Journal of Archaeological Science 59 (2015) 211–218

Contents lists available at ScienceDirect

Journal of Archaeological Science

journal homepage: http://www.elsevier.com/locate/jas

The identification of binding agent used in late Shang Dynasty turquoise-inlayed bronze objects excavated in Anyang

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ARTICLE INFO

Article history:
Received 9 November 2014
Received in revised form
4 April 2015
Accepted 24 April 2015
Available online 11 May 2015

Keywords:
Py-GC/MS
GC/MS
Urushi
Plant oil
Turquoise-inlayed bronze
Binding agents

ABSTRACT

The paper presents the results of the analysis of the binding media used in turquoise-inlay bronze artifacts in late Shang Dynasty, which were excavated in Anyang, Henan Province of China. Techniques applied include pyrolysis gas chromatography and mass spectrometry with thermal assisted hydrolysis and methylation (THM-Py-GC/MS), as well as GC/MS with derivatization reagent of MethPrep II. Marker compounds of urushi including methylated pentadecyl catechol and the oxidation products: 6-(2,3-dihydroxyphenyl) hexanoic acid; 7-(2,3-dihydroxyphenyl) heptanoic acid and 8-(2,3-dihydroxyphenyl) octanoic acid as their methylated forms were found, indicating Urushi (lacquer) was used as binding agents for the inlay. In addition, a series of fatty acids was detected with relative higher concentration of azelaic acid, which represents the presence of plant oil in the sample. Furthermore, a group of glue marker compounds and a series of long-chain fatty acids as well as a group of long-chain alcohols were detected in the sample.

1. Introduction

Yin Ruin, located in the northwest suburb of Anyang City in Henan Province, the capital city of Shang Dynasty, is the only documented Shang capital site in ancient literature that is confirmed by archaeological excavations. In Yin Ruin area, a number of great archaeological findings have been discovered, which include twelve royal tombs, more than one hundred palaces and royal temples building foundations, Huanbei Shang city and Oracle cellars etc. (Institute of Archaeology, Chinese Academy of Social Sciences, 1987). Thus, due to its unique importance in archaeology, Yin Ruin was listed in the UNESCO World Heritage Sites in 2006. The Shang Dynasty tombs, located in Huanyuan Zhuang east in Anyang, were excavated from 1992 to 2002 (Institute of Archaeology, Chinese Academy of Social Sciences, 2007). In tomb M54, many precious bronze swords, arrows, vessels, jade artifacts and ceramics were found (Fig. 1). Especially, one group of objects, namely six bow-shaped bronzes with beautiful turquoise inlay on the surface were unearthed. The turquoise was nicely cut and inlayed as a special pattern – the Tao tie pattern, which represents a mysterious monster from Chinese legend. The function of those objects is still unclear. Some researchers thought that they were used during ritual practice, while others said they were the parts of a carriage, but where and how they were used in the carriage remains unclear.

Turquoise is a hydrous phosphate of copper and aluminum, $(CuAl_6(PO_4)_4(OH)_8 4H_2O)$, which was highly valued and used as ornaments in ancient time in China due to its beautiful colour. In the last decades, many precious turquoise-inlaid artifacts were found by archaeologist from noble tombs (Hao and Hao, 2002; Guo, 2008; Ding and Zhu, 1996; Hu, 1993). The earliest ones are the turquoise Goddess (a human-sized female statue with eyes decorated with turquoises) from the Hongshan Culture (4500–2250 BC) and turquoise-inlaid jade artifacts from the Liangzhu Culture (5000–4800 BC) (Zhang, 1996; Guo, 2008). After its presentation to the public, the technique of how the turquoise inlay was made attracted the attention of the people (Archaeological Team at Dan jiang Dam of Henan Province, 1980; Henan Institute of Cultural Relics and Archaeology, 2004; Shi and Cai, 2007.). At the beginning, there has been a debate on whether binding agents were used for the turquoise inlay until it was realized that there were indeed binding agents between the turquoise and the substrate. The question then arose what kinds of materials were used to fix the

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http://dx.doi.org/10.1016/j.jas.2015.04.021
0305-4403/

Fig. 1. Photo of the tomb M 54 excavated in Huanyuan Zhuang in Anyang city.

inlay during the ancient time. One paper reported that the whitish residues sampled from an Eastern Zhou (770–256 BC) turquoise-inlaid bronze sword are chemically similar to shellac by using Fourier Transform Infrared Spectroscopy (FTIR), Scanning Electron Microscope and Energy Dispersive X-Ray Spectrometer (SEM/EDS) techniques analysis (Cheng et al., 2008). In a more recent publication, a sword with turquoise embedded in its handle from Qiaojiayuan in northwestern Hubei Province (central China), dating back to Chu state (6th–5th BC) was studied. The binding agents to stick the turquoise on the bronze sword were identified as beeswax by using FTIR and X-Ray Diffraction (XRD) techniques (Luo et al., 2012). However, the authors suggested the samples still need to be studied with other analytical methods to see whether ingredients other than beeswax are present. Other materials such as lacquer was used as coating materials for objects and also for binding media in ancient time in China (Bonaduce et al., 2008; Wei et al., 2011). For example, a mixture of Chinese lacquer and lime milk was identified as binding agent to bond the gold foil to the bronze base unearthed at the Sanxingdui site (ca. 2800–800 BC) in southwestern China (Zeng, 2005). It will be also interesting to study the samples from different times and areas to see whether other binding agents were used to inlay turquoise.

In ancient times in China, the possible materials used as binding reagents could be drying oils, lacquer, resins and waxes etc. (Chen, 2003). Lacquer originates as the sap of lac trees and is tapped from the tree. According to the region of the tree origin, there are mainly three types of oriental lacquers – *Rhus vernicifera* (the phenol derivative is urushiol), *Rhus succedanea* (the phenol derivative is laccol) and *Melanorrhoea usitate* (the phenol derivative is thitsiol) (Niimura et al., 1999). These monomers are considered as the most characteristic markers to distinguish particular lacquer (Lu et al., 2006). Lacquer film is a cross-linked polymer that polymerised by laccase and it is insoluble in most solvents. Due to this fact, only a few analytical techniques are available for the scientific investigation. Pyrolysis-gas chromatography and mass spectrometry Py-GC/MS (Niimura et al., 1996, 1999; Niimura and Miyakoshi, 2006; Lu et al., 2006, 2007a, b; Kumanotani, 1995, 1998; Burmester, 1988; Frade et al., 2009) have been mostly applied. The advantage of the Py-GC/MS is that no sample preparation or pre-treatments of the specimen is necessary and only a very small amount of sample is required. However, one of the main problems of the pyrolysis technique is, when confronted to the polar compounds of acidic and alcoholic pyrolysis products, causing a rather low reproducibility of the resulting pyrograms. Moreover, the high fragmentation of natural macromolecules during pyrolysis forms many unspecific compounds. To overcome these problems, Py-GC/MS with thermal assisted hydrolysis and methylation technique were applied (Mazzeo et al., 2004; Cappitelli et al., 2002; Chiavari et al., 2001; Piccirillo et al., 2005; Le Hô et al., 2012; Schilling, 2014). Tetramethylammonium hydroxide (TMAH) is one of the most commonly used reagents for the online methylation of acidic and alcoholic moieties. Py-GC/MS with thermal assisted hydrolysis and methylation (THM) reagent of TMAH were successfully used to simultaneously characterize binding media used in artifacts such as drying oil, lacquer etc. (Schilling, 2012).

The technique of gas chromatography coupled to mass spectrometry (GC/MS) was used to identify binding media of drying oil, resin and wax in artworks or archaeological objects (Cappitelli et al., 2002; Challinor, 1996; Pitthard et al., 2006; Bonaduce et al., 2009). The GC/MS analytical procedure for the analysis of lipids is based on the transesterification of fatty acids and the determination of their relative ratios to identify particular lipids, while the analytical procedure for the analysis of resinous binding media is based on the esterification of resinous acids followed by the identification of particular resins according to their resinous acid methyl esters (Pitthard et al., 2010; Colombini and Modugno, 2009; Valianou et al., 2011). Samples from archaeological context are normally very difficult due to their complex environment and long term ageing. The analyses results of archaeological samples by THM-Py-GC/MS and GC/MS techniques can complement or approve each other to provide unambiguous information. Thus in this study, techniques including THM-Py-GC/MS with in situ methylation reagent of tetramethylammonium hydroxide (TMAH) and GC/MS techniques were carried out for the identification of the binding agents used in turquoise inlayed into the bow-shape bronze artifacts from Shang Dynasty in Anyang Yin Ruin. The results are significant for archaeologist to further study and compare the materials used to inlay turquoise on bronze in different periods, and to find out the inherence and change of the materials used in the history. The information will be also helpful for making conservation treatment strategy in the future.

2. Experimental

2.1. The samples

The binding agent samples were taken with a scalpel from the objects of M54-203 and M54-303, where the turquoise is lost, but

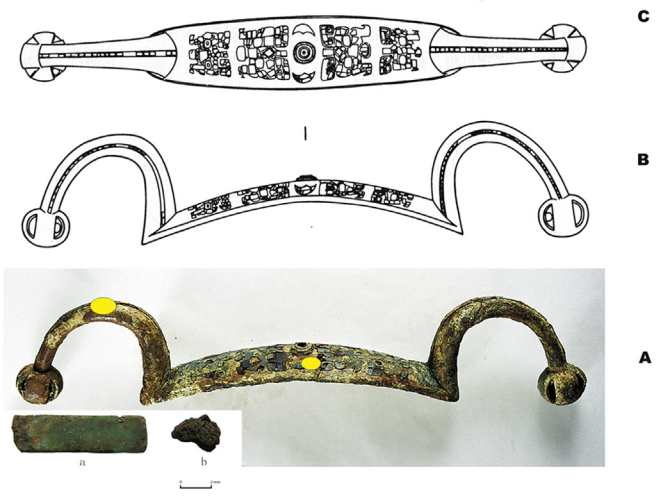

Fig. 2. A. The turquoise inlay bow-like bronze ware (M54-303), the yellow areas indicate where samples were taken; B. Schematic graph of M54-303 side view; C. Schematic graph of M54-303 vertical view; a) one piece of turquoise; b) an assay binding agent sample. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).