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Ancient Chromophores and Auxiliaries: Phrygian Colorants from Tumulus MM at Gordion, Turkey, ca 740 BCE

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Abstract: This paper discusses colorants found in Tumulus MM, the tomb of King Midas or his father, at Gordion, the capital of the Phrygian kingdom. Chromophores, colorants, and auxiliaries are preserved largely independent of the textiles they once colored. The Tumulus MM textiles are now fragmentary due to the degradation processes that occurred inside the tomb chamber. For DHA 26 (Vienna, Austria, 2007), we discussed a group of golden-yellow fragments from Tumulus MM that appeared to be tabby cloth but were skeletal lattices of goethite, αFeOOH (yellow ochre), as identified by FTIR, with SEM/EDS, XRD with molybdenum Kα radiation, NIR, and Raman spectroscopy. The "dyeing" has been replicated using a patented method; originally it may have involved a controlled redox reaction, based on our preliminary experiments. Amidst the goethite lattices, some skeletal fragments were green, with near-black lines within the yarn spiral, identified as indigo by FTIR at the time. Other masses with colorations of red, orange/brown, and purple with deep red veins did not yield identifiable inorganic coloration profiles with SEM/EDS. A purple fragment (2003-Tx-6 Front) was assayed by ICP-MS for mordants and for bromine, but neither could be found. Recently, direct analysis in real time mass spectrometry (DART-MS) enabled us to successfully detect organic colorants. For one fragment, indoxyl, isatin, indigo, and *leuco*-indigo were identified. One striated red-to-brown mass (2003-Tx-3) contained alizarin, purpurin, xanthopurpurin, lucidin, and other madder substituents; it also contained indigo/isatin but neither indoxyl nor *leuco*-indigo. Other beige-brown masses like 2003-Tx-5 sometimes contained alizarin, xanthopurpurin, rubiadin, and lucidin but rarely purpurin or indigo-related compounds. The purple (2003-Tx-6) shared the madder analogues with browner hues. The versatility appears related to that found in Anatolian pile carpets and flat weaves. Our new analyses confirm that the Phrygian textile colorists were indeed superb, versatile dyers.

Keywords: Iron Age; goethite; madder; indigo; Gordion; King Midas; Anatolia; weaving; dyes; City Mound; Phrygia

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1. Introduction

New research has identified the colorants in the royal textiles from Tumulus MM, the tomb of a great Phrygian king—King Midas or his father—who ruled at Gordion, Turkey, in the 8th century BC. The kingdom of Phrygia, then at the height of its power, extended over much of central Anatolia, with the capital at Gordion, located approximately 80 km (50 miles) southwest of modern Ankara (Figure 1) [1] (p. 136). Tumulus MM, called "MM" for "Midas Mound", is the largest burial mound at the site, now preserved to a height of 53 m. The tomb was excavated by the University of Pennsylvania Museum in 1957, under the direction of archaeologist Rodney S. Young [2]; research on the contents of the burial has continued up to the present day.

Figure 1. The Phrygian kingdom in the 8th century BC.

The tomb chamber was constructed of finished pine planks erected on a floor of cedar beams. Surrounding the chamber was an enclosure of juniper logs and rubble packing, and over this was piled the huge mound of earth. The rich burial had contained an impressive collection of bronze vessels, bronze-and-leather belts, bronze fibulae (brooches), pottery jars containing food residues, and 15 pieces of fine wooden furniture, along with numerous textiles associated with the furniture and bronzes [3] (pp. 79–190) [4]. At the north of the chamber lay the remains of the king, lying on a mass of degraded textiles that covered the wood of his open log coffin, which had broken apart and collapsed onto the tomb floor (Figure 2).

Figure 2. View of the remains of the king buried in Tumulus MM, Gordion, lying on the degraded textiles covering his log coffin, as excavated in 1957. Photo courtesy of the Gordion Project, Penn Museum.

The organic finds were remarkably well preserved due to the constant relative humidity that had prevailed inside the tomb chamber, although some deterioration had occurred. The excavators had drilled a series of holes into the surface of the mound in order to locate the chamber. The water used in the drilling, along with a gradual alkaline seepage into the tomb, had compromised the integrity of the wooden furniture and dissolved the fibers of the textiles buried with the king [5]. While some textile fragments were intact, most were recovered as amalgamated, dense, powdery solids. Nonetheless, the colors survived, ranging from a deep yellow to orange, reds, purples, and green. These rare Phrygian textile remains have been analyzed in terms of their materials, weave structures, and colorants [6]. The new research outlined in this paper highlights the dyes, their sources, and the processes used to achieve the results.

Southwest of the cemetery is the City Mound (Citadel Mound), situated above the Sakarya River (Figure 3) [7]. The Phrygians who settled at Gordion are thought to have originated in Thrace, making their way eastward to the central Anatolian plain. A porous gypsum plateau lay to the west of Gordion, while further east were sedimentary lowlands and uplands of basalt and marl [8] (p. 690). Contemporary with or somewhat earlier than Tumulus MM, the Early Phrygian settlement on the City Mound had burned in a fire and was subsequently rebuilt with minor alterations [9] (pp. 8, 10). Archaeologists have been particularly interested in the burnt layer, called the Destruction Level, as it was covered over largely intact, leaving a good record of Phrygian activities at the site ca 800 BC (Figure 4).

Figure 3. Aerial view of Gordion in the early days of excavation, with the City Mound (Citadel Mound) at the lower left and Tumulus MM at the upper right. Photo courtesy of the Gordion Project, Penn Museum.

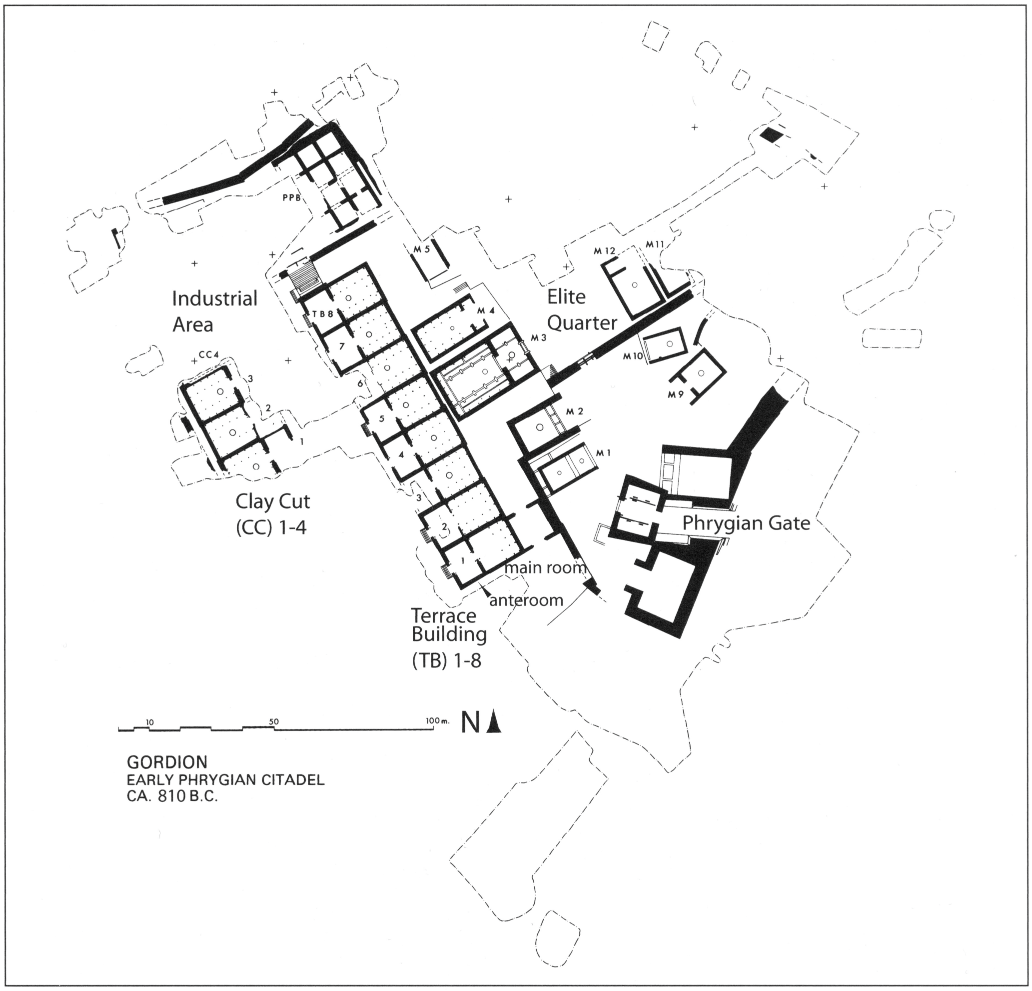

Figure 4. Plan of the City Mound at Gordion during the Early Phrygian period [9] (p. 8).

The burnt level of the City Mound has provided context for the Tumulus MM textiles, both in terms of surviving fragments of cloth and also loom weights and other tools indicating large-scale textile production [10]. Excavations in the central part of the mound revealed numerous buildings of megaron type with anterooms and spacious back rooms containing weaving equipment: needles, knives, combs, more than 1000 spindle whorls, and around 3000 loom weights, most in the range of 400–600 g (Figure 5) [11] (pp. 112–153) [12] (p. 65). In the largest of these buildings, Megaron 3, fragments of charred textiles were recovered, with their patterns visible but lacking their original colors (Figure 6) [13,14] (pp. 15–16). These charred fragments feature tapestry, soumak, and gauze weaves, as well as tablet work, in various gray shades as though the color of the ash might indicate different mordants [15].

Taken together, the textiles from Tumulus MM and the remains from the City Mound provide evidence for wide-scale textile manufacture and use at Gordion, which yielded fabric in a variety of weaves, some with geometric patterning, and in subtle and vivid hues achieved by ingenious dye chemistry. While it has not been shown that the Tumulus MM textiles were woven in workshops on the City Mound, the materials and colorants of these textiles are consistent with the resources present at Gordion. Although the Tumulus MM fabrics do not exhibit elaborate weaves or patterning, such as those from Megaron 3, they were clearly costly items—valuable enough to be deposited as grave goods in the largest tomb at Gordion. Their characteristics indicate an interest and expertise in colorants and dye technology, an advanced knowledge of chemistry and geology, and a good understanding of the natural products—plants and minerals—available in the vicinity. Beyond their inherent cultural value, the dyed textiles from the tomb suggest what the Megaron 3 textiles might have looked like before losing their color to the fire. This paper will focus on the dyes of the Tumulus MM textiles, their chemistry, and their use as colorants for these royal Phrygian cloths.

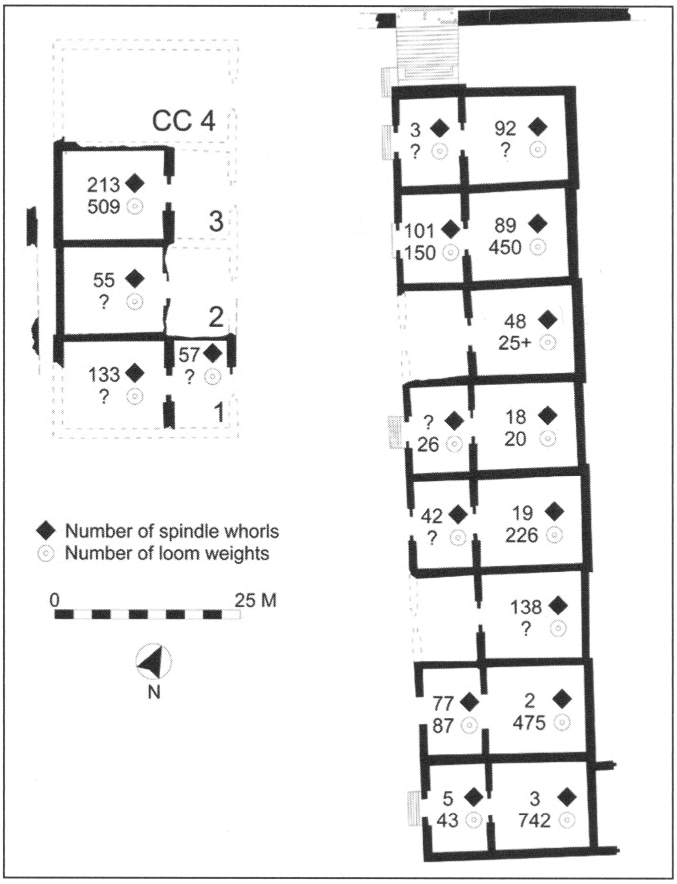

Figure 5. Workrooms in the Terrace Building complex on the Gordion City Mound, with the numbers of loom weights and spindle whorls reported for each room [12] (p. 65). Plan courtesy of Brendan Burke.

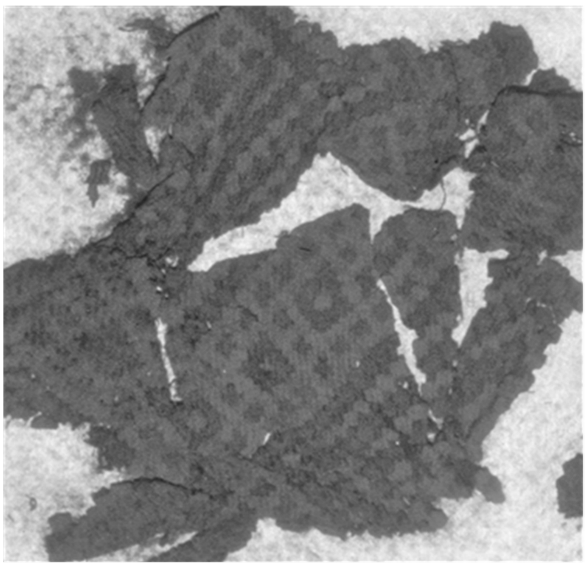

Figure 6. A charred textile fragment from Megaron 3 on the City Mound, stored at the University of Pennsylvania Museum (Bellinger Box 12) [13]. Photo courtesy of Mary Ballard.

2. Materials and Methods

Eleven textile samples from Tumulus MM were lent to the Museum Conservation Institute, Smithsonian Institution, in 2003 for analytical research; these were labeled 2003-Tx-1 through 2003-Tx-11, with 2003 indicating the date that the samples were catalogued for the purpose of study. Initial efforts on fiber, weave, and dye analysis were summarized elsewhere in 2007 [16] and published at length in 2010 [6]. The present paper combines old and new methods and results to provide a full range of archaeological and scientific data regarding the dyes. A synopsis of the defining characteristics of the textile samples, where such features could be obtained, is given in Table 1; a fuller description and extensive imaging are available in the 2010 publication [6].

Table 1. Summary of textile features associated with samples 2003-Tx-1 through 2003-Tx-11 [6].

Compendium of Textile Features Found in Tumulus MM					
Sample	**Color**	**Images (Figures)**	**Fiber**	**Yarn and Count**	**Constuction or Weave**
2003-Tx-1	gold	14, 19	bast	2 Z, S-plied 18 × 21 cm	balanced plain weave
2003-Tx-2 Front	(orange) red	13	—	—	—
2003-Tx-2 Back	gold	15	bast	2 Z, S-plied 18 × 21/cm	balanced plain weave
2003-Tx-3 Front	white-cream	22	—	—	—
2003-Tx-3 Front	brightest red	21, 22	unknown	unknown	unknown
2003-Tx-3 Front	mixed reddish			unknown	
2003-Tx-4 F&B	reddish	23, 24	unknown	unknown	unknown, twining
2003-Tx-5 F&B	type B fibrous	—	unknown	Z twist	twining
2003-Tx-5 F&B	type A	—	—	—	—
2003-Tx-6 Front	reddish/purple layer	25, 26	—	—	—
2003-Tx 6 Front	varied	25, right	unknown	S-twisted	cord
2003-Tx-6 Back	dark red	—	unknown	unknown	twining
2007-Tx-7 Front	gold	17	bast	2 Z, S-plied	plain weave
2007-tx-7 F&B	brown fibrous mass	17, 29	—	—	—
2003-Tx-7 Back	dark fiber A	29	unknown	floss/S	twining
2003-Tx-7 Back	dark fiber B	29	—	—	—
2003-Tx-8 Front	whitish pale tan	27	—	—	—
2003-Tx-8 Front	single fiber/yarn	27	unknown	floss/S	twining
2003-Tx-8 Back	gold	18	bast	2 Z, S-plied 28 × 23/cm	plain weave
2003-Tx-8 Back	dark, fibrous	18	unknown	unknown	unknown
2003-Tx-9 Front	whitish tan	—	—	—	—
2003-Tx-9 Front	gold	—	unknown	—	—
2003-Tx-9 Back	gold	28	bast	2 Z, S-plied ca 35 × 35/cm	plain weave
2003-Tx-9 Back	dark	28	unknown	floss/S	twining
2003-Tx-10	dark	30, 31	flax	2Z, S-plied, 35 × 35 cm	balanced plain weave
2003-Tx-11	dark blue strands	16, 20	bast	2Z, S-plied	balanced plain weave
2003-Tx-11	bicomponent gold strands	16, 20	bast	2Z, S-plied	balanced plain weave

The research detailed in this section is divided into two conventional categories: inorganic and organic. The inorganic studies were carried out during the period 2003–2008 with some recent reconsiderations in 2021–2022 [6,17]. The organic work, except for 2003-Tx-11, was carried out in 2019–2022. The largest volume of color is associated with the coffin textiles (Figures 2 and 7), with additional fragments found in the northeast corner and at the east wall of the chamber. The textile fragments from Tumulus MM were obtained on loan for analysis from the Museum of Anatolian Civilizations, Ankara, Turkey, under the auspices of the Gordion Furniture Project. Their find spots within the chamber are shown on the tomb plan (Figure 8).

Figure 7. Storage drawer of material from Tumulus MM adjacent to the head of the corpse, similar to 2003-Tx-4 Front and Back. Photo courtesy of the Gordion Furniture Project.

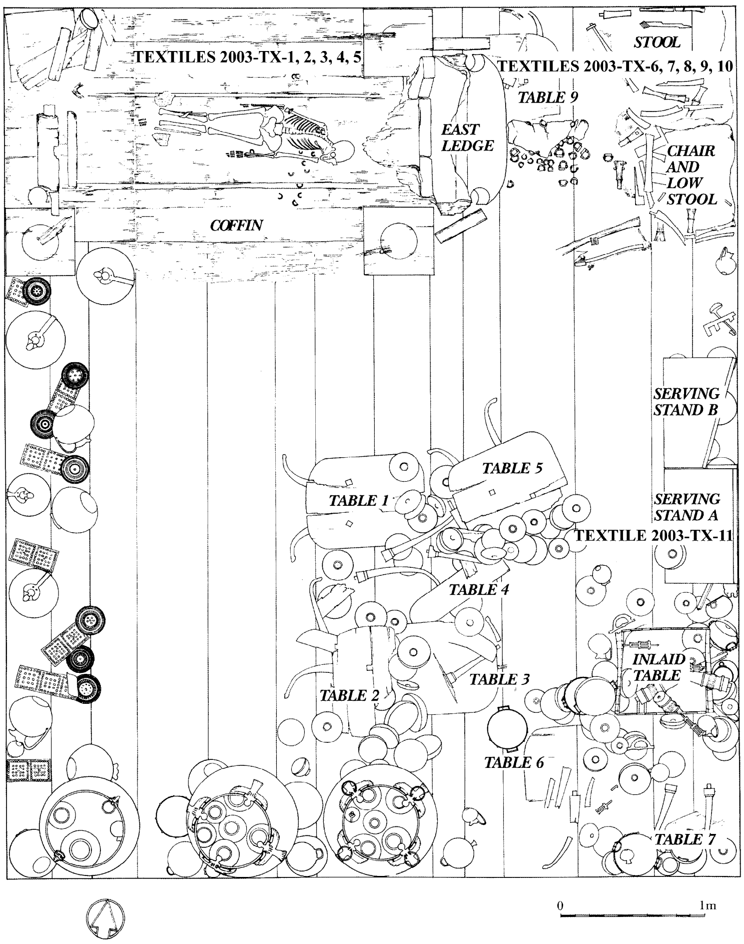

Figure 8. Plan of the Tumulus MM chamber showing the locations of the wooden furniture and textiles. Plan courtesy of the Gordion Project, Penn Museum, and the Gordion Furniture Project.

2.1. Inorganic

The inorganic analyses were carried out using a JEOL JXA-840A Scanning Electron Microscope (SEM) with a Thermo NORAN TN-5502 energy dispersive analytical attachment (EDS) and its compatible NORAN Vantage spectrum processing software. The system was also fitted with a low atomic number detector (Pioneer Premium detector with a Norvar window). Self-sampling powder from the periphery of the sample was transferred to a carbon-coated carbon stub and stored in a desiccant chamber until used. A sketch of the stub was made; sketches and stubs remain archived and available. This equipment was used for the inorganic analysis of all samples except 2003-Tx-10 [6,17].

An Aventa visible through near infrared and shortwave infrared portable spectrometer (VIS-NIR-SWIR) also characterized the inorganic material present in fragment 2003-Tx-2. A Thermo Nicolet Almega XR Dispersive Raman Spectrometer provided further spectra of 2003-Tx-1 [16,18].

A Perkin Elmer Elan 6000 Inductively Coupled Plasma Mass Spectrometer (ICP-MS) connected to a Scott-type Tyron® double pass spray-chamber fitted with a standard crossflow nebulizer as sample-introduction device was used on samples from 2003-Tx-6. A review of this method to search for mordants or inorganic substituents such as bromine has been described elsewhere [19].

The Rigaku D/MAX-RAPID X-Ray Diffraction spectrometer was initially used to confirm the presence of goethite on 2003-Tx-1, but its reliance on K_{β} copper radiation was thought to be inadequate. Additional X-Ray Diffraction spectrometer data were obtained from the Smithsonian National Museum of Natural History using a Rigaku DMax/Rapid; the X-rays are Mo $K\alpha$ with wavelength of 0.71 angstroms. The data were processed in Rigaku AreaMax software and analyzed with Jade software and matched to references in the PDF database [16].

2.2. Organic

A direct analysis in real time for mass spectrometry (DART-MS) [20] probe operated by an SVP controller was mounted in front of a differentially pumped Vapur interface (IonSense, Saugus, MA, USA) on a high-resolution Orbitrap Elite mass spectrometer (Thermo Fisher Scientific, Waltham, MA, USA). A 40 mm stainless steel transfer tube was used in place of the typical ceramic transfer tube on the Vapur interface. Solid fragments 0.5–3 mm wide that had fallen off larger pieces of compressed and degraded textiles were collected from material containers and, prior to analysis, stored in paper or aluminum foil to prevent any further contamination by contact with residues from modern materials. The miniscule fragments were too brittle and irregularly shaped to be mounted in forceps without crushing, and fragments were manipulated for analysis by forceps in hand to pass in the 7 mm gap between the DART probe and transfer tube (Figure 9). DART analysis was performed at 350 °C helium. MS data were acquired in the profile mode at 120 k resolving power with a maximum ion trap fill time of 100 ms [21].

High-performance liquid chromatography (HPLC) was carried out on samples from 2003-Tx-2 Front in order to determine whether there was any protein fiber (i.e., wool felt) in the orange-red mass. Analysis was performed using a St. John Model 2000 Amino Acid Analyzer with Alcott 708AL Autosampler. Post-column derivatization with ortho-phthalaldehyde (OPA) and 2-mercaptoethanol (MCE) were used as detecting reagents [22].

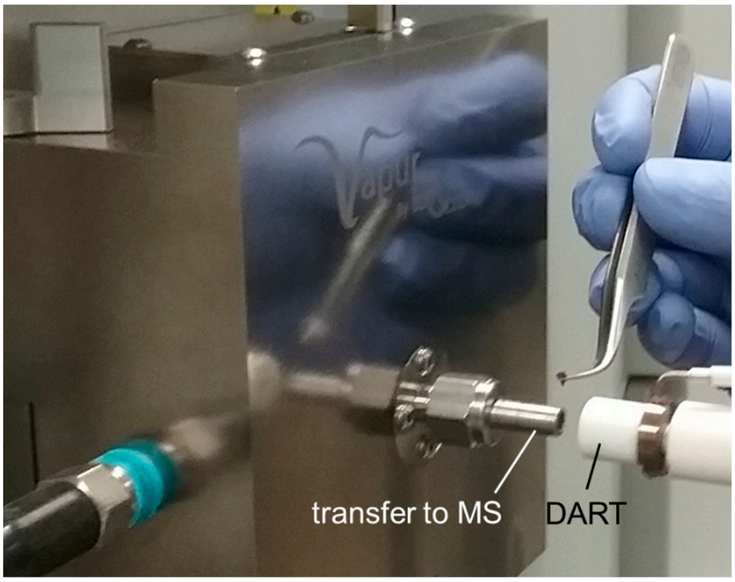

Figure 9. Textile fragment about to be manipulated for DART-MS analysis.

3. Results

Where the results by instrumental analysis deal with a single fragment, the results are described. Where the instrumental results provide data for more than a single fragment, the analyses have been combined into tables based on the inorganic or organic spectra. The Tumulus MM textiles are listed according to their find spots (from the coffin, the northeast corner, and the east wall) and their color: Table 2 for indigo, and Tables 3 and 4 for Madder.

Table 2. Results for indigo from DART-mass spectrometry for samples 2003-Tx-1 through 2003-Tx-11 from Tumulus MM [21].

<table>
<tr><th colspan="9">Indigo Group Compounds, Neutral Chemical Formula, and Intact Ion m/z</th></tr>
<tr><th rowspan="3">Sample</th><th rowspan="3">Color</th><th>Indigo</th><th>Indican</th><th>Isatan A</th><th>Isatan B</th><th>Indoxyl</th><th>Leuco-Indigo</th><th>Isatin</th></tr>
<tr><th>$C_{16}H_{10}N_2O_2$</th><th>$C_{14}H_{17}NO_6$</th><th>$C_{17}H_{17}NO_9$</th><th>$C_{14}H_{15}NO_6$</th><th>C_8H_8NO</th><th>$C_{16}H_{12}N_2O_2$</th><th>$C_8H_5NO_2$</th></tr>
<tr><th>263.082</th><th>296.113</th><th>380.098</th><th>294.096</th><th>134.06</th><th>265.096</th><th>148.039</th></tr>
<tr><td>2003-Tx-1 F</td><td>gold</td><td></td><td></td><td></td><td></td><td></td><td></td><td></td></tr>
<tr><td>2003-Tx-2 F</td><td>(orange) red</td><td>√</td><td></td><td></td><td></td><td></td><td></td><td></td></tr>
<tr><td>2003-Tx-3 F</td><td>white</td><td></td><td></td><td></td><td></td><td></td><td></td><td></td></tr>
<tr><td>2003-Tx-3 F</td><td>brightest red</td><td rowspan="2">√</td><td rowspan="2"></td><td rowspan="2"></td><td rowspan="2"></td><td rowspan="2">√</td><td rowspan="2"></td><td rowspan="2">√</td></tr>
<tr><td>2003-Tx-3 F</td><td>mixed reddish</td></tr>
<tr><td>2003-Tx-4</td><td>reddish</td><td>√</td><td></td><td></td><td></td><td></td><td></td><td></td></tr>
<tr><td>2003-Tx-5 F</td><td>type A</td><td></td><td></td><td></td><td></td><td></td><td></td><td></td></tr>
<tr><td>2003-Tx-5 F</td><td>powder</td><td></td><td></td><td></td><td></td><td></td><td></td><td></td></tr>
<tr><td>2003-Tx-6 F</td><td>reddish/purple</td><td rowspan="2">√</td><td rowspan="2"></td><td rowspan="2"></td><td rowspan="2"></td><td rowspan="2">√</td><td rowspan="2"></td><td rowspan="2">√</td></tr>
<tr><td>2003-Tx-6 B</td><td>reddish/purple</td></tr>
<tr><td>2003-Tx-7 F</td><td>tan</td><td></td><td></td><td></td><td></td><td></td><td></td><td></td></tr>
<tr><td>2003-Tx-7 B</td><td>brown fibrous mass</td><td></td><td></td><td></td><td></td><td></td><td></td><td></td></tr>
<tr><td>2003-Tx-7 B</td><td>dark fiber A</td><td></td><td></td><td></td><td></td><td></td><td></td><td></td></tr>
<tr><td>2003-Tx-7 B</td><td>dark fiber B</td><td></td><td></td><td></td><td></td><td></td><td></td><td></td></tr>
<tr><td>2003-Tx-8 F</td><td>white, tan</td><td></td><td></td><td></td><td></td><td></td><td></td><td></td></tr>
<tr><td>2003-Tx-8 F</td><td>fiber/yarn</td><td></td><td></td><td></td><td></td><td></td><td></td><td></td></tr>
<tr><td>2003-Tx-8 B</td><td>dark, fibrous</td><td></td><td></td><td></td><td></td><td>√</td><td></td><td>√</td></tr>
<tr><td>2003-Tx-9 F</td><td>whitish tan</td><td></td><td></td><td></td><td></td><td></td><td></td><td></td></tr>
<tr><td>2003-Tx-9 B</td><td>dark</td><td>√</td><td></td><td></td><td></td><td>√</td><td></td><td>√</td></tr>
<tr><td>2003-Tx-10</td><td>dark</td><td></td><td></td><td></td><td></td><td></td><td></td><td></td></tr>
<tr><td>2003-Tx-11</td><td>blue strand</td><td>√</td><td></td><td></td><td></td><td>√</td><td>√</td><td>√</td></tr>
<tr><td>2003-Tx-11</td><td>bicomponent</td><td>√</td><td></td><td></td><td></td><td></td><td></td><td>√</td></tr>
</table>

Table 3. Results for madder from DART-mass spectrometry for samples 2003-Tx-1 through 2003-Tx-11 from Tumulus MM [21].

<table>
<tr><th></th><th></th><th colspan="8">Madder Group Organic Compounds, Neutral Chemical Formula, and Intact Ion m/z</th></tr>
<tr><th>Sample</th><th>Color</th><th>Alizarin or Xanthopurpurin</th><th>Purpurin</th><th>Munjistin</th><th>Lucidin</th><th>1-Methoxy-2-methylanthraquinone</th><th>Alizarin 1 (or 2)-methyl Ether, or Rubiadin</th><th>Xanthopurpurin Dimethyl Ether</th><th>2-Hydroxyanthraquinone</th></tr>
<tr><td></td><td></td><td>$C_{14}H_8O_4$</td><td>$C_{14}H_8O_5$</td><td>$C_{15}H_8O_6$</td><td>$C_{15}H_{10}O_5$</td><td>$C_{16}H_{12}O_3$</td><td>$C_{15}H_{10}O_4$</td><td>$C_{16}H_{12}O_4$</td><td>$C_{14}H_8O_3$</td></tr>
<tr><td></td><td></td><td>241.049</td><td>257.045</td><td>285.040</td><td>271.061</td><td>253.087</td><td>255.066</td><td>269.081</td><td>225.055</td></tr>
<tr><td>2003-Tx-1</td><td>gold</td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td></tr>
<tr><td>2003-Tx-2 F</td><td>(orange) red</td><td>√</td><td>√</td><td></td><td>√</td><td>√</td><td>√</td><td>√</td><td>√</td></tr>
<tr><td>2003-Tx-3 F</td><td>white</td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td></tr>
<tr><td>2003-Tx-3 F</td><td>brightest red</td><td rowspan="2">√</td><td rowspan="2">√</td><td rowspan="2"></td><td rowspan="2">√</td><td rowspan="2">√</td><td rowspan="2">√</td><td rowspan="2">√</td><td rowspan="2"></td></tr>
<tr><td>2003-Tx-3 F</td><td>mixed reddish</td></tr>
<tr><td>2003-Tx-4</td><td>reddish</td><td>√</td><td>√</td><td></td><td>√</td><td>√</td><td>√</td><td></td><td></td></tr>
<tr><td>2003-Tx-5 F</td><td>type A</td><td>√</td><td></td><td></td><td>√</td><td></td><td>√</td><td>√</td><td></td></tr>
<tr><td>2003-Tx-5 F</td><td>powder</td><td>√</td><td></td><td></td><td></td><td></td><td></td><td></td><td></td></tr>
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<tr><td>2003-Tx-6 B</td><td>reddish/purple</td></tr>
<tr><td>2003-Tx-7 B</td><td>tan</td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td></tr>
<tr><td>2003-Tx-7 B</td><td>brown fibrous mass</td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td></tr>
<tr><td>2003-Tx-7 B</td><td>dark fiber A</td><td>√</td><td></td><td></td><td></td><td>√</td><td>√</td><td>√</td><td></td></tr>
<tr><td>2003-Tx-7 B</td><td>dark fiber B</td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td></tr>
<tr><td>2003-Tx-8 F</td><td>white, tan</td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td></tr>
<tr><td>2003-Tx-8 F</td><td>fiber/yarn</td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td></tr>
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<tr><td>2003-Tx-9 F</td><td>whitish tan</td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td></tr>
<tr><td>2003-Tx-9 B</td><td>dark</td><td></td><td></td><td></td><td></td><td>√</td><td>√</td><td>√</td><td></td></tr>
<tr><td>2003-Tx-10</td><td>dark</td><td>√</td><td></td><td></td><td>√</td><td>√</td><td>√</td><td>√</td><td></td></tr>
<tr><td>2003-Tx-11</td><td>blue strands</td><td></td><td></td><td></td><td></td><td>√</td><td>√</td><td>√</td><td></td></tr>
<tr><td>2003-Tx-11</td><td>bicomponent</td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td></tr>
</table>

Table 4. Additional results for madder from DART-mass spectrometry for samples 2003-Tx-1 through 2003-Tx-11 from Tumulus MM [21].

		Madder Group Organic Compounds, Neutral Chemical Formula, and Intact Ion *m/z*							
Sample	**Color**	**2-Methoxyanthraquinone, or 1-Hydroxy-2-methylanthraquinone**	**Pseudopurpurin**	**Damnacanthal**	**Rubianin**	**Christofin**	**Physcion**	**Physcionanthranol A/B**	**Copareolatin Dimethylether**
		$C_{15}H_{10}O_3$	$C_{15}H_8O_7$	$C_{14}H_{10}O_5$	$C_{20}H_{18}O_9$	$C_{17}H_{14}O_5$	$C_{16}H_{12}O_3$	$C_{16}H_{14}O_4$	$C_{17}H_{14}O_6$
		239.071	301.035	283.061	403.103	299.092	285.076	271.097	315.087
2003-Tx-1	gold								
2003-Tx-2 F	(orange) red	√		√		√	√	√	√
2003-Tx-3 F	white								
2003-Tx-3 F	brightest red	√		√		√	√		
2003-Tx-3 F	mixed reddish								
2003-Tx-4	reddish	√		√					
2003-Tx-5 F	type A	√							
2003-Tx-5 F	type B powder								
2003-Tx-6 F	reddish/purple	√				√	√	√	√
2003-Tx-6 B	reddish/purple								
2003-Tx-7 B	tan layer								
2003-Tx-7 B	brown fibrous mass								
2003-Tx-7 B	dark fiber A	√				√	√	√	√
2003-Tx-7 B	dark fiber B								
2003-Tx-8 F	whitish pale tan								
2003-Tx-8 F	single fiber/yarn								
2003-Tx-8 B	dark, fibrous	√							
2003-Tx-9 F	whitish tan								
2003-Tx-9 B	dark	√							
2003-Tx-10	dark	√				√	√		
2003-Tx-11	blue strands					√			
2003-Tx-11	bicomponent								

3.1. *Inorganic*

3.1.1. ICP–MS

No bromine was found on 2003-Tx-6F, among six samples taken in the deep purple areas. Note that the ablation system was modified to identify labile halides such as bromine, and was found to be a somewhat awkward but feasible method to identify mordants in antique textiles, based on comparison with a collection with known, identified samples [19,23,24].

3.1.2. SEM/EDS

The results in Table 5 show the elements as a percentage of weight/volume as reported by the instrumentation. The results of this instrument are qualitative; precise quantities cannot be determined. An exception was made to the reporting of these results because the differences in values of some of the results are extreme, as with samples 2003-Tx-1 and 2003-Tx-11 [6,16,17,25,26].

Table 5. Results from Energy Dispersive Spectroscopy for samples 2003-Tx-1 through 2003-Tx-11 from Tumulus MM [6,15,17].

Amalgamated SEM/EDS Charts of Tumulus MM Samples 2003-Tx-1 through 2003-Tx-11													
Sample	**Color, Magnification, Sample Runs (if not 4)**	**Weight Percentage of Elements by Position in the Periodic Table**											
		Na	**Mg**	**Al**	**Si**	**P**	**S**	**K**	**Ca**	**Ti**	**Fe**	**Ni**	**Cu**
2003-Tx-1 F	gold 100X	0.48	—	0.52	1.12	0.60	0.18	—	—	—	97.05	—	—
2003-Tx-2 F	red 1000X	—	2.92	17.45	30.32	2.87	10.88	7.59	6.63	—	18.97	—	—
200x-Tx-3 F	white	—	1.12	5.92	13.11	1.75	25.21	1.43	36.89	—	6.12	—	8.36
200x-Tx-3 F	brightest red	—	2.92	10.02	15.76	4.98	7.08	2.24	18.16	—	7.25	—	31.39
200x-Tx-3 F	mixed reddish	—	3.44	10.04	12.83	4.69	8.98	1.97	20.07	—	5.61	4.49	29.21
2003-Tx-4	reddish 500X	—	3.41	13.59	33.98	4.68	9.40	5.61	17.01	—	11.48	—	4.21
2003-Tx-5 B	type A surface	0.95	2.35	8.23	22.27	1.69	23.10	2.50	30.72	—	6.88	—	—
2003-Tx-5 F	type B fibrous	1.20	4.33	11.87	36.07	2.24	12.86	3.90	17.15	—	9.90	—	—
2003-Tx-6 F	type A upper	—	2.59	9.81	25.05	1.29	6.30	3.89	11.89	—	10.03	—	28.41
2003-Tx-6 B	reddish/purple	—	2.86	8.75	13.76	4.08	15.61	1.95	23.40	—	4.75	—	24.83
2003-Tx-7 B	tan layer 500X	—	0.92	2.04	5.59	0.59	30.84	0.65	46.36	—	3.65	—	9.35
2003-Tx-7 B	brown fibrous mass	—	1.06	5.44	9.44	1.50	1.51	0.70	1.73	—	78.65	—	—
2003-Tx-7 B	dark fiber A	—	2.43	15.18	42.71	1.72	3.83	7.53	2.57	1.36	19.74	—	—
2003-Tx-7 B	dark fiber B	—	0.55	25.09	12.53	4.85	24.34	16.20	5.28	0.51	9.94	—	—
2003-Tx-8	white, tan 100X (3)	—	2.14	4.48	15.32	0.98	23.08	1.97	34.96	—	4.40	—	12.42
2008-Tx-8 B	dark fiber 90X (2)	—	2.77	5.16	1.88	2.07	12.22	1.26	25.22	—	3.11	—	36.23
2003-Tx-8	strand 100X (3)	—	3.09	5.21	13.20	2.23	5.70	1.55	28.77	—	3.61	—	35.75
2003-Tx 8	dark, fibrous 100X (3)	—	3.27	5.38	13.42	2.18	6.00	1.56	31.11	—	2.95	—	34.61
2003-Tx-9 F	white tan 45X (3)	—	3.23	7.38	23.11	1.52	15.22	2.52	19.95	0.41	5.85	—	20.80
2003-Tx-9	dark 45X (1)	—	4.11	8.57	25.58	1.57	5.58	3.56	10.60	0.85	8.22	0.83	30.52
2003-Tx-9	dark fiber 45X (2)	—	1.41	3.40	9.03	—	29.57	1.20	39.02	—	3.30	—	12.37
2003-Tx-11	dark strands (6)	—	0.40	0.80	2.28	0.81	0.85	0.51	1.60	—	90.06	—	2.56
2003-Tx-11	bicomponent (3)	—	1.57	1.42	3.36	5.54	1.35	0.89	7.30	—	63.29	—	14.76

3.1.3. VIS-NIR-SWIR Spectroscopy

The results of the spectra compared the goethite minerals in its database to fragment 2003-Tx-1. Critical points match in the visible and near infrared at 761 nm and 920 nm, respectively (Figure 10). Generally, natural iron pigments contain clays, and the mixtures will vary [18,27].

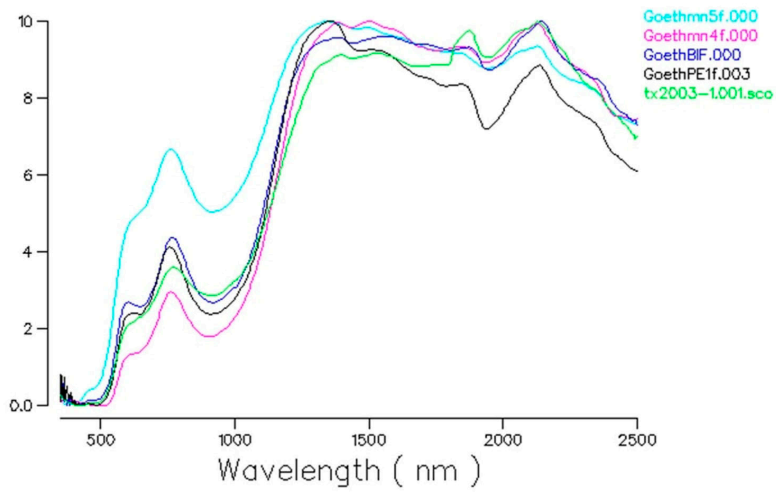

Figure 10. Fragments of 2003-Tx-1 are compared with five samples of known goethite from the Aventa geological reference library. Measurements plot pseudo reflectance versus wavelength [18].

3.1.4. XRD

In the case of 2003-Tx-1, the initial XRD was considered indeterminate; the use of X-rays from a molybdenum source was recommended. The comparison to a synthetic, pure standard is both more accurate and more precise (Figure 11) [16,28].

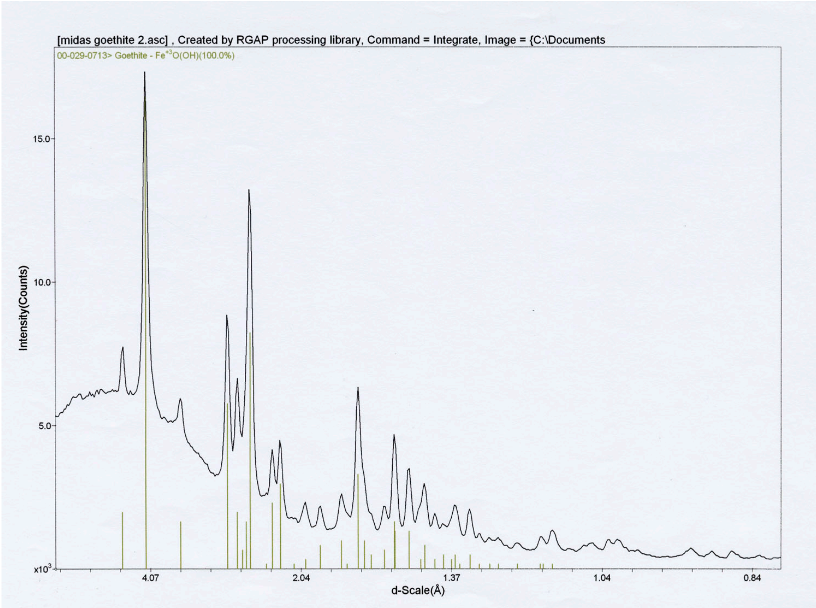

Figure 11. Spectrum taken with Rigaku DMax/Rapid with a Mo Kα wavelength of 0.71 angstroms X-Ray Diffraction Spectrometry. Measurements plot a scale x10^3 between 5 and 15 versus a d-scale in Angstroms (Å) [6,22].

3.2. Organic

3.2.1. DART-MS

Spectra from each Tx sample were examined for ions related to indigo ($C_{16}H_{10}N_2O_2$), madder ($C_{14}H_8O_4$), and Tyrian purple ($C_{16}H_8O_2N_2Br_2$), as well as other materials (Tables 2–4). No madder samples were found to contain munjistin (C.I. 75370, $C_{15}H_8O_6$, *m/z* 285.0399) or pseudopurpurin (C.I. 75420, $C_{15}H_8O_7$, *m/z* 301.035); their *m/z* were absent from all samples. Isomers, because they have identical formulae and *m/z*, are not separated by this method. No forms of bromoindigo were encountered [21].

The timing of the DART analysis was noted to compensate for unstable manual positioning, leaving collection periods before and after analysis to compare signal to background. The qualitative presence of a dye compound was confirmed by sustained appearance in mass spectra during the analysis window. Although in some samples the protonated molecule signal for dyes was quite large, even above all others observed in the spectrum (Figure 12a), in others the abundance was so low that it could be discerned only by the high resolution of the mass measurement (Figure 12b). Given the history of the samples, the origin of the other organic compounds observed in spectra is speculative.

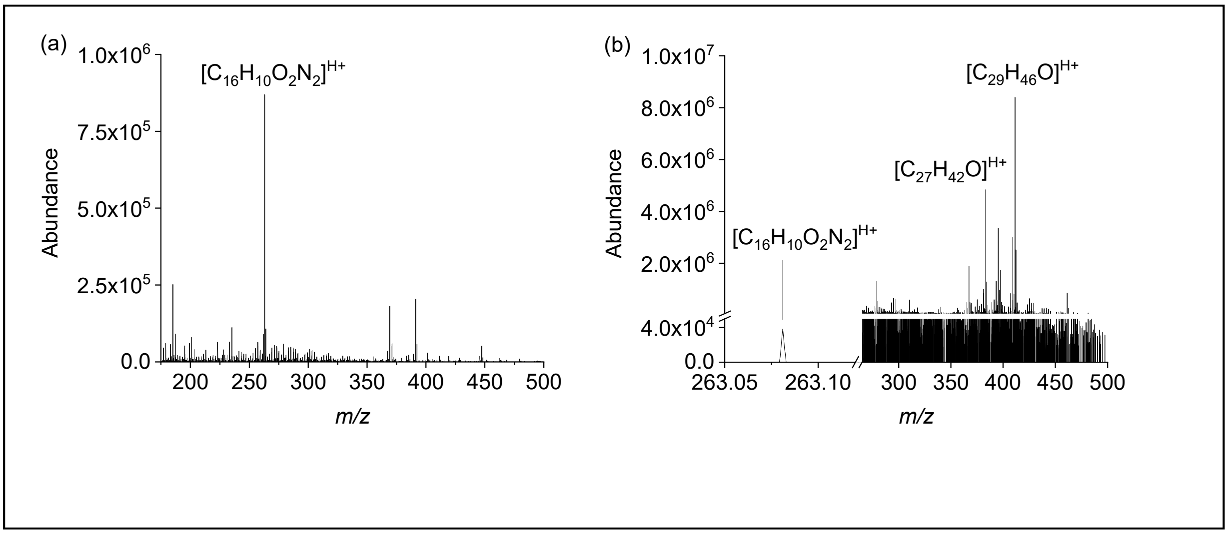

Figure 12. DART mass spectra of fragments (**a**) 2003-Tx-9 and (**b**) 2003-Tx-6 highlighting indigo [22].

3.2.2. FTIR

When the initial search for fibrous materials in 2003-Tx-1 failed using polarized light microscopy (PLM), a back-up method using FTIR was attempted as a last resort. An unexpected result occurred using the spectral library attached to a Thermo Nicolet 6700 Fourier Transform Infrared Spectrometer with Centaurus microscope and Golden Gate micro Attenuated Total Reflectance (ATR) accessory: inorganic goethite. More predictably, FTIR-ATM was also able to discern indigo in 2003-Tx-11 [6,16].

3.2.3. HPLC

No protein was found on the front side of 2003-Tx-2 in the orange-red mass (Figure 13) [22].

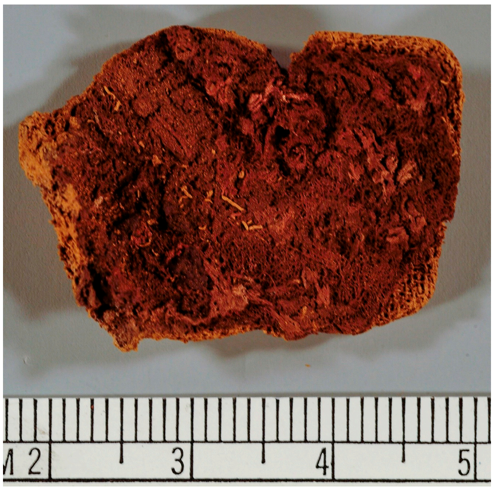

Figure 13. 2003-Tx-2 Front.

4. Discussion

4.1. Iron, Goethite

The amalgamation of materials into a single spectrum limits the reliability of the spectrum when the material is composed of multiple components, as with a dyed textile. For organic analysis, a dyed textile with 3% organic dye relative to the 97% weight of fabric would reflect the composition of the fabric and not the dye. Similarly, inorganic analysis without separating the components limits the usefulness of the analysis. Goethite is typically found as a clay, a mixture of components [29,30]. In the case of 2003-Tx-1, its best mineral match is a banded iron formation from the Karoo of South Africa, the "Tiger Eye" Mine, with a golden-brown color. In the best of circumstances, such a goethite mineral is summarized as follows:

> *FeO(OH), with common substituents Al, Mn, Ni; polymorphous with lepidocrocite. The most common iron oxide mineral in the regolith. Structure: double chains of Fe-O octahedra linked laterally. Yellow-brown, forming as compact aggregates of sub-micron-sized crystals or as dispersed micro-crystals; common as cutans on ferruginous nodules.* [18]

With over two millennia of leachate and microbiological decay, the presence of a highly pure goethite component reflecting a prior life as a textile colorant is extraordinary. Beyond the fragments 2003-Tx-1, 2003-Tx-2 Back, and 2003-Tx-11 (Figures 14–16), similar goethite-colored weaving can be seen as part of laminated textile packages from the tomb (Figures 17 and 18). While the yarns of the goethite-colored weavings studied here are hollow and entirely devoid of fiber, it is clear that these fragments do represent a dyed textile product, once fully colored and malleable.

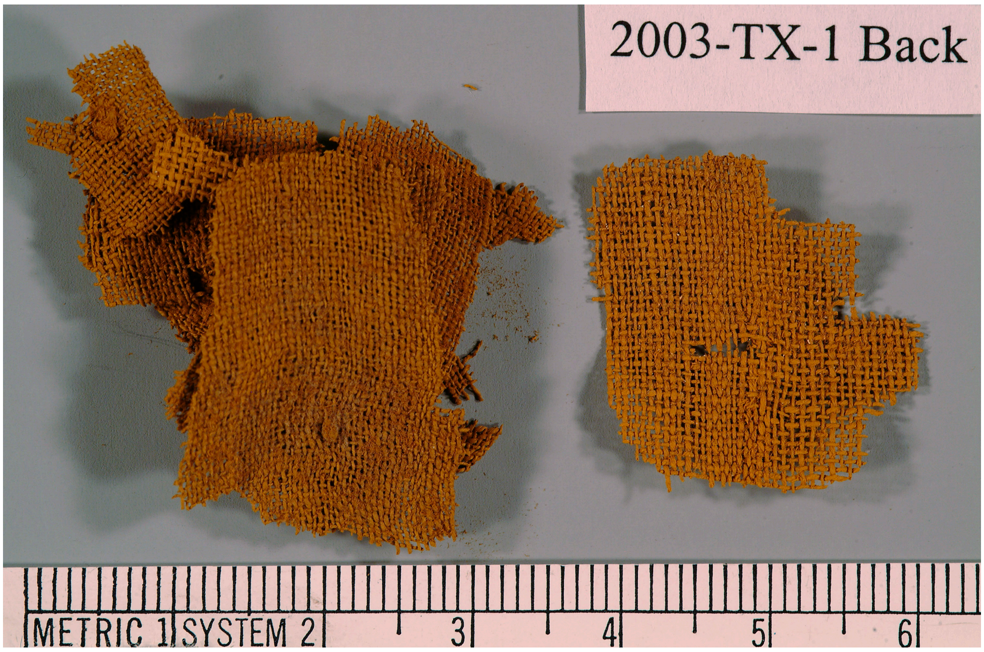

Figure 14. 2003-Tx-1 Back.

Figure 15. 2003-Tx-2 Back.

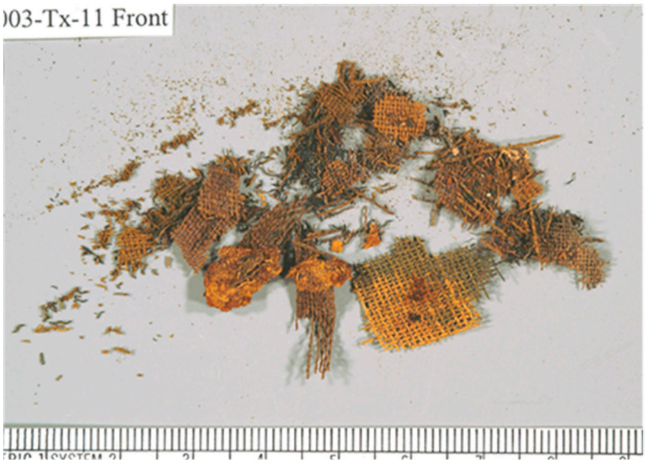

Figure 16. 2003-Tx-11 Front (fragment group).

Figure 17. 2003-Tx-7 Front.

Figure 18. 2003-Tx-8 Back.

In recent decades, a reasonably stable version of goethite-coated polyester was developed under laboratory conditions while exploring the potential for making fabrics conductive. The inventor kindly recreated his treatment on modern linen on our behalf (Figure 19) [16,31–34]. This suggests that under the right circumstances, it is possible to produce a laboratory version—or to manufacture fabric of this sort. The modern facsimile is flexible and has a soft handle; it is a purer yellow, more a limonite, as might be expected with modern purified chemical agents.

Figure 19. Three forms identified as goethite with VIS-NIR-SWIR spectroscopy. In the background, a piece of modern polyester coated with goethite; on glassine paper, some fragments of 2003-Tx-1; at upper right, modern linen coated with goethite.

Yet, the feasibility of goethite-treated cloth for use as a garment or furnishing fabric is somewhat questionable. The modern samples and the ancient ones are "ring dyed": it is the surface layer that has been coated. As a surface layer, the coating would be subject to abrasion and wear. Depending on the depth of surface and size, goethite coating might be somewhat irritating to the skin, and scratchy and hard (5–5.5) on the fibrils, comparable to a fine sandpaper on the Mohr's scale.

Fragment 2003-Tx-11 (Figure 16) provides interesting insight into an unusual means of coloration that was developed by the Phrygians. Goethite is present, with some of it dissolved and some tinged green or blue-green. When examined under a low-powered microscope, the golden strands were found to have been dabbed with indigo before the yarns were plied (Figure 20). That is, it appears that the oxidized indigo solution was lifted by brush hairs and dotted onto a yarn where it might coalesce as droplets or dabs. Here, the goethite seems a lighter shade, a thinner coating or film of the mineral. Was this complex fabric placed in Tumulus MM as an experimental success and an example of ingenuity? Whatever the significance of this colorful cloth, its striped yarn is intriguing now.

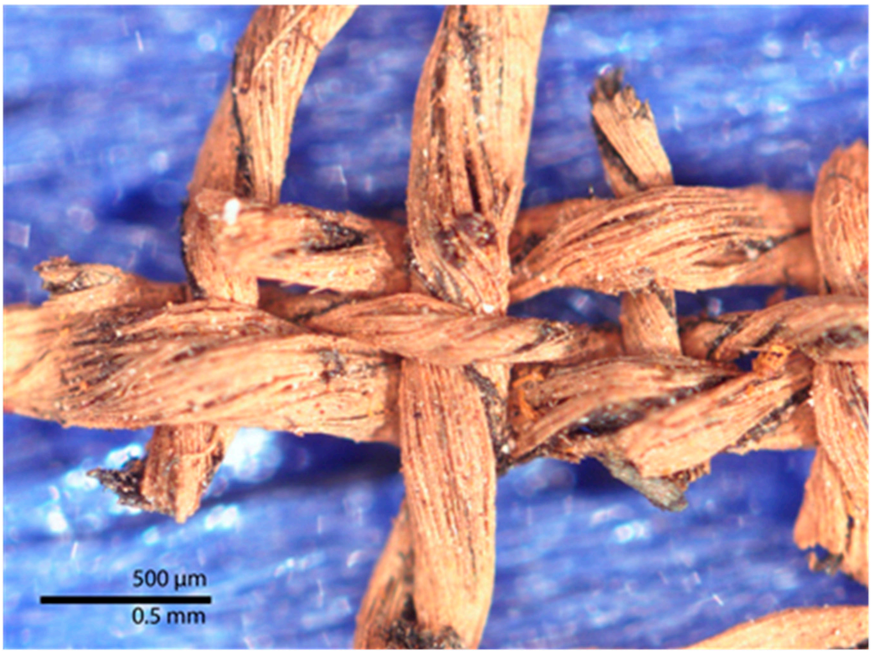

Figure 20. Detail of 2003-Tx-11 showing indigo between single strands of goethite-infused fibers (lying on a modern medical antistatic fabric).

4.2. Indigo

The fragment 2003-Tx-11 with its lighter goethite layer and semi-dyed, *leuco*-indigo state suggests that goethite had a second, perhaps more common use: to make a green color that would fade so slowly that the fading would match the rate of fabric wear, unlike the fading rates of fugitive yellow plant dyes. For indigo itself, it might have been processed from woad that could have been cultivated in Anatolia or from indigo that could not [35] (pp. 335–408). There is no plant record of woad seeds or vegetation at Gordion [36]. The ingenuity and frugality used to produce a more uniform dyeing is seen in the presence of its being dabbed on one of the two singles subsequently plied together. Here, indigo was partnered with goethite, already in place on the adjacent strand (see Figure 20). Various reduction methods were utilized for dyeing indigo; these might well have been adjusted to accommodate goethite [37–39].

While fragment 2003-Tx-11 is the only textile sample from Tumulus MM with *leuco*-indigo ($C_{16}H_{12}N_2O_2$), several others have stable forms: indigo (indigotin) the oxidized dye, as well as two unreacted oxidized forms isatin and indoxyl (Table 2). This presence of multiple forms of indigo on the samples from 2003-Tx-3 (Figures 21 and 22), 2003-Tx-4 (Figures 23 and 24), 2003-Tx-6 (Figures 25 and 26), 2003-Tx-8 (Figures 18 and 27), and the back of 2003-Tx-9 (Figure 28) may have contributed to the shades of maroon, purple, or brown. The combined presence of chemistry and color suggests the possibility that two bath dyeings might have been used: a vat for indigo and a mordant dyeing for madder. Fragment 2003-Tx-11 promotes the concept of creative planning and dyeing with indigo; the distinctive contrast between the front and back of fragment 2003-Tx-2 (Figures 13 and 15) does not. The others lie somewhere in between.

Figure 21. 2003-Tx-3 Front.

Figure 22. 2003-Tx-3 Back with spherical clover-burr (a plant seed burr).

Figure 23. 2003-Tx-4 Front.

Figure 24. 2003-Tx-4 Back.

Figure 25. 2003-Tx-6 Front.

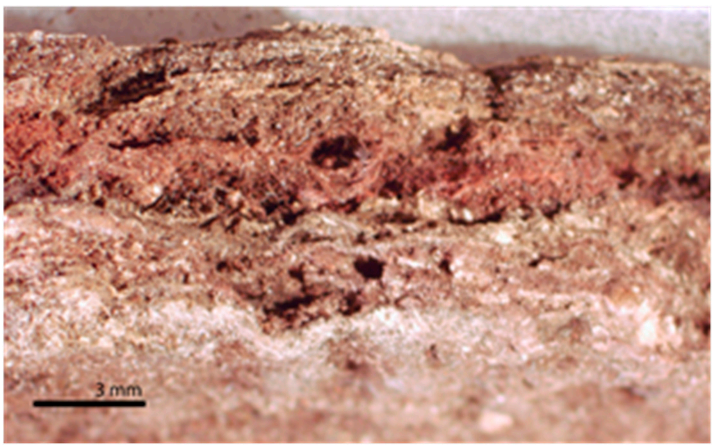

Figure 26. Side view of the upper right edge of 2003-Tx-6 exposing diverse colored layers.

Figure 27. 2003-Tx-8 Front.

Figure 28. 2003-Tx-9 Back.

4.3. Madder

For the textile fragments in Tumulus MM dyed with madder-related dyeings, the treatment is more likely to be wholesale immersions, but the various constituents of madder may or may not be present (Tables 3 and 4). Only 2003-Tx-2 Front (Figure 13), the red matte fragment, and 2003-Tx-6 (Figures 25 and 26), the reddish-purple fragment, contained almost the full list of the chemical components of madder found among the Tumulus MM textiles. These include alizarin, purpurin, lucidin, 1-methoxy-2-methylanthraquinone, rubiadin, xanthopurpurin dimethyl ether, 2-hydroxyanthraquinone, and 2-methoxyanthraquinone (Table 3); 2003-Tx-6 lacks damnacanthal (Table 4). All the Tumulus MM madder-containing fragments lack munjistin, pseudopurpurin, and rubianin, all typical of *Rubia tinctorum*.

With the exception of 2003-Tx-2 the madder fragments fall into two distinct hue ranges: the purple and reddish-purple fragments of 2003-Tx-3 (Figures 21 and 22) and 2003-Tx-6 (Figures 25 and 26) and the softer, darker brown-beiges of 2003-Tx-8 and 2003-Tx-9 Back (Figures 27 and 28). The latter may have been processed with a different end-use in mind, or they may have received their final coloration by different techniques, such as repeated dyeings, i.e., repeated dyebaths.

Fragments 2003-Tx-8 Front and Back (Figures 18 and 27) and 2003-Tx-9 (Figure 28) did not contain alizarin, purpurin, or lucidin but were also brown. Avoiding these components, the dye produced a brown shade, perhaps with the aid of inorganic components, such as aluminum, iron, and copper (Table 5)). In fact, they are a near match for the dark fibers of

2003-Tx-7 Back, which did have alizarin and a number of other chromophores they lacked (Figure 29, Tables 3 and 4)).

Figure 29. 2003-Tx-7 Back.

Perhaps the most unusual fragment of the madder group is the seemingly unfinished fragment 2003-Tx-10. This consists of several apparently identical layers of fine plain weave fabric now laminated together. They have been molded over time as though around the stretcher of a stool or some other shape (Figures 30 and 31). 2003-Tx-10 was overlooked for SEM/EDS, possibly because it appears as though its dyeing had not been completed. Nonetheless, madder dye components were identified—alizarin, lucidin, 1-methoxy-2-methylanathraquinone, rubiadin, xanthopurpurin dimethyl ether (Table 3) and others (Table 4). In some places, the dark madder appears to have been dabbed or smeared on with a viscous material. In other places it has merged with the fiber and darkened it as a dye. Despite its fine, delicate weave count, 2003-Tx-10 alone among the textiles from Tumulus MM is well enough preserved well to identify the type of fiber (flax), as confirmed by conventional polarized light microscopy (Table 1).

Figure 30. Fragment 2003-Tx-10 Back.

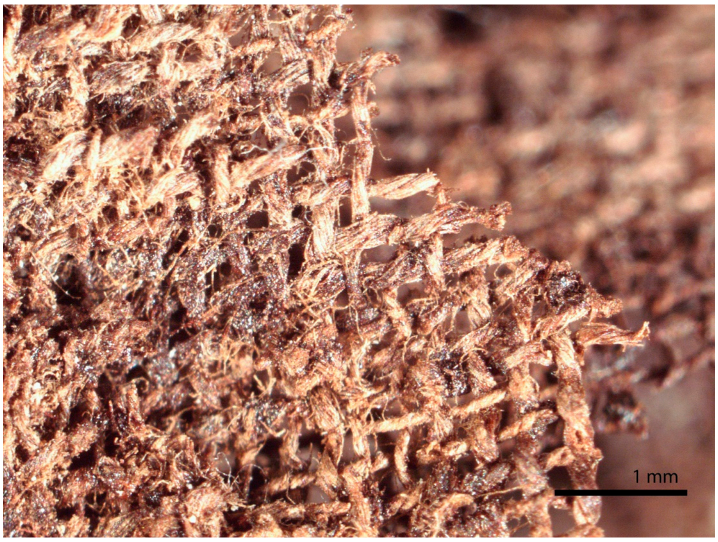

Figure 31. Detail of a single layer of 2003-Tx-10 on the back.

2003-Tx-10 has the lucidin previously found in samples Tx-1 through Tx-6 (Tables 3 and 4)) but lacks the purpurin found in the reddish-purple samples. The lack of purpurin, and sometimes alizarin, may indicate the use of other red chromophoric plants as components of the dye liquors. Helmut Schweppe lists Abyssinia (modern Ethiopia) as a source for *Oldenlandia umbellata* L. or chay root, which contains alizarin and lucidin but no purpurin and no xanthopurpurin [40]. At the time of the construction of Tumulus MM, the Kushite empire on the Upper Nile or the D'mt (Da'amat) kingdom in east Africa might have provided a source closer than India for Phrygian trade. Schweppe also suggests that some components present in the plant might not be taken up by fiber in the dyeing [40] (p. 195); other botanists, dyers, and dye chemists have reported similar issues with *Rubia peregina* (Wild Madder), *Rubia tinctorum* (Madder), and *Galium* sp., all of which are native to Anatolia [35] (pp. 107–166), [41]. Indeed, the textile fragments from Tumulus MM that contained madder lack a full, clear, parallel with any particular classic madder. Future analyses employing MS/MS may resolve this question.

4.4. Mordants

The specific identification of high iron content was confirmed for two fragments as the result of a mineral "dyeing". Early in this study, ICP-MS analysis for bromine was utilized to look for metal mordant ratios, using modern reference standards of mordanted wools, mordanted dyed wools, and previously analyzed historic samples. Nothing comparable to the established ratios was found for 2003-Tx-6, due to loss, diagenesis, contamination, or all of these factors [19,24]. Alum has elsewhere been identified as "Phrygian stone" and described by Charles Singer as an indication of the earliest chemical industry [35] (pp. 20–49), [42]. This interesting topic is outside the scope of the present paper and the self-sampling procedure used in these analyses. The processes used cannot satisfactorily separate functional mordants from soil, seepage, and dirt after 2700 years. Instead of hypothesizing about which metal moiety or moieties may have been active, permission for destructive testing might be sought in the future, in order to provide specific samples that could be cross-sectioned, imbedded, and polished for SEM/EDS with XRF capacity for quantitative analysis. After thorough discussion and permissions for such destructive testing, samples from the City Mound textiles and the Tumulus MM fragments might be successfully assayed and surveyed in this manner.

4.5. Gums and Resins Such as Myrrh

Present on 2003-Tx-10 and 2003-Tx-11 is some type of viscous gum or resin, as yet unidentified, which held the dyestuffs of madder and indigo, respectively, in place. Both gums and resins produce a wide swath of compound peaks in spectra, to the extent that they are ionizable by DART. To characterize such complex samples with DART-MS or pyrolysis gas chromatography-electron impact ionization-MS, results would have to be compared to a reference database of salient gums and resins from that historical context.

5. Conclusions

For those familiar with the Greco–Roman legends of Midas and his "golden touch", the golden-hued goethite-treated textiles from Tumulus MM suggest a tantalizing link to the fabulously wealthy Phrygian king. For the purples of 2003-Tx-3 and 2003-Tx-6, dye scholars and technologists such as Harald Böhmer make a convincing case for iron-mordanted fiber or fabric in single bath madder dyeing being acidified. But these two examples from Tumulus MM both contain forms of stable indigo, and one (2003-Tx-6) has a lower range of iron (Table 5) [43]. Among the various samples analyzed for the present study, there remain confusing patterns of components, hue, and depth of shade. These cannot easily be explained by such things as the selection of old madder roots vs. younger plants, by the re-use of unexhausted or contaminated dye baths, by intentional additional auxiliaries, or by the use of mixed or contaminated mordants [43]. A somewhat haphazard dye process could produce a uniform effect, if the fibers were dyed prior to spinning to even out coloration—creating a heather-like effect.

Somewhat more specificity might be needed to weave small repeating patterns as seen in the fragments from the City Mound (Figure 6). Indeed, skeins could be sorted as lots, and a raised pile, as formed for toweling or carpets, would blend close shades quite well. This might suffice for a single village product. Yet, for commercial scale, a reproducible product and color would be required. Fundamentally, an advanced knowledge of the properties of the dye plants, preparatory methods prior to dyeing, and the effect of auxiliaries and assists are essential. This lends substantial credence toward an extension of Singer's theory to include dyes and dyeing as part of the first chemical industry, where accuracy and precision are necessary. Paradoxically, it also supports the importance of substitution, because the same level of knowledge is required to achieve the same color, to maintain a consistent product over time, when supplies and sources change from year to year [44].

Given the colorants identified in Tumulus MM and the textile equipment excavated in the Terrace Building complex on the City Mound, one can posit a highly developed textile industry at Gordion that was chemically advanced, technically sophisticated, and industrial in scope. One still cannot say how the textiles from Tumulus MM and the operation on the City Mound were related. Whatever the purpose of the charred textiles found on the mound—utilitarian or prestige, luxury gifts or tribute, furnishings or clothing—future study of these fragments may yet establish a correlation. We hope that this paper will serve as incentive for such research, and will underline the importance of colorants, dyeing techniques, and mordants in the ancient Near East, as dyes and colored textiles must have played a major role in economic and social organization, as attested for the kingdom of Phrygia.

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