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Baltic amber or Burmese amber: FTIR studies on amber artifacts of Eastern Han Dynasty unearthed from Nanyang

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ABSTRACT

There is no case of scientific and technological analysis on archaeological amber of Han Dynasty in China. To estimate the provenance micro-destructively, we have utilized GC/MS (Gas Chromatography-Mass Spectromete) and FTIR (Fourier transform infrared spectroscopy) analysis on the amber artifacts which were excavated from the stone-carved tomb M18 around the 1st century in Nanyang City, Henan Province. GC/MS result suggests that the amber with amount lower than 150 μg is inadequate to detect significant markers. The FTIR spectra have high similarity to Burmese amber without the Baltic shoulder and the absorption peak near 887 cm^{-1}. From this, it appears that the raw materials of these ambers were from Burma and that Burmese amber was transported to the Central China through Yunnan by free circulation in Han Dynasty.

1. Introduction

Amber is a fossil resin derived from different types of conifers through a polymerization process over millions of years. According to mineralogy, amber could be classified as a gemstone of organic origin [1]. Although all hardened amber resins share some common compounds, there are many amber species and varieties due to the region of conifer growth. Amber also shows in a variety of different colors: yellow-orange, pale lemon yellow, brown, black, red, green, and blue. The main areas producing amber are Baltic countries, Burma, Dominica, New Zealand and Northeast China [2].

Amber has a long history of utilization as ornaments. It has also been considered to have healing power in many cultures. In Chinese, amber is called Hu-Po, which means “tiger's soul”. According to archaeological data, the earliest known amber products in China was found in the first sacrificial pit of Sanxingdui Site around 3000 years ago [3]. But there are sporadic discoveries of amber products during and before the Warring States Period (475–221 BCE) [4]. The earliest record of amber in China appeared in Lu Jia's book which was written around 200 BCE From his explain, amber was precious as gold and jade; moreover, people at that time believed that amber was produced in water [5].

Amber artifacts of Han Dynasty (202 BCE–220 CE) have been found in many provinces of China, especially in Southern China (Fig. 1). Detailed information about these sites is shown in Table S1. The number of amber products unearthed in each tomb is generally small. Many archaeological amber pendants and beads are carved into animal and geometric shapes with Chinese local style. A few of the raw amber materials are processed into seals for practical use. The tomb owners are princes and kings, or officials and nobles of high rank. From this point of view, amber in the Han Dynasty was still limited to royal families and upper classes.

However, there were no fewer than 60 discoveries of amber artifacts of Han Dynasty in China [6]. No scientific instrument has ever been used to study these archaeological ambers. On the one hand, merely based on document literatures, some scholars speculated that most of the raw materials of amber in Han Dynasty come from the Baltic Sea and fewer from Burma [5]. But this conjecture has not been tested and validated by any scientific evidence. On the other hand, some researchers only conducted infrared spectrum analysis on the amber products of the museum which have no definite archaeological information. They concluded that the four amber products from Han Dynasty (208 BCE–220 CE) to Jin Dynasty (266–420 CE) were from the Baltic [7]. In addition, it was thought that the Baltic amber had been transported to the Korean peninsula in 6th century [8].

But except for Baltic amber, what other kinds of amber have entered to China then? The lack of scientific basis for the discussion on the source of amber in the Han Dynasty promotes us to carry out relevant work and

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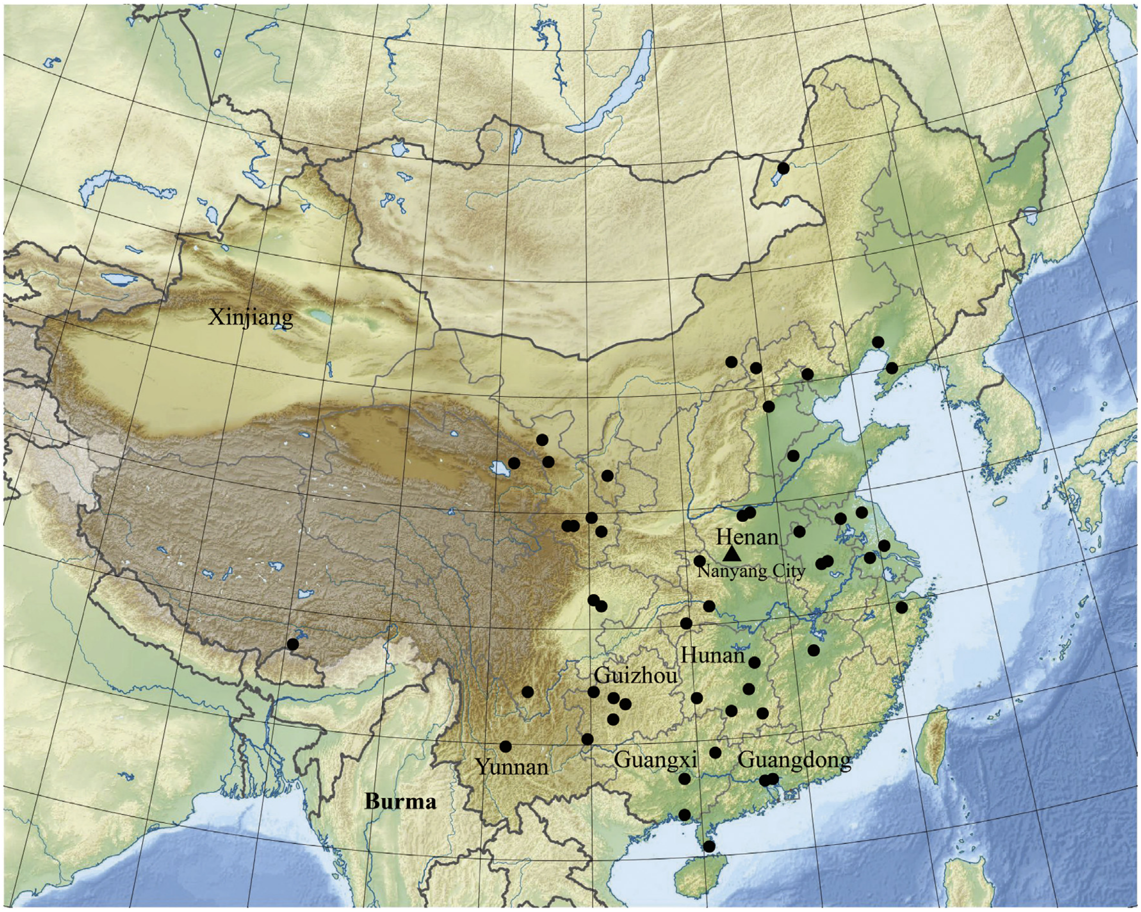

Fig. 1. The distribution of Chinese sites with Han Dynasty amber finds.

Fig. 2. The amber artifacts from the Nanyang city in this study. From left to right is sample 1, 2 and 3.

draw attention from related fields. This study takes ambers unearthed from Nanyang as an example and sheds light on this issue (Fig. 2).

2. Materials and methods

2.1. Archaeological samples

The amber samples in this study were unearthed from the stone-carved tomb M18 in the natatoria of Nanyang sports center. The tomb owner is a senior officials in the Eastern Han Dynasty (25–220 CE). When it was excavated in 2015, various relics amounting to hundreds of pieces were found including potteries, bronzes, golds, jades, crystals and agates. The number of amber artifacts is 5 in total. They all have perforations and similar color and transparency. After consultation with Institute of Cultural Relic Research of Nanyang City, we selected 3 of them which have neater surface and better preservation. The descriptions and pictures are shown in Table 1 and Fig. 1. The other two ambers are an oval bead and a geometric ornament. They are all relatively intact and no fragments have been found at the archaeological site. Since cultural relics are quite precious, we have only to adopt small-invasive methods for research. After detailed consulting with the local institution and the archaeologists, we obtained permission to sample from a small area in the perforation of amber artifact sample 3, which will do no damage to its appearance.

2.2. GC/MS analysis

Samples peeled off are shown in Fig. 3. Approximately 150 μg was extracted three times using 3 ml of dichloromethane/methanol (2:1 *v*/*v*; sonication for 15 min). After centrifugation, the extraction was combined and evaporated until dryness under a stream of nitrogen. The retained dry residue was then treated with a mixture of 50 μl of acetonitrile, and 100 μl of BSTFA for 30 min at 60 °C. After evaporation of the derivatization reagent, the resulting trimethylsilyl derivatives were redissolved with 90 μl of *n*-hexane. 10 μl of internal standard (n-tetratriacontane) was added.

GC/MS analysis was performed with 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 phase thickness of 0.1 μm. A 1 μl volume of the sample was injected in the splitless mode. The oven temperature program was as follows: initial temperature 70 degree Celsius (°C) for 1 min; increased to 100 °C (1 min) at 15 °C/min; then increased to 320 °C at 10 °C/min; 320 °C was maintained for 10 min. Helium was used as the carrier gas. The injector and aux-heater temperatures were set at 300 and 320 °C, respectively. The qualitative analysis was carried out under full-scan acquisition mode within the 50–650 u range.

Table 1
The basic information of amber artifacts excavated from the Nanyang city.

No.	Shape	Description
Sample 1	Amber seal	The color is blood red and the surface is mottled. The transparency of decreases due to soil percolation. The original cutting marks and shape are clear. The knob of the amber seal is a beast in a prostrate position and there is a perforation in the middle. But no engraving on the seal indicates that it may be a semi-finished product.
Sample 2	Amer bird	The color is blood red, the surface is slightly mottled. The knife marks are clearly visible. There is a perforation in the middle of the bird's body and the hole edge is naturally worn. It should be the result of long-term wearing with a string.
Sample 3	Amer bead	The color is dark red with poor transparency and glossiness. The surface has small disintegration and damage. The sample is symmetrical with small round protuberances at both ends and two ridges in the middle. The side has a perforation and the hole mouth has natural wear marks.

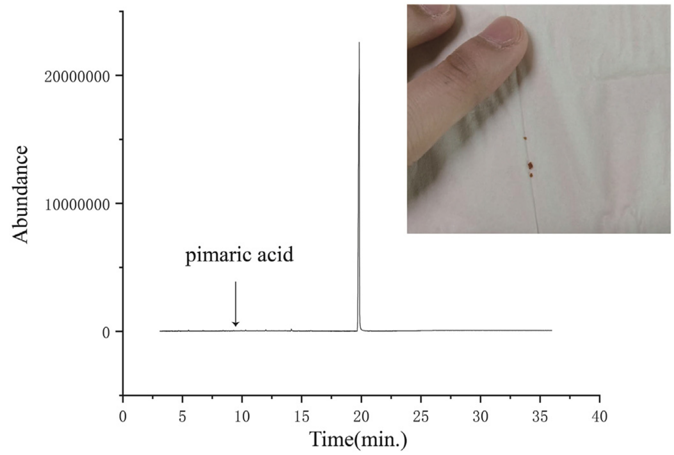

Fig. 3. Gas chromatogram of the sample 3.

2.3. FTIR measurement

Infrared (IR) spectroscopy is probably the most widely used and practical method for the structural characterization and discrimination of amber types. Because the polymerization process preserves all the original functional groups of the compounds found in amber structure with the exception of C=C double bond which suffers a saturation process by exposure to air [9,10]. The ambers from different localities exit the different IR absorption bands and strength according to different polymeric grade. The first extensive IR studies on amber were begun in the 1960s by Curt W. Beck of the Amber Research Laboratory [11]. Many amber types have been recognized on the basis of characteristic IR spectra subsequently.

Fourier transform infrared spectroscopy (FTIR) is a more advanced method which provides high spectral resolution and short collection times. It could be used as a non-destructive technique without sample preparation, through the use of attenuated total reflection with a diamond crystal [12]. Therefore, in this study, FTIR analysis was performed and the source of the amber was estimated from the review of these and previous results.

FTIR spectra of amber samples were obtained with infrared spectrophotometer (ALPHA, Bruker, Germany) without any pre-treatment. The spectra were recorded in attenuated total reflection mode. All the spectra were acquired between 4000 and 600 cm^{-1} with 24 accumulations and a spectral resolution of 4 cm^{-1}.

3. Results and discussion

3.1. Result of GC/MS

The gas chromatogram of sample 3 is shown in Fig. 3. Because the amount of sampling is awfully small and the experiment opportunity is only once, the result is not very good. Many undesired peaks including internal standard, column loss, and some silane compounds etc., drowned the marking signals of amber. The detected marker was only pimaric acid at 9.509 and the matching degree was 13%.

Previous studies have shown that good results can be achieved at 500 μg [8], more than three times the amount used this time. Hence, the unsatisfactory results of this study suggest that the sampling amount of archaeological amber should reach 500 μg for the sake of prudence.

3.2. Result of FTIR

However, we have to focus on the FTIR part. Fig. 4 presents the FTIR spectra of archaeological amber samples (1–3). The data of four other ancient amber artifacts (A–D) in museum collections which considered

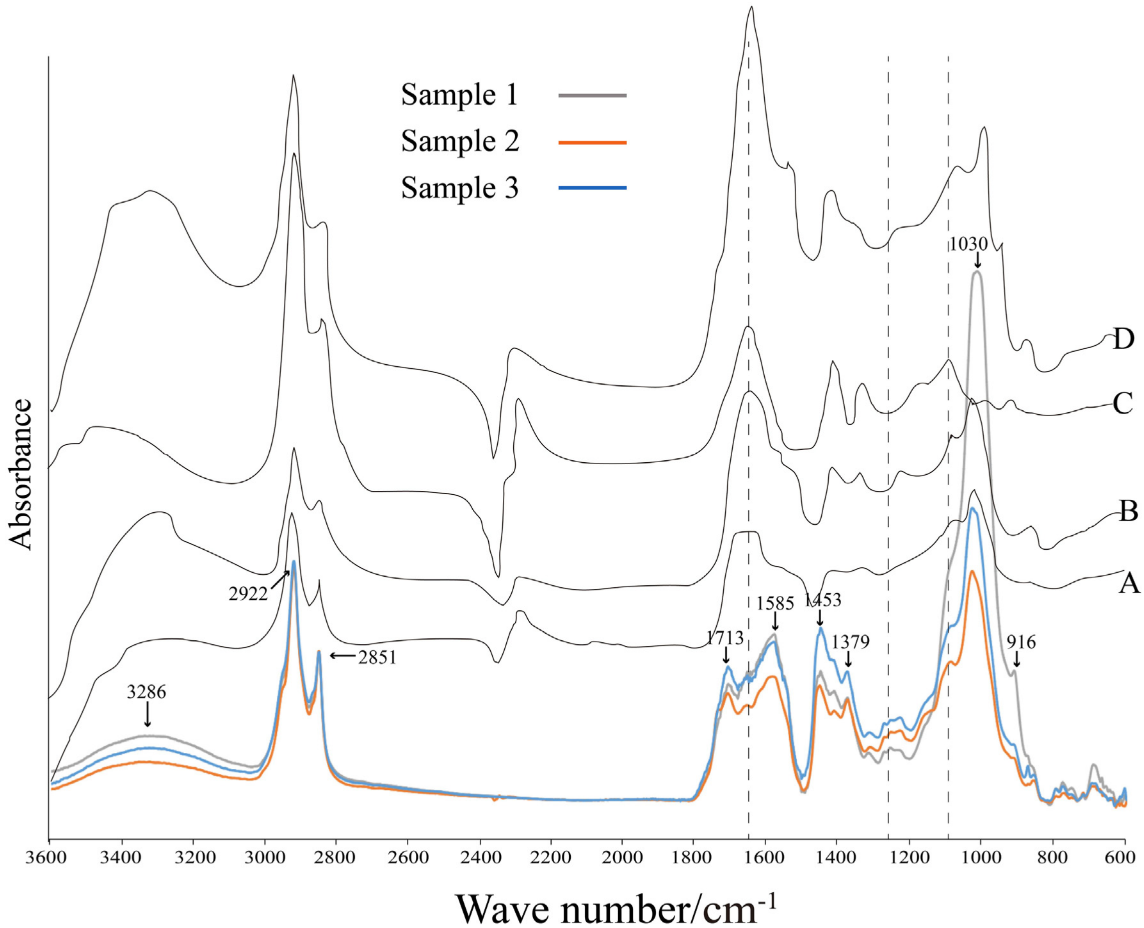

Fig. 4. FTIR spectra of archaeological amber samples 1–3 and four other ancient ambers for comparison.

as Baltic amber are also shown for comparison [7]. The determination is affected by the heterogeneity of the amber, as consequence the obtained spectra depend on the analysed part of the sample. All of them have similar spectra, irrespective of the physical appearance. Absorption peaks are caused by molecular vibrations that make up the polymer skeleton. The spectra shows the characteristic absorption bands of vibrations in a number of functional groups. The presence of functional groups are equally distributed. Therefore it could be considered that the analytic information supplied by FTIR is acceptable.

A gentle absorption peak near 3286 cm^{-1} is due to the OH stretching bands of alcohols and/or carboxylic acids. The bands corresponding to the alkyl stretching show, between 3000 and 2800 cm^{-1}, a characteristic pattern with a principal band at 2922 cm^{-1} and a secondary bands at 2851 cm^{-1} of comparable intensities. The symmetric vibrations of CH_3 occurs at 2922 cm^{-1} while the symmetric stretching absorption band of the methylene group occur at 2851 cm^{-1}. This wave-number range indicates an important level of methyl groups in amber structure. Two other bands can be assigned to alkyl groups: the first between 1460 cm^{-1} and 1420 cm^{-1} involve bending vibration of CH_2 and asymmetric bending vibration of CH_3, the second at 1379 cm^{-1} is only due to symmetric bending vibration of CH_3. It shows that the basic skeleton of amber is aliphatic structure [2]. A strong absorption peak at 1713 cm^{-1} is assigned to the C═O stretching and it is a typical infrared absorption peak of petrochemical resin. Compounds such as abietic acid, pimaric acid, succinic acid, communic acid are the examples in case of amber [8]. A strong absorption peak at 1585 cm^{-1} is attributed intramolecular H bonds of the alcohols group. A relatively strong absorption at 1480 cm^{-1}–1300 cm^{-1} is due to the C—H bending mode. The peak near 1030 cm^{-1} is attributed to C—O stretching vibration of the ester group, while its intensity and precise location on the cm^{-1} axis vary depending on the influence exerted by the ester C═O double bond [12].

The infrared spectra of amber from different habitats have some common characteristics. But there are still differences in the positions or relative strengths of some absorption peaks. Wang et al. (2015) have demonstrated that there are no notable differences in the FTIR characteristics with reflection mode and tabletting method. We have estimated the archaeological ambers based on previous study on geological amber samples from the Baltic, Burma, Dominica and Fushun, China (Table 2). Following are some detailed comparisons and illustrations:

a. Regardless of the IR technique applied, ambers from different localities have similar spectra in the 2800–3000 cm^{-1} region. There is no

Table 2
FTIR characteristics and comparisons of amber from different provenances (based on [13,14];'-' represents not notable).

Band, cm^{-1}	Functional groups	Baltic amber	Burmese amber	Dominican amber	Fushun amber
3082	C=C stretching	Weak	–	Weak	–
3060–3027	C=C stretching	–	–	–	–
2850–2926	H asymmetric stretching	Strong	Strong	Strong	Strong
1710–1737	C=O stretching	Strong	Strong	Strong	Strong
1696–1705	C=O stretching	–	Weak	Weak	Weak
1450–1458	H asymmetric bending	Strong	Strong	Strong	Strong
1373–1384	C-H symmetric bending	Strong	Strong	Strong	Strong
1220–1250	C-O stretching	–	–	Medium	–
1160–1220	C-O stretching	Medium	–	–	–
886–888	C=C deformations	Medium	–	Medium	Weak

absorption peak near 3082 cm^{-1} appearing in the archaeological ambers which is different from Baltic amber and Dominican amber. Actually, the peak in samples A–D is not significant either.

b. There are vibration frequency shifts determined by the degree of ethers and esters formation, correlated to the number of functional groups from the chain and showing evidence on the intramolecular bounds. For example, a shift in the infrared bands ascribed to C—C bend from 1585 cm^{-1} to the ambers in this study while it occurs around 1640 cm^{-1} to most ambers. This position is marked with dotted lines in Fig. 4. Sample A has a flat hump and samples B–D have sharp peaks indeed. It suggests a transition from conjugated to isolated double bonds in these archaeological ambers, which may be related to the formation time [9].

c. A significant shoulder near 1250 cm^{-1}–1110 cm^{-1} called 'Baltic shoulder' is known to appear mainly in Baltic amber [12]. This phenomenon can be clearly observed in samples A–D. Moreover, there is always a absorption peak at 1160-1220 cm^{-1} caused by C—O stretching in Baltic amber [2]. Sample B has a remarkable peak within this area. However, the archaeological ambers do not possess the above characteristics.

d. An important difference in spectra is registered for absorption bands from 950 to 850 cm^{-1} region. A sharp peak near 887 cm^{-1} is assigned to $C{=}CH_2$ out of plane bending and is derived from C=C double bond. Its intensity depends on the age of fossil resin [2]. However, one peak seemingly appears near 917 cm^{-1} in the spectrum of sample 1, while samples 2–3 are not obvious here. The absence of the band 887 cm^{-1} indicates that the contraction-reticulation of the polymeric chain is finished [15]. But samples B–D have absorption peak within the 950–850 cm^{-1} region, though shifting may happen in some situations. It also shows that they were formed late. In summary, from the FTIR spectra, the archaeological samples and reference samples are definitely not from the same origin.

Zircon U—Pb dating shows the formation age of Burmese amber is 98.79 ± 0.62 Ma. Baltic amber was formed in the early Tertiary (around 65 Ma). Approximate age of Dominican amber is 26–15 Ma. The age of Fushun amber is between Burmese amber and Baltic amber [16]. As polymerization proceeds, cross-linkage between chains of labdanoid diterpene takes place as copal changes to amber and continues as amber structurally matures. The decreasing amount of exocyclic methylene double bonds weakens the peaks near 1645 cm^{-1} and 888 cm^{-1} in infrared spectra gradually [17]. The existence of these peaks indicates that the polymerization time of amber is relatively short and the formation age is late. In short, according to the formation time, the order of amber from several areas is as follows: Burmese amber, Fushun amber, Baltic amber and Dominican amber. Based on this, the archaeological ambers should belong to Burmese amber. Moreover, Burmese amber is usually blackish brown in its color with low transparency, and its surface often covered with white powder. This is consistent with these archaeological ambers.

In fact, some literatures of the Han Dynasty recorded the source of amber. There are three main statements: Kophen (the kingdom of Kabul, now Kashmir region), Roman Empire, Ailao Country (now in Yunnan Province). These places are not the actual provenances of amber due to the limited knowledge of the ancients. But they are certainly important stops on the amber route to China. From the distribution of Chinese sites with Han Dynasty amber, they are not so centralized in the capital area. Hence, it is likely that ambers were freely circulated and traded, not absolutely monopolized by the central government. The entering of Burmese amber to China is mainly after Emperor Wudi of Han Dynasty opening the passage with India. The archaeological amber artifacts from Nanyang indicate that Burmese amber was more common in Central Plains at that time.

4. Conclusions

The archaeological ambers of the Han Dynasty unearthed in Nanyang have same color and transparency as Burmese Amber. Thier FTIR spectra do not possess the Baltic shoulder and the absorption peak near 887 cm^{-1}, also consistent with Burmese amber rather than Baltic amber and Fushun amber. They should be exported to the Central China through Yunnan from Burma by free circulation. Additionally, GC/MS result indicates that the amber sample lower than 150 μg is insufficient to detect significant markers and 500 μg is a recommended amount.

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