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Scientific investigation of the paint and adhesive materials used in the Western Han dynasty polychromy terracotta army, Qingzhou, China

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ABSTRACT

A royal tomb of early period of the Western Han dynasty (206 B.C–8 A.D) was excavated by archaeologists in Qingzhou County, Shandong Province in 2006. Over 2000 polychromy terracotta soldiers, horses, chariots, servants etc. were unearthed from the tomb. All the terracotta figures are one quarter or one sixth as large as the livings, most of them were painted with well designed patterns. In order to gain complete information about the materials and techniques used for the polychromy on the terracotta army, five samples from the painted areas were taken. In addition, one sample from the area to adhere one leg to the ploychromy horse body was also obtained. The analytical techniques applied include XRF, FTIR, Py-GC/MS and GC/MS. Chinese purple, cinnabar, lead red and ochre were used as pigments, while animal glue was identified as binding medium and adhesive in the polychromy terracotta army in the Han Dynasty. The results definitely will provide new evidence about the materials and technologies used in Han Dynasty. Especially, the binding medium identified is different in comparison with Qin Shihuang's terracotta army (259–210 BC).

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1. Introduction

A Han dynasty royal tomb was excavated in Xiangshan, Qingzhou county, Shandong province, China in 2006. The tomb pit is about 7.3 m long (south to north) and 5.1 m wide (east to west). It dates back to early Western Han period (206–8 AD). About 2000 polychromy terracotta army, carriages and horses were found in this pit (Liu, 2006). All the terracotta figures are one quarter or one sixth as large as the livings. They were arranged in a certain order to imitate the scene of a real situation. The figures of the terracotta army were made with different clothing style and painted in very well designed patterns. Fortunately, they are well preserved with bright colour; most of the colours used are red, white and purple. It is another great discovery after Qin Shihuang's terracotta army (259–210 BC), which definitely provides new evidence of the Han dynasty cloth style, the techniques of making pottery and colour paints etc. Archaeologists and art historians conclude the results of the new discovery and suggest that the Chinese in the Qin and Han dynasties probably made a regular practice of burying the bodies of their royals and nobles with a symbolic military escort. By comparing with the polychromy of Qin Shihuang's terracotta army, the size of Qingzhou Han dynasty terracotta army is smaller. Small terracotta armies were also found in other Han dynasty tombs, such as in Yangling, Shanxi and Xuzhou, Jiangsu province, which indicate the thought of the people in Han dynasty has changed in comparison to Qin dynasty. The people in Han dynasty started to use smaller terracotta figures as a symbol to achieve the same purpose as in Qin dynasty.

In the past, several studies of materials used for the polychromy of pottery in China have been reported. The earliest painted pottery found in Zhicheng county, Hubei province (4400–3300 BC), was studied resulting cinnabar as pigment on the pottery plate (Chen and Yang, 1984). Another important painted pottery was found in Dadiwang site (late Yang shao Culture, 3000 BC). The main pigments identified were chalk and cinnabar (Zheng, 1986), but until now little was known about the binding media in the paintings. Recently, egg was reported as binding medium used in polychromy Qin Shihuang's terracotta army (Bonaduce et al., 2008), while animal glue was identified as binding medium in Dunhuang wall paintings by HPLC technique (Li, 1995; Su, 2000), as well as in the wall paintings from Tang dynasty tombs (Wei et al., 2011a). In order to compare the techniques and materials used in paints in different periods and to provide scientific support for the protection of those valuable cultural relics, two of the Han dynasty

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polychromy terracotta army and a horse excavated in Xiangshan, Qingzhou county are investigated in this study, which are depicted in Fig. 1a–c.

In the literature, a number of instrumental techniques were applied for the identification of pigments, such as X-ray Fluorescence Analysis (XRF) (Neelmeijer et al., 2000), X-ray Microanalysis in a Scanning Electron Microscope (SEM/EDX) (Manzano et al., 2000) or X-ray Diffraction (XRD) (Mantler et al., 2000). The study of pigments in Chinese artefacts, such as Chinese purple and blue also known as Han blue ($BaCuSi_4O_{10}$) and Han purple ($BaCuSi_2O_6$) by Raman and SEM has been reported (Ma et al., 2006). Han purple and Han blue are synthetic barium copper silicate pigments that were developed in China at least 2000 years ago. It is known that those pigments were in use by the late Western Zhou dynasty (800 BCE) until the end of the Han dynasty (Liu et al., 2007). Those pigments were found in artifacts of beads, earrings, and octagonal sticks, as well as in paint layers of the terracotta army from the Qin dynasty (221–207 BCE) and on wall paintings of Han dynasty tombs (206 BCE–220 CE) (Heinz et al., 2010). Recently, Chinese purple was also identified in the paint layer of those Han dynasty terracotta army (Zhang et al., 2010). The identification of organic materials is still a challenge due to the complexity of the organic compounds, which are not stable, thus making it necessary to use and combine information from several steps of investigations. The main techniques used for the characterization of binding media in artworks include Fourier Transform Infrared Spectroscopy (FTIR) (Capitelli and Koussiaki, 2006), High Performance Liquid Chromatography (HPLC) (Peris-Vicente et al., 2005), Gas Chromatography Mass Spectrometry (GC/MS) (Andreotti et al., 2006 and Marinach et al., 2004) and Pyrolysis Gas Chromatography Mass Spectrometry (Py-GC/MS) (Piccirillo et al., 2005 and Capitelli et al., 2002). As known, GC analysis requires the transformation of the polar and non-volatile organic compounds into more volatile ones and these derivatives, typically following a preceding extraction and hydrolysis step, can be identified. Common derivatization reagents for this task are N-methyl-N-(terbutyldimethylsilyl) trifluoroacetamide (MTBSTFA), (m-trifluoromethylphenyl) trimethylammonium hydroxide (TFTMAH) (Pitthard et al., 2006), and trimethyl sulfoniumhydroxide (TMSH) which have been reported being effective for the analysis of fatty acids (Baumer et al., 2009; Dron et al., 2004; Wei et al., 2011a). Similarly, hydrolysed amino acids from proteinaceous binders of paintings can be effectively derivatized by the use of MTBSTFA in pyridine (Colombini et al., 1998) and ethyl chloroformate (ECF) (Mateo Castro et al., 1997; Wei et al., 2011a; Valianou et al., 2011). The identification of proteins is based on the relative concentration of the stable amino acids (Schilling and Khanjian, 1996; Pitthart et al., 2010; Wei et al., 2011a). Moreover, proteomics methods were also applied to identify the proteinaceous binding medium in artworks (Leo et al., 2012).

Analytical techniques including FTIR, XRF, Py-GC/MS and GC/MS were applied in this scientific investigation. However they must be natural organic materials, such as: drying oil, resin, gum or proteinaceous materials. In order to cover a wide range of materials, different analytical methods were applied.

2. Experimental

2.1. Samples

During this study, two types of samples are used, especially for binding media analysis: reference samples made of drying oils, resins and proteinaceous materials including egg, casein and animal glue were prepared in the Conservation Science Department, Kunsthistorisches Museum, Vienna, Austria (Pitthard et al., 2006). Five samples were extracted from the two of the figurines (Fig. 1a, b) and were analyzed for pigment and binding medium identification. Additionally, one adhesive sample from the polychromy horse (Fig. 1c) was obtained – in order to investigate the adhesive material used (see Table 1).

2.2. Natural and artificial UV ageing

The reference samples were prepared by casting them in thin films on glass slides. Naturally aged samples were stored for five years in the laboratory at room temperature. In order to imitate the real samples (such as samples from the Han dynasty terracotta), the reference materials were artificially aged. By exposing the samples in a SOL 2 sunlight simulation chamber (Dr. K. Hönle GmbH UV Technologies, Munich, Germany) equipped with a Xenon lamp,

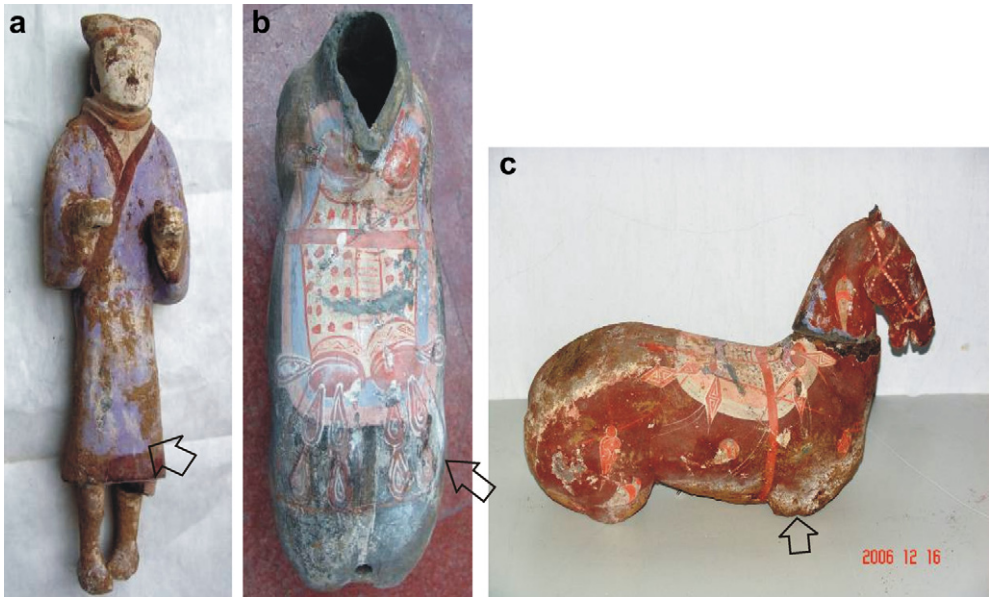

Fig. 1. a–c. Polychromy terracotta a) terracotta figure No. 286; b) terracotta figure No. 657; c) terracotta horse No.4. The arrows indicate where the samples were taken.

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