 2002). Studies have also shown that ruminant (e.g., bovine

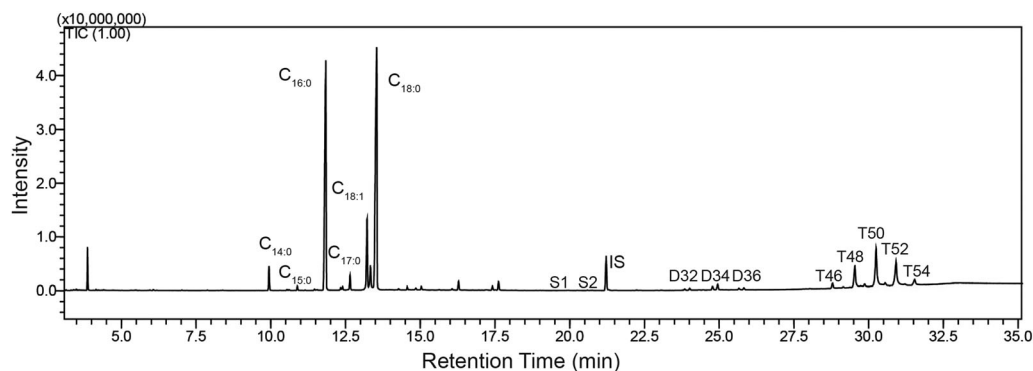


FIGURE 5 Total ion current (TIC) chromatogram of the residue sample by solvent extraction (trimethylsilylated extracts). $\text{C}_{14:0}$, $\text{C}_{15:0}$, $\text{C}_{16:0}$, $\text{C}_{17:0}$ and $\text{C}_{18:0}$ are saturated fatty acids (determined as their trimethylsilyl (TMS) esters) containing 14–18 acyl carbons, respectively; $\text{C}_{18:1}$ is mono-unsaturated fatty acid (determined as TMS esters) containing 18 acyl C atoms; S1 is cholesterol (determined as a TMS derivative); S2 is beta-sitosterol (determined as a TMS derivative); IS represents the internal standard (*n*-tetraatriacontane); D32, D34 and D36 are diacylglycerols (determined as their TMS derivative) containing 32, 34 and 36 acyl C atoms, respectively; T46, T48, T50, T52 and T54 are triacylglycerols containing 46, 48, 50, 52 and 54 acyl C atoms, respectively.

and ovine) and non-ruminant (e.g., porcine) adipose fats and ruminant milk fat can be distinguished based on their TAG distributions (Regert 2011). The adipose fat of non-ruminant and ruminant species presents a narrower distribution of TAGs ranging from C_{44} to C_{54} , while the presence of short-chain fatty acids in milk fat presents a broad distribution of TAGs ranging from C_{28} to C_{54} (Dudd and Evershed 1998; Mukherjee *et al.* 2007). The triacylglycerol distribution from this residue, ranging from C_{46} to C_{54} , falls in the narrow TAGs distribution that corresponds to animal adipose fats.

However, preferential degradation and loss of compound means that the distribution of fatty acids and triacylglycerols alone is not sufficiently distinctive to distinguish different fats (Dudd and Evershed 1998). The application of gas chromatography combustion isotope ratio mass spectrometry (GC-C-IRMS) in archaeological residue analysis has made it possible to characterize more specifically the origin of animal fats (Evershed *et al.* 1994; Craig *et al.* 2005; Evershed 2008). The model set up by Copley *et al.* (2003) has been widely applied for the determination of archaeological animal fat origins by plotting $\delta^{13}C$ values of $C_{16:0}$ and $C_{18:0}$. Residues whose $\Delta^{13}C$ value ($\delta^{13}C_{18:0} - \delta^{13}C_{16:0}$) falls to < -3.3 per mil are consistent with fats of a ruminant dairy origin, whilst those between -3.3 and 0 per mil are ruminant carcass fats and > 0 per mil are non-ruminant carcass fats. (Fig. 6) (Copley *et al.* 2003). This strategy of GC-C-IRMS to determine more precisely the origin of the sources of the archaeological lipids has been successfully applied to reveal the ingredient of ruminant adipose fat in a Roman cosmetic product dated to the mid-second century CE (Evershed *et al.* 2004).

The acid extraction and simultaneous methylation of lipids was submitted to GC-C-IRMS analysis following GC-MS screening (see Fig. S5 in the additional supporting information). The $\delta^{13}C$ values of $C_{16:0}$ and $C_{18:0}$ in the residue are -14.2‰ and -15.9‰ , respectively, and the $\Delta^{13}C$ value is -1.7‰ consistent with ruminant adipose fats (Fig. 6), such as cattle and sheep. Furthermore, the relatively positive $\delta^{13}C_{16:0}$ and $C_{18:0}$ values indicate the abundant consumption of C_4 plants (e.g., millet) by the ruminant animals (Dunne *et al.* 2012). Thus, it can be concluded that this residue is using ruminant animal fat (fed with C_4 plants) as matrix for dispersing and wrapping of white MHC particles to form a cream product.

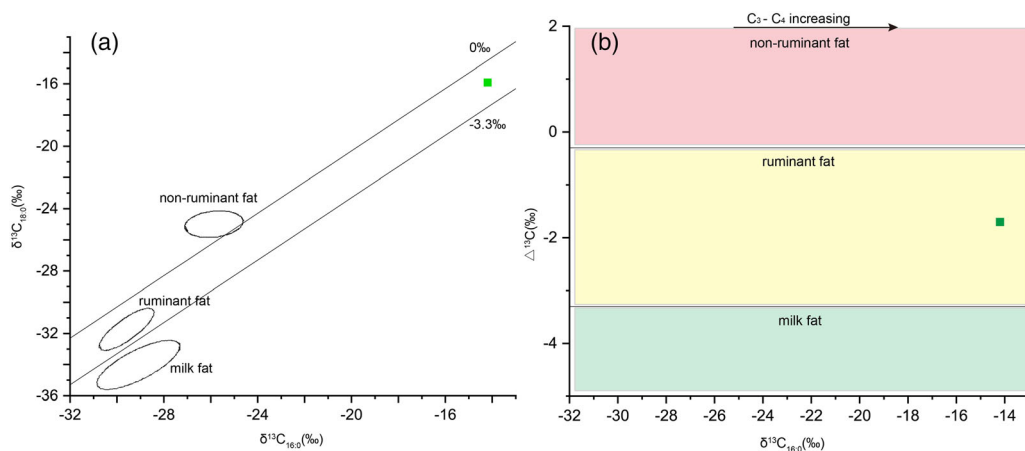


FIGURE 6 Gas chromatography combustion isotope ratio mass spectrometry (GC-C-IRMS) results of the tested samples $\delta^{13}C_{18:0}$ versus $\delta^{13}C_{16:0}$ (a) and $\Delta^{13}C$ versus $\delta^{13}C_{16:0}$ (b). In both graphs, a green square represents the isotopic values of the tested residue. In (a), the black circle represents the data set of a modern reference based on the C_3 plants food web (Copley *et al.* 2003).

DISCUSSION

Origin of the animal lipids

Although palaeographical descriptions have been used for the reconstruction of the agricultural and dietary activities taking place during the Spring and Autumn Period, almost no records exist to elucidate animal husbandry of the Rui state located in the transition zone between the agricultural region and the nomadic region at the southern edge of the Loess Plateau. The local vegetation is mainly dominated by *Poaceae* within the Wei River Basin, and the variations in pollen concentrations of *Pinus* and *Artemisia* possibly indicate a climatically driven increasing aridity (Li *et al.* 2009; Zhuang and Kidder 2014). The geographical and climatological environment of Liujiawa site on the transition zones between the Loess Plateau and the Wei River Plain favour the cultivation of crops, especially the C₄ plant millet with abundant sunlight and rainfall under the continental monsoon climate (temperate semi-arid region) which has been previously revealed by human bone isotope analysis from Liangdaicun Site (adjacent to the Rui state region near the Liujiawa site) (Ling *et al.* 2017). The human settlement variance may have promoted animal husbandry while diminishing the relevance of hunting activities in animal exploitation (Du *et al.* 2020).

As general phenomena in ancient northern China, domestic ruminant animals have different feeding strategies according to animal bone collagen isotope analysis. For instance, analysis of the bulk C isotope of collagen from sheep and cattle from the Taosi site (c.2300–1900 BCE) showed that the mean bulk $\delta^{13}\text{C}$ value of sheep is -17.22% , while the mean bulk $\delta^{13}\text{C}$ value of cattle is -11.25% . The sheep are speculated to have been grazing in natural pasture, while the cattle, whose bulk $\delta^{13}\text{C}$ values were positively shifted, were thought to have been pen-raised. The latter is attributed to the livestock having been fed with by-products of millet (a C₄ plant) (Chen *et al.* 2012, 2016; Hu 2018). This difference in the raising strategies of sheep and cattle appears to have remained as longstanding traditions in ancient northern China (Chen *et al.* 2018). Thus, the ruminant fat matrix with positively shifted $\delta^{13}\text{C}$ values in this study is considered most likely to have originated from domesticated cattle in the pens-raising strategy with a ‘strictly controlled’ C₄ diet.

Exploitation of stalactites along with the Taoist School Cave Cultus

The mineral ingredient MHC within the animal lipid matrix was purposefully collected from limestone caves, and this is probably linked with Taoist School activities. The Taoist School (道家) is a philosophical school originating in the Spring and Autumn Period; its maturity was symbolized by the mentor of Lao Zi (c.571–471 BCE). The Spring and Autumn Period and the subsequent Warring States Period (475–221 BCE) witnessed the emergence of the Taoist School with the doctrine of longevity, immortality and salvation. The Taoists were in favour of cave dwellings and would choose prestigious caves as a preferential place for Taoist rituals, since caves were considered metaphorically as the ‘womb’ that could give birth to neogenesis and palingenesis (Jiang 2003). The exploitation of caves in this ritual context inevitably led to the finding of cave minerals, especially the white stalactites.

Stalactites are commonly deposited in different forms in limestone caves composed of carbonate rocks. Ancient people, particularly following the advent of Taoist School Cave Cultus, believed stalactites were formed by the holy liquid from the souls of hills: stalactites occur in *Yang* caves, being congealed from the *qi* of *Yang* (*Yin* and *Yang* are the two opposing principles in nature in ancient Chinese philosophy, *qi* of *Yang* means pneuma of *Yang*) (Yoke 2007).

High-quality stalactites were associated with whiteness or ‘the gloss of jade’, and specifically occurred in prestigious hills and caves with particular rock compositions, shapes and environmental conditions. The intrinsic whiteness together with their special shape was linked to medical/cosmetic/alchemy potentials (Huaizhi and Yuantao 2000).

Moonmilk, as a special speleothem, is usually a soft white plastic mud (in its wet state) and powdery material (in its dry state). It has alluring properties such as intrinsic whiteness and unique shapes with the concentric layers of microcrystalline carbonates greatly admired (Léveillé *et al.* 2000), which may have been purposefully collected in mineral-collecting activities in the search for white stalactites with cosmetic/medical use (Banerjee *et al.* 2019). MHC forms in special microenvironments (e.g., high Mg/Ca ratio, high pH or the presence of algae etc.) would be in accord with the holy description of moonmilk in historical texts, likely causing it to be regarded as highly valuable for medical and cosmetic purposes in terms of texture, colour and shape (Léveillé *et al.* 2000). The collected minerals were selected and ground for days or weeks (as described in ancient medical books) in order to obtain pure and fine particles. Porous Ca carbonate is used as a cosmetic ingredient due to its extremely good absorbency as an absorbent for sweat and sebum (Mitsui 1997). The spherical nature of the carbonate (e.g., MHC in this study) also enhanced its extensibility when applied to the skin. Moonmilk collection from limestone caves, as a key part of the production of the cosmetics, implies that this period could document an increasing cosmetic use and production involving Taoist School Cave Cultus activities around the Rui state urged on by the aristocratic class (e.g., the male occupant of M49 in this study).

Earliest face cream in China

The residue found inside the bronze jar, a cream product using cattle adipose fat as a matrix for the MHC particles, is indicative of its function as a cosmetic cream or cosmeceutical product. The animal fat as a source of glycerolipid provided functions of emollient, moisturizing and grooming for the skin as well-being vehicles to carry other agents (Evershed *et al.* 2004; Ribechini *et al.* 2011; Baraldi *et al.* 2020). The cream recipe is similar to prescriptions in ancient medical books (e.g., the *Fifty-two Prescriptions* (五十二病方)). The *Fifty-two Prescriptions* as a medical manuscript was unearthed from tomb Mawangdui III (168 BCE) of the West Han dynasty in 1973 and is currently the earliest written list of medical prescriptions unearthed in China (Zhong and Ling 1975). It is regarded as a pre-Qin period medical book and it first mentions the medicinal use of animal fats, including treating 11 kinds of dermatoses with 70 prescriptions (52 prescriptions for an external cream-based therapy). Within the *Fifty-two Prescriptions*, different animal fat matrices were differentiated with non-ruminant adipose fat (e.g., porcine) recorded as *Gao* (膏) and ruminant adipose fat (e.g., bovine and ovine) recorded as *Zhi* (脂). A prominent feature of these therapies involves the extensive use of animal adipose fat as matrix dispersing inorganic mineral powders or officinal ingredients for medical/cosmetic ointment-making. One prescription in the *Fifty-two Prescriptions* is particularly assumed to be a cosmetic face cream rather than a therapeutical ointment because most of the ingredients (*Angelica dahurica*, *Asarumforbesii maxim*, *Cinnamomum obtusifolium*, *Magnolia liliiflora* and cattle fat) have only cosmetic and fragrant properties.

Over Chinese history, another record unequivocally specified the use of cattle fat as a matrix for the making of face cream appeared rather late in *The Essential Techniques for the Welfare of the People* (齐民要术) by agronomist Sixie Jia written between 533 and 544 CE. Our analysis result has indicated the Liujiawa ancestors were most likely using cattle fat to provide the glycerolipid material in the cream. Considering that MHC has a whitening effect, the cream with

a cattle fat matrix in this study should be a face-whitening cream. To our knowledge, the Liujiawa case is the earliest evidence for the use of cattle adipose fat as a cream matrix for cosmetic formulations in the pre-Qin period, specifically around the time range of the Liujiawa site (700–640 BCE), directly demonstrating the handicraft industry's use of cattle fat. This was over 1100 years earlier than the record by agronomist Sixie Jia in *The Essential Techniques for the Welfare of the People*.

Rise of the cosmetic industry in the early period of Spring and Autumn

Archaeologically, these kinds of small and exquisite bronze jars, similar to the bronze jar where the residue was found and analysed in this study, have been observed in a wide area during the early phase of the Spring and Autumn Period (see Fig. S6 in the additional supporting information) (Li 2009). These containers were usually present in the tomb of the high-ranking class (mostly kings, queens or nobilities). The finding of the well-sealed bronze ware with a large quantity of residue inside has lent support to the hypothesis that the function of the jar was as a cosmetic container which verified the archaeologists' speculation (Li 2009).

The results of our analyses, together with the wide area of distribution of these containers, implies that the cosmetics might be mostly used as a high-end product led by aristocratic class, and similar cases can be found in other ancient societies and civilizations (Doménech-Carbó *et al.* 2012; Mai *et al.* 2016) as well as in later Chinese dynasties (Yu *et al.* 2017). Cosmetic manufacturing had already become a specialized industry for the supply to the nobility in the early stage of the Spring and Autumn Period, and the involvement of a sorcery/alchemy-related ingredient (e.g., the collection of cave minerals) enriched the aestheticism with mystic elements. In fact, historical records from the pre-Qin period described face whitening through cosmetic use as a source of cultural pride. The whitened face with unnatural complexions could conceal defects on the skin and mask a layer of luminous homogeneity, enhancing the facial bilateral symmetry in contrast with the black eyelashes and black hair. Also, the whitened face eliminates wrinkles, creating an identity of youthfulness and beauty with a manner of majestic which is appealing to the aristocratic class.

Another interesting point lies in the male's use of white cosmetics, which has scarcely been described since the Spring and Autumn Period (mostly female figures were described). In accord with our findings, historical records also suggested the pre-Qin period (pre-221 BCE) was an emerging era for white makeup cosmetics advocating facial attractiveness with white luminance. This aesthetic taste of the aristocratic class involving cave minerals reflected the increasing awareness of aesthetics and metaphysics in the Spring and Autumn Period that had influenced the subsequent aesthetic taste in history. Furthermore, although lead-based cosmetics have been extensively used in ancient China (Schafer 1956), our study shows the diverse choice of materials had taken place in the early development of the Chinese cosmetic industry.

Globally, it also yielded an interesting point when comparing the ancient cosmetic cream products in the East and in the West with reference to the material use and making procedures. The composite cosmetics made of inorganic minerals and lipid-based cream can be found in ancient Egypt with lipids (possibly olive oil) as a matrix for potentially toxic lead-based metallic salts (lead soaps) (Walter *et al.* 1999; Cotte *et al.* 2005). Especially, a similar Roman cosmetic recipe was reported from the second century CE in London with ruminant adipose fat as a matrix mixed with starch and SnO₂. It was concluded to have acted as a cosmetic cream which shares surprising features with modern moisturizing creams (Evershed *et al.* 2004).

CONCLUSIONS

Residue analysis verifies the earliest cosmetic cream product in China: not only has it pushed back the historical description for cosmetic use of ruminant adipose fat (most likely cattle fat) to the early phase of the first millennium BCE, but also it highlighted the special MHC use resulting from the exploitation of cave minerals along with the Taoist School Cave Cultus which adds mystic elements to the aestheticism of cosmetics. The special ingredients and the popularization of similar bronze vessels disclosed the rise of an incipient cosmetics industry in the Spring and Autumn Period which still acts as an important part of our daily life. This archaeological residue study showed that apart from being a culinary ingredient, animal products were also explored in the handcraft industry of cosmetics-making. It has also deepened our knowledge of natural mineral usage, revealing a special aesthetic taste in the early Iron Age of ancient China and has contributed to the worldwide study of cosmetics development.

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[Correction added on 3 March 2021, after first online publication: Additional funders have been added in the last 2 sentences of Acknowledgements section.]

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SUPPORTING INFORMATION

Additional supporting information may be found online in the Supporting Information section at the end of the article.

Figure S1. Plane graph of tomb M49 with the numbered funeral artefacts. The location of the studied bronze vessel (code M49:142) is indicated by the red rectangle. The numbering of the items was reported by Chong *et al.* (2019).

Figure S2. Part of the residue under a microscope. The observation was observed using a camera as well as light microscopy (a Keyence 600 model).

Figure S3. X-ray diffraction (XRD) result of the residue sample.

Figure S4. Energy-dispersive X-ray spectrometer (EDS) system analysis result of the residue.

Figure S5. Total ion current (TIC) chromatogram of the residue sample by acid extraction. C_{14:0}, C_{15:0}, C_{16:0}, C_{17:0} and C_{18:0} are saturated fatty acids (determined as their methyl esters) containing 14–18 acyl carbons, respectively; C_{18:1} is mono-unsaturated fatty acid (determined as methyl esters) containing 18 acyl C atoms; and IS represents the internal standard (*n*-tetratriacontane).

Figure S6. Archaeology sites unearthed with similar types of small bronze vessels to M49:142 in the Liujiawa site in the Spring and Autumn Period (770–476 BCE): 1, Liujiawa site; 2, Liangdaicun site; 3, Shangguocun site; 4, Guoguo site; 5, Songzhuang site; 6, Xianrentai site; 7, Longmenkou site; 8, Xiaowangzhuang site; 9, Qijiayu site; 10, Dongjiang site; 11, Xulou site; 12, Xueguogucheng; 13, Liujiadianzi site; 14, Lijiazhuang site; 15, Quantoucun site; 16, Xinwangji site; and 17, Liugezhuang site. Dots are drawn with reference to Li (2009), as well as other archaeological reports.