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The rise of the cosmetic industry in ancient China: insights from a 2,700-year-old face cream

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ABSTRACT Cosmetic has a long history in China while its origin has remained unclear. It potentially originated in the Spring and Autumn period (770-476 BC) but little is known about its early manufacture and use. The Liujiawa Site, located at the southern edge of the Loess Plateau in northern China, was the late capital of the *Rui* State in the early to middle 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. Here, we report 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, made of ruminant adipose fat mixed with monohydrocalcite coming from cave moonmilk, was likely used as cosmetic face cream by the nobleman of ancient *Rui* State. This work provides an early example of cosmetic production in China and, together with the prevalence of similar cosmetic containers during this period, 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*

1. Introduction

The global cosmetic industry (products designed to help people to meet cultural norms of 'beauty') was valued at over 500 billion US dollars in 2017 and is expected to reach a market value of over 800 billion US dollars by 2023 (Orbis Research 2020). Today, cosmetics (arises from Greek word '*kosmeticos*', 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 signaling 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 back to the pre-Qin period (before 221 BC) (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 in any level of detail.

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, Nesměrák *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 direct biomolecular analysis of ancient cosmetic residue in China has been limited, despite the crucial role which China has played in the economic emergence of the cosmetic 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 to 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 BC) in central China. The clue of cosmetic origin is important given that the

origins of widespread cosmetic industry and economy are to be found in this time period of ancient China (Zhao *et al.* 1990).

Recently, in the course of the excavation in Liujiawa Site (about 700-640 BC) (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 northwest of the head of the occupant (a male of aristocratic class identified from the set of funerary bronze weapons) of the tomb (Fig. 1C and Fig. S1 in Supporting Information) (Chong *et al.* 2019). The jar and the lid were found sealed together during excavation (Fig. 2A). Upon opening under controlled conditions, the jar was found to be filled with an agglomeration of yellowish white lumps (Fig. 2C, Fig. S2 in Supporting Information) weighing approximately 6 grams in total. These special types of bronze vessels that prevailed in contemporary tombs of early and middle Spring and Autumn Period were archaeologically speculated as 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 this residue 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 (770-476BC).

2. Materials and Methods

2.1 Site and sample background

Liujiawa Site is located at Liujiawa village, Chengcheng County, Shaanxi Province, China (Fig. 1). It comprised of both residence and cemetery areas and spans both sides of the Lujia River, a deep loess tableland with a total area of nearly 3 square kilometers. 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 princedom, *Rui* State, dating to the early stage of Spring and Autumn period, more specifically, from a time range of ca.700-640 BC in terms of paleography 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 subsistence, social organization, and cultural practices in this part of China during this period (Chong *et al.* 2019).

During the course of its 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 soil outside, artistic decorative patterns became visible on the surface (Fig. 2B). Following the discovery of 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 Liujiawa Site.

2.2 FTIR analysis

The residue sample was analyzed by 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 aggregate 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.

2.3 XRD analysis

XRD analysis was applied to the residue sample by a Rigaku MiniFlex II Desktop X-ray diffractometer using Cu Kα (λ = 1.5406 Å) radiation. A small amount of the mixture was ground into a fine powder and then dispersed evenly on a square silicon tablet (1.5cm × 1.5cm) using 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.

2.4 SEM analysis

Scanning electron microscopy (SEM) was conducted on a Phenom XL coupled with 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 with 15 kV, spotsize 1.2 nA and EDS analysis was conducted with 15 kV, spotsize 8 nA in low vacuum mode.

2.5 Inorganic carbon and oxygen isotope analysis

8 mg of powder was collected in 1.5 ml centrifuge tube. The sample was soaked in 1M acetic acid for 10 minutes to remove diagenetic carbonates, followed by three rinses in distilled water and freeze-drying for 24 hours. After reaction with 100% phosphoric acid, stable carbon and oxygen 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. $\delta^{13}C$ and $\delta^{18}O$ values were calibrated using International Standards (IAEA-603 ($\delta^{13}C$ = 2.5‰;

$\delta^{18}O$ = -2.4‰); IAEA-CO-8 ($\delta^{13}C$ = -5.8‰; $\delta^{18}O$ = -22.7‰); USGS44 ($\delta^{13}C$ = -42.2‰)) and an in-house standard (MERCK ($\delta^{13}C$ = -41.3‰; $\delta^{18}O$ = -14.4‰)). Replicate analysis of MERCK standards suggests that machine measurement error is *c.* ± 0.1‰ for $\delta^{13}C$ and ± 0.2‰ for $\delta^{18}O$.

2.6 GC/MS analysis

Solvent extraction. About 20 mg of residue powder was weighed out into a clean labelled vial and 2 ml of chloroform/methanol (2:1 v/v) was then added. The solution was sonicated for 15 minutes before centrifuging at 3000 rpm for 10 minutes. 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 nitrogen and then transferred into a reaction flask. One (1) ml of solution of chloroform/methanol (2:1 v/v) was added into the vial to wash and was also transferred into the reaction flask and then dried under a gentle stream of nitrogen. Fifty (50) µl *n*-hexane and 100 µl BSTFA (bis (trimethylsilyl) trifluoroacetamide with 1% trimethylchlorosilane) was then added to the reaction flask for the derivatization process, undertaken at 70 °C for 1 hour. It was dried under a stream of nitrogen and then processed with 500 µl *n*-hexane together with 10 µl *n*-tetratriacontane (1µg/µl) 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 was transferred to a cleaned vial and 4 ml methanol was added before 15 minutes of ultrasonication. Eight hundred (800) µl concentrated sulphuric acid was added and the vials were kept at 70 °C for 4 hours. The solution was then centrifuged at 3000 rpm for 5 minutes and the liquid extract was carefully pipetted off into a clean, labelled tube. Four (4) ml *n*-hexane was 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 nitrogen. Ninety (90) µl *n*-hexane was added and transferred to a vial with addition of 10 µl *n*-tetratriacontane (1µg/µl) as an internal standard. The solution was then ready for GC/MS and GC-C-IRMS analysis. To check for contamination, blank extraction and analysis were simultaneously carried out under the same experimental procedure.

The extracts were analyzed using a 7890A gas chromatograph and 5975C mass detector (Agilent Technologies, CA) in 70 eV electron impact (EI) mode. Analytes were separated using an Agilent DB-5HT capillary column of 15 m × 0.32 mm with a film thickness of 0.1 µm. One (1) µl volume of the sample was injected in a splitless mode. The oven temperature program was as follows: initial temperature 50°C for 1 minute; ramped at 15°C per minute to 100°C and maintained for 1 minute, then ramped at 10°C per minute to 375°C and

isothermally maintained for 10 minutes. Helium was used as the carrier gas. The injector and auxiliary-heater temperatures were set at 300°C 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.

2.7 GC-C-IRMS analysis

Extracted fatty acid methyl esters (FAME) prepared using the acid extraction protocol were also analyzed 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 a temperature of 1000 °C. The Gas Chromatography system is 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). Two (2) μl of each sample was injected with oven temperature held at 50 °C (2 minutes) 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 minutes. Triplicate measurements of the standard were performed prior to the test to determine instrument precision (±0.24‰) and accuracy (±0.30‰) tested with *n*-alkanoic acid ester standard of known isotopic value (Indiana standard F8-3). The stable carbon isotopic values of the methanol used for the extraction were measured. The isotopic shift due to the carbon introduced by the methylation was corrected by a mass balance equation (Regert 2011).

3. Results

3.1 The source of inorganic mineral

Under the microscope, the yellowish lumps contain many gray-white particles (Fig. S2, Supporting Information). The aggregate of these white particles were only observed in the residue inside the sealed jar while they were not observed in 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 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 lipid matrix (Fig. 3). Asymmetric C–O stretching vibration is visible at 1408 cm^{-1} and 1484 cm^{-1} (peak 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 *et al.* 2007, Jones *et al.* 2012). Other peaks were also in accordance well with identified IR features of MHC (Coleyshaw *et al.* 2003, Rasmussen *et al.* 2012). The identification of MHC was further confirmed by XRD analysis in which almost all of the peaks are attributable to

those of MHC (Fig. S3 in Supporting Information). Besides the carbonate component of the residue, IR bonds between 3000 cm^{-1} and 2800 cm^{-1} (peak b, c and d, correspond to C–H stretching vibrations) and around 1736 cm^{-1} (peak 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 calcium 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 *et al.* 1974). Furthermore, MHC formation from other stable carbonates (*e.g.*, calcite distributed within the loess) during 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 microenvironment (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 *et al.* 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 in shape forms (Onac 1995, Cirigliano *et al.* 2018) that depend on its microenvironment while low magnesium (Mg) tends to form spherulite-like MHC (Rodriguez-Blanco *et al.* 2014). This is in accord with our EDS analysis which reveals minor presence of Mg (Fig. S4 Supporting Information). Moreover, the carbonate in the residue has a $\delta^{18}O$ of -9.0 ‰ and $\delta^{13}C$ of -8.6 ‰. Given that $\delta^{18}O$ of carbonates are primarily determined by water in the environment in which they form, a $\delta^{18}O$ below -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 should be noted that 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 *et al.* 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).

3.2 The origin of 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 TIC chromatogram of the solvent extract documents a high proportion of saturated $C_{16:0}$ and $C_{18:0}$ *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 lower P/S ratio (<1.3) (Romanus *et al.* 2007). The P/S value of the analyzed sample is 0.81 and together with the high $C_{18:0}$ 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 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 *et al.* 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 *et al.* 1998). The application of gas chromatography combustion isotope ratio mass spectrometry (GC-C-IRMS) in archaeological residue analysis has made it possible to more specifically characterize the origin of animal fats (Evershed *et al.* 1994, Craig *et al.* 2005, Evershed 2008). The model set up by M. S. Copley et al (2003) has been widely applied for the determination of archaeological animal fat origins through plotting $\delta^{13}C$ values of $C_{16:0}$ and $C_{18:0}$. Residues whose $\triangle^{13}C$ value ($\delta^{13}C_{18:0}$-$\delta^{13}C_{16:0}$) falls below -3.3 per mil are consistent with fats of a ruminant dairy origin, whilst those between -3.3 per mil and 0 per mil are ruminant carcass fats and above the 0 per mil are non-ruminant carcass fats. (Fig. 6) (Copley *et al.* 2003). This strategy of GC-C-IMRS to more precisely determine 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 middle of the second century AD (Evershed *et al.* 2004).

The acid extraction and simultaneous methylation of lipids was submitted to GC-C-IRMS analysis following GC/MS screening (Fig. S5 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 $\triangle^{13}C$ 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.

4. Discussion

4.1 The origin of the animal lipids

Although paleographical descriptions have been used for the re-construction of the agricultural and dietary activities taking place during the Spring and Autumn period, almost no records exist to elucidate animal husbandry of *Rui* State located in the transition zone between the agricultural region and 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 *et al.* 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 C_4 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 *Rui* State region near 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 carbon isotope of collagen from sheep and cattle from the Taosi Site (ca. 2300-1900 BC) showed that the mean bulk $\delta^{13}C$ value of sheep is -17.22‰ while the mean bulk $\delta^{13}C$ value of cattle is -11.25‰, the sheep is speculated to have been grazing in natural pasture while the cattles whose bulk $\delta^{13}C$ values were positively shifted were thought to have been pen-raised: this is attributed to the livestock having been fed with by-products of millet (a C_4 plant) (Chen *et al.* 2012, Chen *et al.* 2016, Hu 2018). This difference in the raising strategies of sheep and cattle appear to have remained as long-standing traditions in ancient northern China (Chen et al, 2018). Thus, the ruminant fat matrix with positively-shifted $\delta^{13}C$ values in this study is considered most likely to originate from domesticated cattle in the pens-raising strategy with a 'strictly controlled' C_4 diet.

4.2 The 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, and its maturity was symbolized by the mentor of *Lao Zi* (ca. 571-471 BC). The Spring and Autumn Period and the subsequent Warring States Period (475-221 BC) witnessed the emergence of *Taoist School* with the doctrine of longevity, immortality and salvation. The Taoists were in favor 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 with medical/cosmetic/alchemical potentials (Huaizhi *et al.* 2000).

Moonmilk, as a special speleothem, is usually a soft white plastic mud (in its wet state) and powdery material (in dry state). Moonmilk has alluring properties such as intrinsic whiteness and unique shapes with concentric layers of microcrystalline carbonates admired (Léveillé *et al.* 2000), which may have been purposefully collected in mineral collecting activities in searching 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, color 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 calcium carbonate are used as cosmetic ingredient due to its extremely good absorbency quality as 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 by the aristocratic class (*e.g.*, the male occupant of M49 in this study).

4.3 The 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 cosmetics cream or cosmeceutical product. The animal fat as 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*)). *Fifty-two Prescriptions* as a medical manuscript was unearthed from tomb Mawangdui III (168 BC) of West Han Dynasty in 1973 and is currently the earliest written list of medical prescriptions unearthed in China (Zhong *et al.* 1975). It is regarded as a pre-Qin period medical book and it firstly mentions the medicinal use of animal fats, including treating 11 kinds of dermatoses with 70 prescriptions (52 prescriptions for external cream-based therapy). Within the *Fifty-two Prescriptions*, different animal fat matrix was differentiated with non-ruminant adipose fat (*e.g.*, porcine) recorded as *Gao* (*膏*) and ruminant adipose fat (*e.g.*, bovine & ovine) recorded as *Zhi* (*脂*). A prominent feature of these therapies involves extensively used 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 cosmetic face cream rather than therapeutical ointment as most of the ingredients (*Angelica dahurica*, *Asarumforbesii Maxim*, *Cinnamomumobtusifolium*, *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 in between 533-544 AD. 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 whitening effect, the cream with cattle fat matrix in this study should be face whitening cream. To our knowledge, the Liujiawa case is the earliest evidence for the use of cattle adipose fat as cream matrix for cosmetic formulations in the pre-Qin period, specifically around the time range of Liujiawa Site (700-640 BC), directly demonstrating the handicraft industry use of cattle fat. This was over 1,100 years earlier than the record by agronomist Sixie Jia in *The Essential Techniques for the Welfare of the People*.

4.4 The 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 analyzed in this study, have been observed in a wide area

during the early phase of Spring and Autumn period (Fig. S6, Supporting Information) (Li 2009). These containers were usually present in the tomb of high rank 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 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 of nobility in early stage of the Spring and Autumn period, and the involvement of sorcery/alchemy related ingredient (*e.g.*, the collection of cave minerals) enriched the aestheticism with mysticism 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 can conceal the defects on the skin and mask a layer of luminous homogeneity, enhancing the facial bilateral symmetry in contrast with the black eyelashes and the black hair. Also, the whitened face eliminates the 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 was scarcely 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 BC) was an emerging era for white makeup cosmetics advocating facial attractiveness with white luminance. This aesthetic taste of 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 Chinese cosmetic industry.

Globally, it also yielded an interesting point when comparing the ancient cosmetic cream products in the East and in the West in 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 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 AD in London with ruminant adipose fat as matrix mixed with starch and SnO_2. It was concluded to have acted as cosmetic cream that shares surprising features with modern moisturizing creams (Evershed *et al.* 2004).

5. Conclusion

Residue analysis verifies the earliest cosmetic cream product in China: it has not only pushed forwards the historical description for cosmetic use of ruminant adipose fat (most likely cattle fat) to the early phase of the first millennium BC, but also highlighted the special MHC use resulting from the exploitation of cave minerals along with the *Taoist School Cave Cultus* that adds mysticism elements for the cosmetics aestheticism. The special ingredients and the popularization of similar bronze vessels disclosed the rise of an incipient cosmetics industry in the Spring and Autumn period that still acts as an important part of our daily life. This archaeological residue study showed that apart from being culinary ingredient, animal products were also explored in the handcraft industry of cosmetic 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 cosmetic development.

Conflict of interest

The authors declare that they have no conflict of interest.

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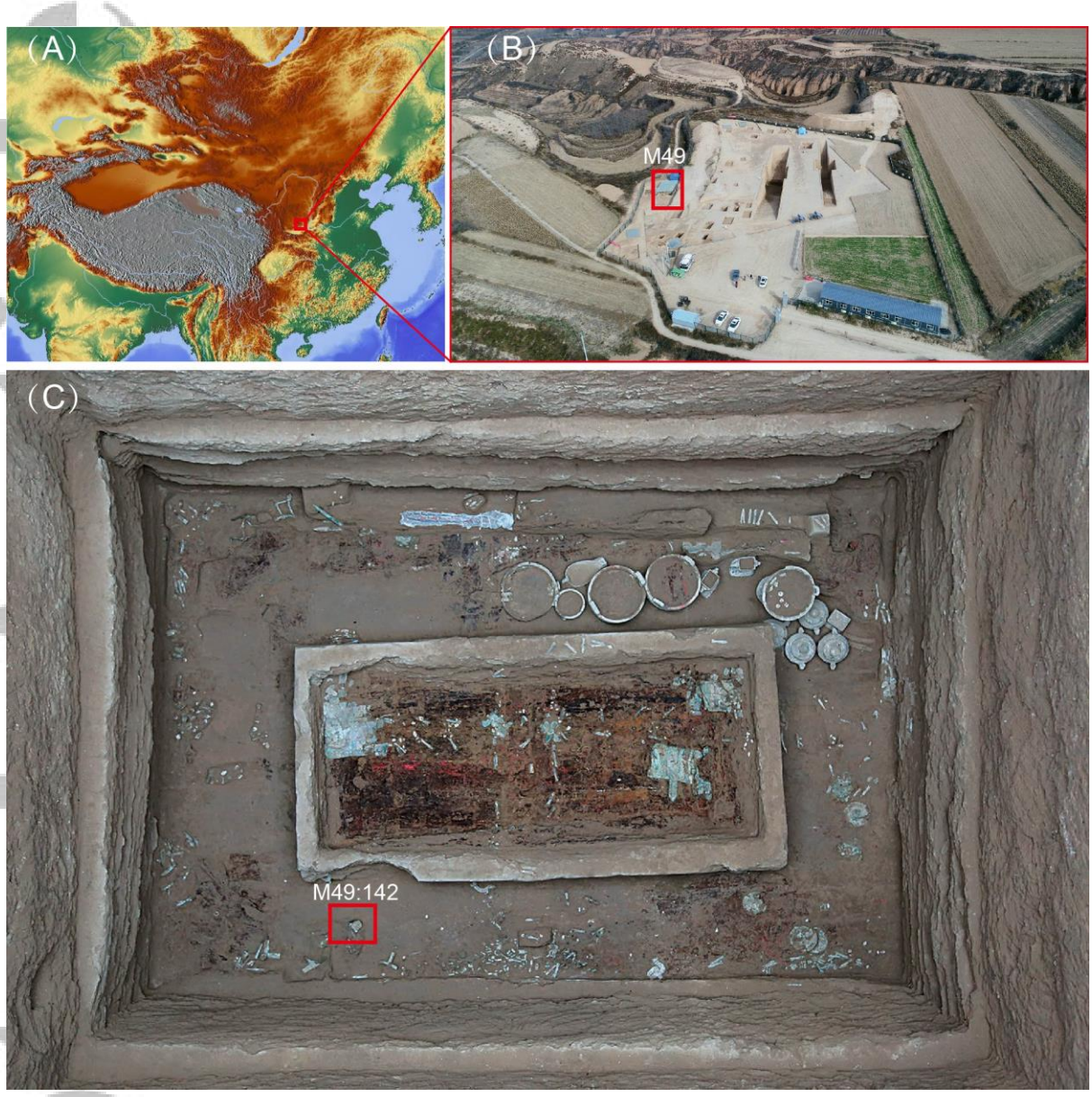

Figure 1 (A) the location of Liujiawa Site indicated by the red rectangle, (B) the landscape of Liujiawa Site and the location of tomb M49 indicated by the red rectangle, (C) the buried artifacts within the tomb M49 and the location of the bronze jar M49:142 indicated by the red rectangle. The plane graph of artifacts in tomb M49 is provided in Fig. S1, Supporting Information.

Figure 2 (A) the bronze jar in situ, (B) the decoration on the bronze jar after cleaning, (C) a large quantity of agglomeration of yellowish white lumps inside the bronze jar.

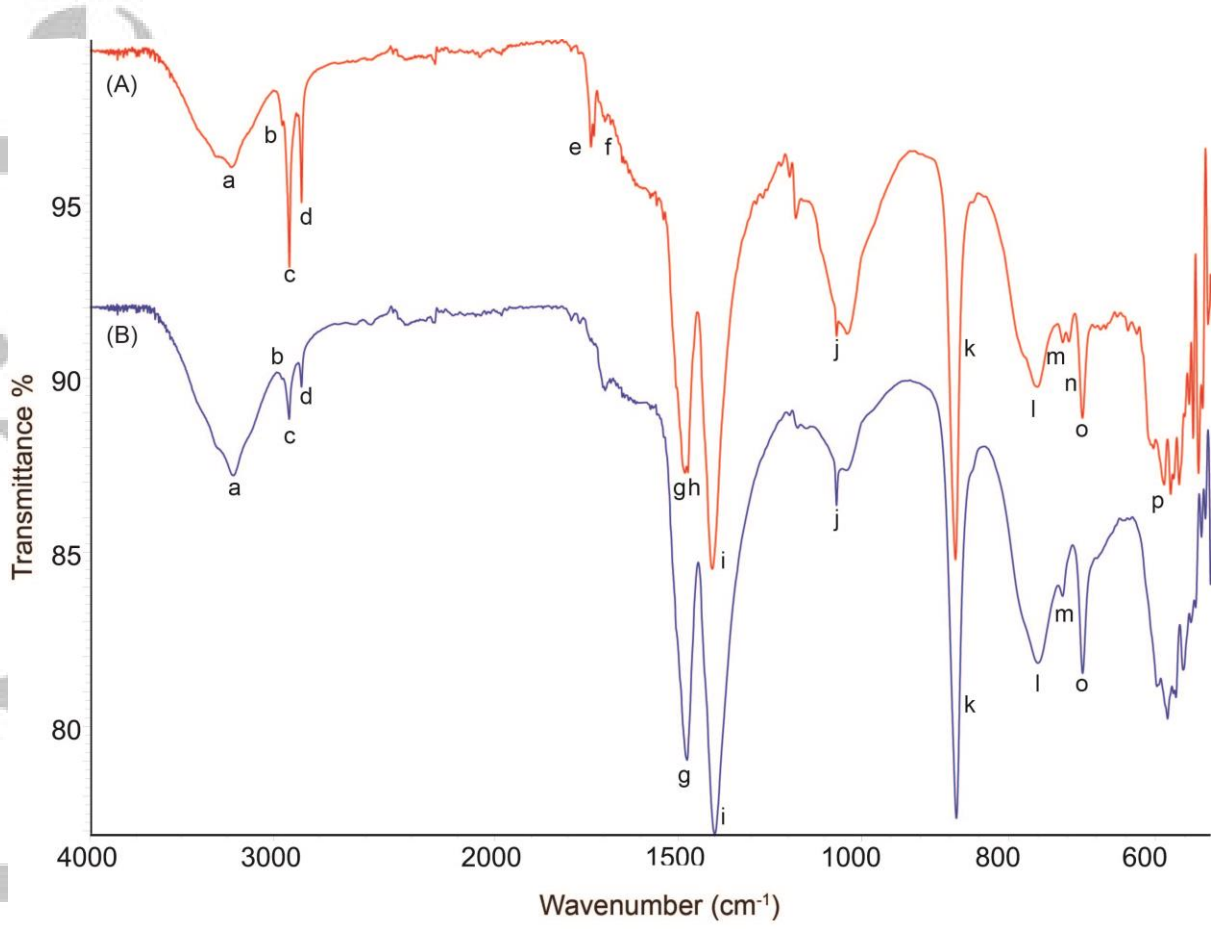

Figure 3 ATR–FTIR spectra of the residue sample: (A) the spectrum collected from the yellowish powder and (B) the spectrum collected from the white particles.

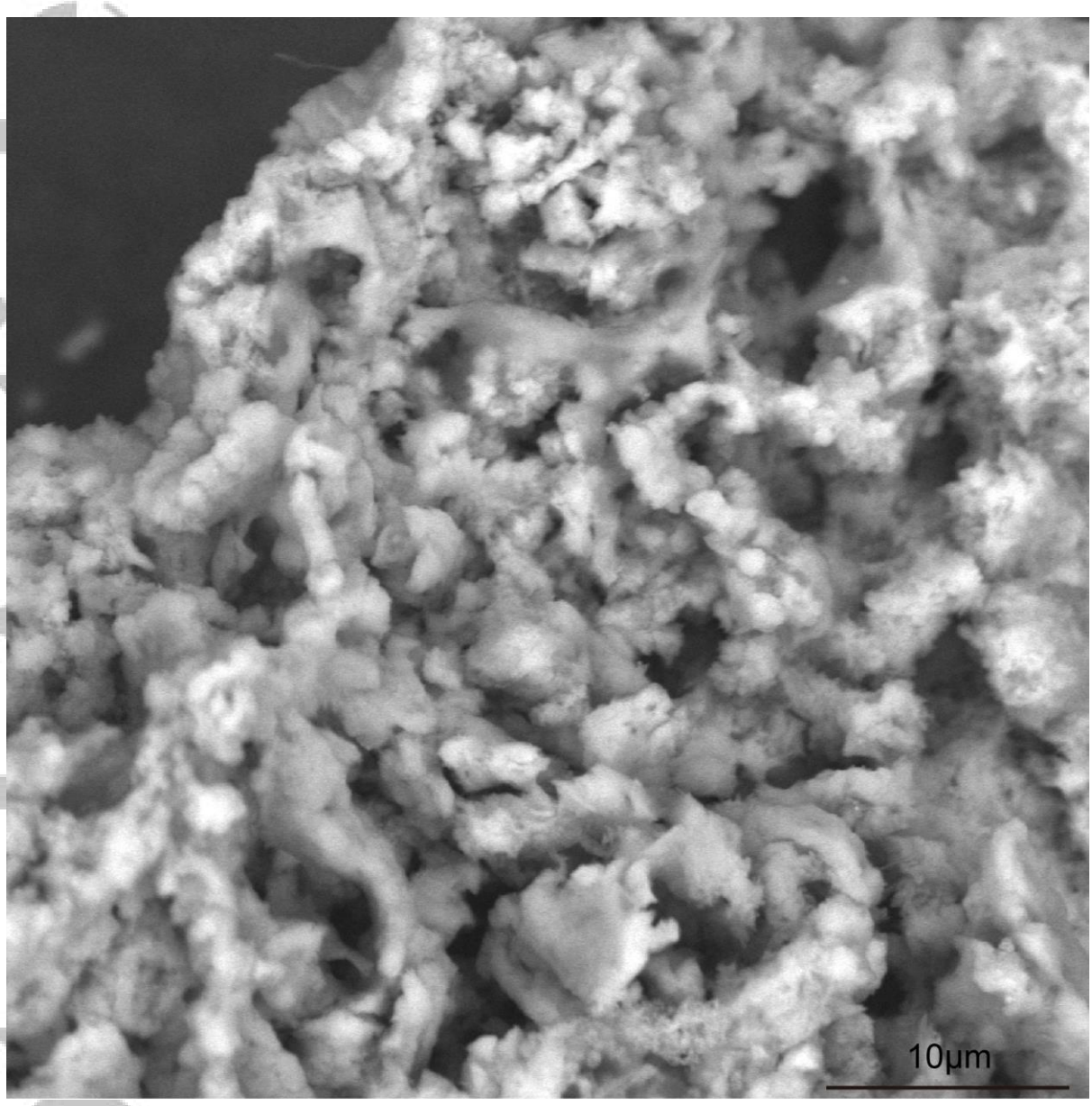

Figure 4 the SEM observation of the residue.

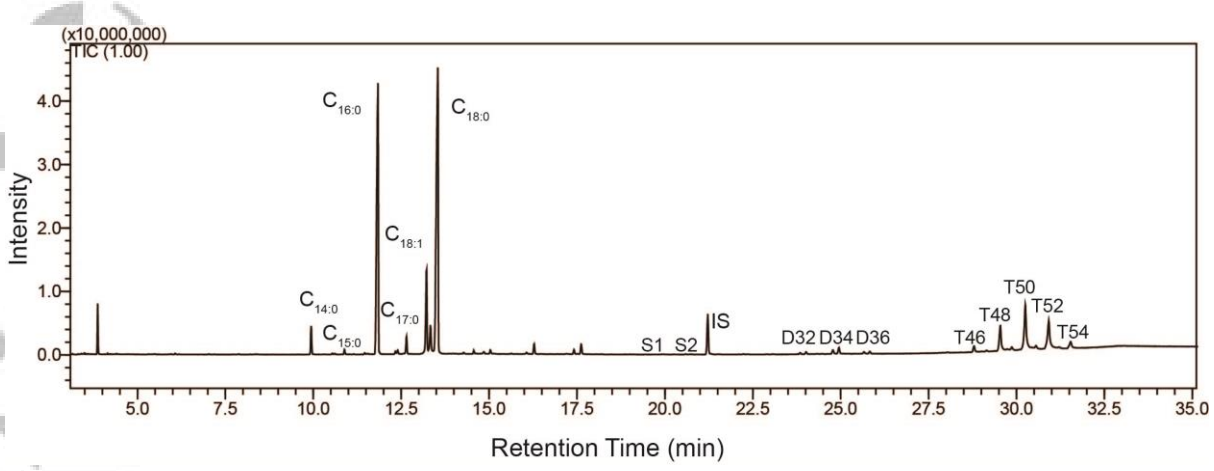

Figure 5 The TIC chromatogram of the residue sample by solvent extraction (trimethylsilylated extracts). $C_{14:0}$, $C_{15:0}$, $C_{16:0}$, $C_{17:0}$, $C_{18:0}$ are saturated fatty acids (determined as their TMS esters) containing 14-18 acyl carbons, respectively; $C_{18:1}$ is mono-unsaturated fatty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

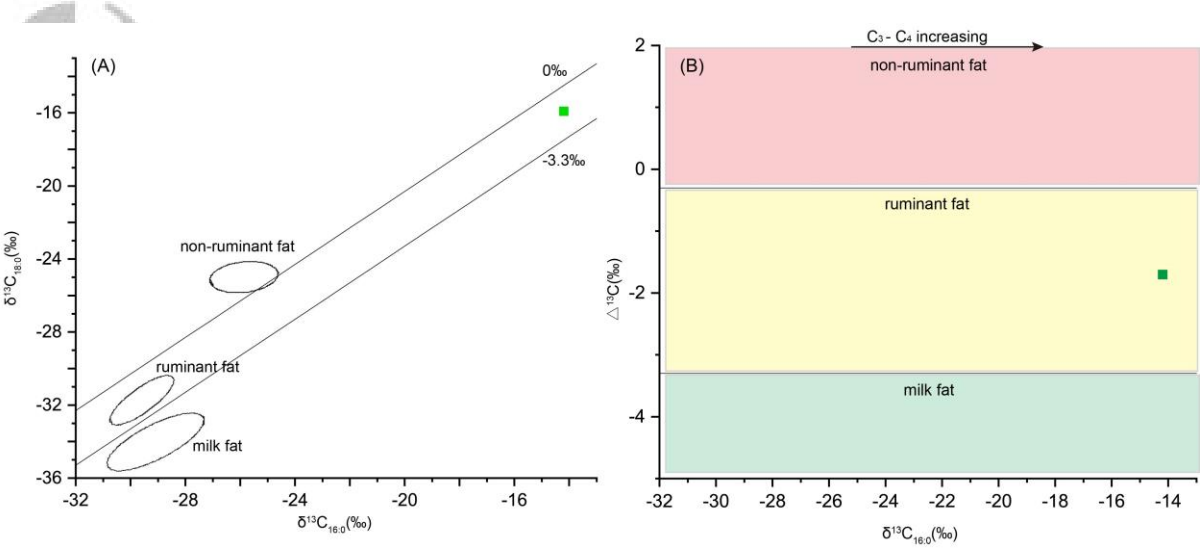

Figure 6 The GC-C-IRMS results of the tested samples $\delta^{13}C_{18:0}$ vs $\delta^{13}C_{16:0}$ (A) and $\triangle^{13}C$ vs $\delta^{13}C_{16:0}$ (B). in (A) and (B), green square represents the isotopic values of the tested residue. In (A), the black circle represents the data set of modern reference based on C_3 plants food web (Copley *et al.* 2003).