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A multi-analytical techniques based approach to study the colorful clothes and accessories from mummies of Eastern Central Asia

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ABSTRACT

A wide variety of well-preserved textile finds and leather objects from four archaeological sites, situated in the Xinjiang Uyghur Autonomous Region (China), covering a time span from the beginning of the 1st millennium BCE to the 1st or even 3rd century CE, were analyzed by state-of-the-art analytical techniques with regard to the utilized fiber and dyestuff materials. The examined textiles consist of wool, silk or plant-based fibers and have been dyed with flavonoid-, indigoid- and anthraquinone-type dyes obtained from different plants or from scale insects. Red and black colored decorations on leather objects have been manufactured from cinnabar and carbon-based black pigments. The results offer insights into the dyeing techniques and raw materials used in prehistoric Xinjiang and reveal a complex and highly refined technology.

1. Introduction

In the Xinjiang Uyghur Autonomous Region (further Xinjiang), situated in the northwestern part of China, several graveyards and ancient sites with numerous well-preserved and fully clothed mummified human corpses are documented. Aside from the corpses many artifacts and accessories of daily life have been preserved in the graves, among them wooden bows, leather sheaths and textile bags (e.g. Beck et al., 2014; Li et al., 2013; Schröder et al., 2016; Wagner et al., 2009.). Very early mummified remains belong to the Bronze Age and are known for example from archaeological sites of Yanghai (Kramell et al., 2014) and Qäwrighul (Mallory & Mair, 2000). The conservation of these organic materials over thousands of years is owed to the extremely dry climate, the salt content of the soil and cold winters. The results from interdisciplinary research of this finds contributes to gain valuable insights into a period of time long gone and without written documentation. They help to understand and to reconstruct ancient technologies and channels of trade used at that time. The investigation of clothing and accessories (Gleba & Mannering, 2012) with regard to fibers and the colorants used for their dyeing is a key issue of these interdisciplinary studies.

Some previous publications already described some results of investigations on colored textile materials from the Xinjiang region, especially from the finding sites of Zaghunluq (probable period of use correlating with phase C in Yanghai, i.e. 7th - 3rd century BCE), Yanghai (consists of three distinct burial zones, probable period of use: 1200 BCE–200 CE), Yingpan (probable period of use: Han to Jin dynasty, i.e. 206 BCE–420 CE) and Sampula (Zhang et al., 2008; Liu et al., 2011; Xie et al., 2001; de Hofenk & van Bommel, 2001; Liu et al., 2013). Not only textiles but also accessories such as hunting equipment and glass artifacts (e.g. beads, pendants and other decorative goods (Liu et al., 2012)) were designed colorfully.

In this study, a wide variety of radiocarbon-dated textile finds from the archaeological sites of Sampula, Niya, Wupu and Aisikexia'er have been investigated by state-of-the-art analytical techniques to determine the kind of fibers and dyestuffs having been used. Additionally, for the first time, colored decorations of leather objects from the finding site of Niya were examined.

2. Materials and methods

2.1. Site setting and archaeological context

The archaeological sites selected for the current study represent archaeological cemeteries of Sampula (Wagner et al., 2009; Wang & Xiao, 2001), Niya (Hulsewé, 1979), Wupu (Schröder et al., 2016;

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Wang, 1999) and Aisikexia'er (Fig. 1). These places are situated in the oases around the Tarim Basin (Fig. 1) occupied with the vast Taklamakan Desert (for further informations see Supplementary data).

The samples analyzed and discussed in this paper originate from textile or leather clothing objects and accessories. All sampled objects are stored in the archaeological collections in Ürümqi, Hami and Turfan, respectively (Table 1).

2.2. Analytical techniques

The analytical techniques included optical microscopy (OM), scanning electron microscopy (SEM), the combination of SEM with energy dispersive X-ray spectroscopy (SEM-EDX), X-ray Diffraction (XRD), Fourier transform infrared (ATR-FTIR) in attenuated total reflection mode, Raman and diffuse UV–Vis-reflectance spectroscopy. Furthermore high performance liquid chromatography was combined with diode array detection (HPLC-DAD) and mass spectrometric detection (LC-MS/MS; materials, techniques, instrumentation and extraction methods are specified in the supplementary data).

3. Results and discussion

3.1. Fiber material and coloration of textile objects

3.1.1. Non-destructive or minimally invasive preliminary investigations concerning fiber material and coloration

The topographic documentation of the various samples and the space-resolved elemental analysis of fibers and adhesions were performed by optical microscopy, SEM and SEM-EDX studies as previously reported (Kramell et al., 2014). In addition ATR-FTIR spectroscopic investigations were used to confirm unequivocally the assignment to plant or animal derived fibers (compare (Margariti et al., 2011)).

Scale structures typical for wool and characteristic vibrational bands of the protein matrix of hair keratin (Doherty et al., 2008; Church et al., 1997; Akhtar et al., 1997) were observed on investigated samples of clothes from graveyard sites of Wupu, Aisikexia'er and Sampula (Table 2). In the case of the Niya site additional silk and plant derived fibers have been used for the production of textiles (typical properties and characteristic vibrational bands of the protein matrix of silk fibroin and of the skeletal structure of plant fibers have previously been reported in literature (Monti et al., 1998; Kavkler & Demšar, 2011; Farke, 1986)). The plant material based yarns belonged to an inclined strap of a skirts waistband from grave M5 (object ID 95MNIM5-18, sample ID 95MNIM5-18B, Fig. 2).

Ubiquitous elements like C, N, O, S, Na, Si, Cl, Al, Ca, Mg, K, P and Fe were detected in dyed and undyed samples by SEM-EDX. These results do not permit any conclusions concerning the original process of coloration or mordant dyeing, inasmuch as the presence of these elements might also be explained as the result of a subsequent contamination during the use of the clothes or they might originate from the surrounding of the grave. However, it should always be kept in mind (especially for reconstruction of materials) that iron salts alter the colorfulness of red mordant dyes significantly. As described by Joosten et al. (Joosten et al., 2006) this "post mordanting effect" usually results in a darkening of red mordant dyes.

First references and conclusions concerning the colorants or the group of dyes were obtained from the non-destructive investigation of the crude samples (without any previous sample preparation steps or extractions) by UV–Vis-reflectance spectroscopy. The results from these measurements were used to decide which conditions have to be selected for the extraction of the samples. As a result, reflectance spectra (see Supplementary data) obtained for bluish historic fibers indicate the presence of indigoid-type dyestuffs. Diffuse reflectance spectra (see supplementary data) of reddish historic fibers (madder colorings) were similar to authentic references. However, inflection points of the historic woolen samples occurred at about $\lambda = 590$ nm and showed a small shift of approximately 20 nm compared to respective colored woolen references stained with Al salt. The shift of the inflection point could be explained by various causes. One explanation is an altered composition in respect of the metal ions (Gulmini et al., 2013).

3.1.2. Identification of colorants in historic textiles

Destructive analyses of dyestuffs were performed by HPLC-DAD and LC-ESI-MS/MS.

The main coloring components of red-shaded samples from the archaeological graveyard sites of Sampula, Niya, Wupu and Aisikexia'er were anthraquinones, viz. alizarin, purpurin, xanthopurpurin and rubiadin (Table 2). As previously stated (Kramell et al., 2014), it seems

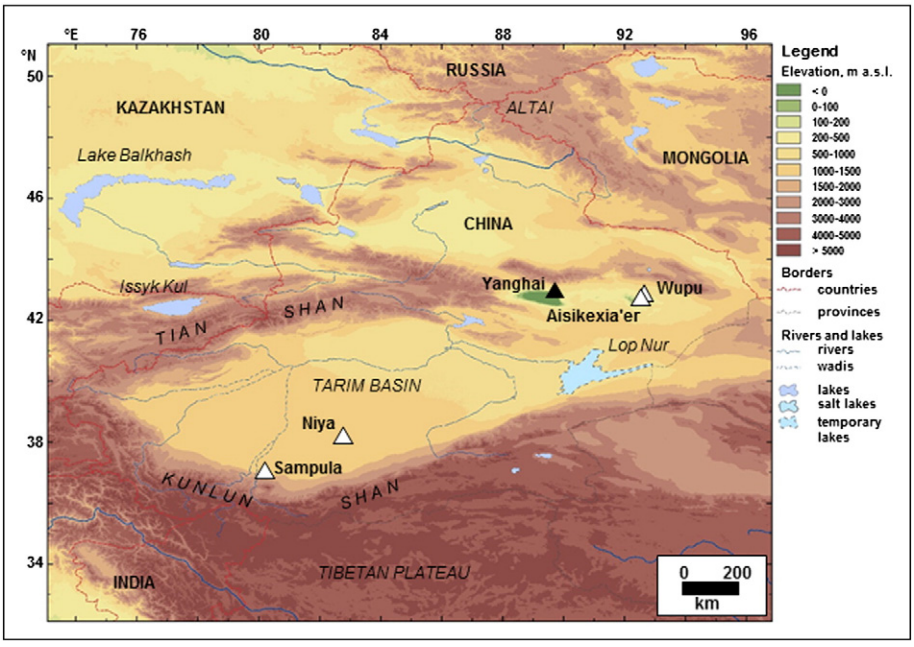

Fig. 1. Map showing major topographic features of the region and the location of selected archaeological graveyards in the Turfan Depression (Xinjiang, China). Modern cities and political borders are shown for better orientation.