Experimental Skin Processing with Ferruginous Material. Macro- and Microproperties. Preliminary Results

Introduction

Leather processing is supposed to had been one of the commonest activity in Palaeolithic hunter – gatherers’ societies. Ethnographic sources claim that hide processing was a multistage work, beginning with a fresh hide cleaning, through a whole cycle of drying, softening or smoking to get a satisfying material for making clothes, shelter construction or other functions. A variety of tools were used, mainly including scrapers.

It is known from ethnographic observations (Hayden 1993), that some stages of hide processing require some agents that facilitate cleaning or softening. Haematite is one of them. Its presence has long been proved in archaeological records, as sediment colouring in pit fillings, cultural layers, on tools surfaces and as a raw material itself in the shape of lumps at some archaeological sites. A problem usually discussed is a practical function of haematite. It is commonly accepted that the rock (or mineral) was used in colouring leather, maybe in its preservation, softening and quick drying; distinct differences in effect were observed when red and yellow ochre were applied “the yellow ochre remained stiff, thick and rough whereas the piece treated with red ochre dried rapidly, lost 1 mm in thickness and started to get softer” (Wadley et al. 2004, 662). All applications are probable. A symbolic and ritual aspect of red ochre and haematite by Palaeolithic people used to be highlighted (Woźny 2005).

Numerous and various potential ochre and haematite applications (Wreschner 1980; Wadley et al. 2004) provoke to us if a determined processing and function can be identified through the analysis of their microstructure. This question arouse during the observation of microstructural variability of paintings, differing in chronology and techniques, which were performed with the red ferrous colourants (Trąbska 2007). It can be assumed that red colouring observed in ar-
chaeological sites, ascribed to powder production in hide processing should appear either due to deposition of remnants of crushed and powdered haematite/ochre and is not directly connected with the leather, or due to utter destruction of a processed leather, with only haematite/ochre powder left. We decided to verify, though partly, the hypotheses concerning both the application of haematite in hide processing and microstructural “fingerprints” of the used material. A direct impulse stems from observation made during functional and structural analyses of artefacts from the Magdalenian site Dzierżysław 35 (Ginter et al. 2002). Revealed traces on tools point at hide scraping with the use of haematite. Additionally, haematite was found there in various forms: figurines and probable remnants of rubbing off powder (op. cit., Trąbska 2004).

Material and methods

Materials used for experiments are as follows: a) dried and hard, unprocessed wild boar leather, with remnants of fat and epithelium, b) scrapers made by one of us (MW-K) from Baltic erratic Cretaceous flint, c) eight “haematite” artefacts from Dzierżysław 35, varying in colour and hardness, but macroscopically identical with processed artefacts, with striations or rubbed surfaces, d) one sample of a natural haematite clay from Klucze quarry (Upper Silesia Province), used as a pigment contemporary, and e) one sample of a contemporary pigment used by artists (Table 1). For the two samples we know their phase composition; they, actually, are not pure haematite but natural mixtures of haematite, clay minerals, quartz and other natural substances. As it is assumed that other samples of raw material used in this work are of similar composition, they are named “haematite”. Six “haematites” (for nine used in the experiment) were comparatively hard to rub them on a surface or reduce it to a powder (Table 1). Size of “haematite” samples used in experiments does not exceed 2 x 1.5 cm. Surfaces of processed leather fragments were observed with the use of scanning microscopes: Jeol 5200 with Link-Isis EDS microanalyser and EDS/BSE NanoNova SEM SEI Company apparatus.
Experimental work

Fragments of wild boar leather were processed twofold: in several cases “haematite” was rubbed on a surface, the latter became red and the remnants of powder were left. In other cases a “haematite” lump was scraped with the flint tool over a hide surface, the powder sedimented and coloured the hide that was then scraped with scrapers. Small lumps: a mixture of “haematite”, fat and leather epithelium were partially removed and partially rubbed into leather surface. Certain “haema-
“Haematite” lumps were so hard (sample 723) that required an intensive scraping to produce a powder.

### Table 3
Results of hide processing with the use of “haematite”. Phot. D. Bobak

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mode of processing</th>
<th>“Haematite” sample</th>
<th>Photography of a processed hide fragment</th>
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<tbody>
<tr>
<td>0</td>
<td>“Haematite” powder scraped on a leather surface, that was then scraped with the flint tool (scraper)</td>
<td>3832 Fig. 3</td>
<td><img src="image" alt="Photography of a processed hide fragment" /></td>
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<tr>
<td>1</td>
<td>Commercial pigment</td>
<td>Fig. 4</td>
<td><img src="image" alt="Photography of a processed hide fragment" /></td>
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<td>1a</td>
<td>2274</td>
<td>Fig. 5</td>
<td><img src="image" alt="Photography of a processed hide fragment" /></td>
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<tr>
<td>2</td>
<td>“Haematite” powder scraped on a leather surface, that was then scraped with the flint tool (scraper)</td>
<td>2695 Fig. 6</td>
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<td>2</td>
<td><img src="image1.png" alt="Image 1" /></td>
<td><img src="image2.png" alt="Image 2" /></td>
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<tr>
<td>2a</td>
<td>“Haematite” powder scraped on a leather surface, that was then scraped with the flint tool (scraper)</td>
<td>6782 Fig. 7</td>
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<td><img src="image3.png" alt="Image 3" /></td>
<td><img src="image4.png" alt="Image 4" /></td>
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<td>3</td>
<td>Limonite powder scraped on a leather surface, that was then scraped with the flint tool (scraper)</td>
<td>5189 Fig. 8</td>
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<tr>
<td>3a</td>
<td>“Haematite” powder (made of a very hard specimen) scraped on hair</td>
<td>7196</td>
<td>Fig. 9</td>
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<tr>
<td>4</td>
<td>“Haematite” powder scraped on a leather surface, that was then scraped with the flint tool (scraper)</td>
<td>5462</td>
<td>Fig. 10</td>
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<tr>
<td>4a</td>
<td></td>
<td>5462</td>
<td>Fig. 11</td>
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<td>5</td>
<td>Leathered covered with natural haematite clay</td>
<td>“natural haematite”: haematite clay</td>
<td>Fig. 12</td>
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<tr>
<td>5a</td>
<td>Very hard “haematite” powder, intensely scraped on a leather surface, that was then scraped with the flint tool (scraper)</td>
<td>723</td>
<td>Fig. 13</td>
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Results of experimental and microscopic observations

“Haematite” and limonite processed hides were intensely coloured (Table 3). A hue varied from orange through red to reddish-brown, depending on a colour of a raw “haematite” and amount of an added powder. “Haematite” powder becomes a colourant at very low concentration of powder (in other words: single powder grains make a hide macroscopically red. Figs. 14–21). Undoubtedly scraping facilitated impregnation of “haematite” powder in leather pores, colouring it more intensely. The use of powder facilitated removal of fat remnants from a hide surface, softening it, in some cases even a dozen or so minutes.
Particles of “haematite” powder on processed hide surfaces are extremely tiny, ranging from 10 to 100 micrometers (one micrometer equals $10^{-6}$ m). The tiniest particles were observed on the sample no. 2, the largest on surface of hair. Particle shape is irregular, oval (only single observations: sample 16; Fig. 16), lumpy (samples 1, 2, 3a, 4; respectively Figs. 15, 17, 18, 19) and flaky (sample 0; Fig. 14). Variation of shape is not significant: particles habit is typical for fine grained and rubbed haematite and ochre.

Chemical analyses of processed surfaces reflect general pattern of a raw material chemical composition. Concentration of iron is very low and does not exceed a few percent (Figs. 14a–21a). Only sample 0 is characterised by high iron content due to specific mode of processing: enormously high amount of powder was used. Other elements: silica, alumina and potassium are components of clay minerals (comp. Table 1). They improve “smearing capability” of “haematite” on any surface. No admixtures of hard grains were observed (quartz, feldspars): it can be assumed that they were removed unintentionally in the course of processing as they were identified in XRD phase analysis (Table 1). Carbon and, to a lesser degree, sulphur and chloride are related to the leather composition, though not all of them were recognised in every sample and we do not know why.
Fig. 14. Sample 0. Microstructure of hide surface processed with "haematite". An arrow points at "haematite" grains. Flaky occurrences of ferruginous material: without chemical analysis they cannot be discerned from surroundings.


Fig. 14a. Sample 0. High iron concentration due to specific processing (comp. Table 2).

Fig. 15. Sample 1. Tiny “haematite” particles, occasionally aggregating in larger lumps, pointed by arrows.

Ryc. 15. Próbka 1. Drobne cząstki „hematytu”, czasem tworzące wyraźne skupienia, wskazane przez strzałkę.

Fig. 15a. Very low concentration of iron and other “haematite” elements: typical composition of a processed leather surface.

Ryc. 15a. Bardzo niska koncentracja żelaza i innych pierwiastków wchodzących w skład „hematytu”: typowy skład chemiczny powierzchni opracowanej skóry.
Fig. 16. Sample 1a. An oval grain of a limonite powder: a unique image in the examined set of samples.

Fig. 17. Sample 2. Iron compounds have here shape of fine lumps, recognizable only due to chemical analysis.

Ryc. 17. Próbka 2. Substancje żelaziste są bardzo drobnoziarniste, morfologicznie możliwe do zauwazania tylko dzięki analizie mikrochemicznej.

Fig. 17a. Sample 2 and 2a. The results of a chemical microanalysis is representative for the two samples and, again, point at very low concentration of iron.

Fig. 18. Sample 3a. Iron compounds are easily recognisable here as lumps. They are very strongly attached to the hair surface.

Fig. 19. Sample 4. Irregular lumps of iron compounds located loosely in hide corners. This particle rapidly disappeared from the microscope observation field.


Fig. 19a. Sample 4 and 4a. Chemical analysis of a hair surface.

Fig. 20. Sample 5. Very low concentration of “haematite” powder. Only single particles can be identified due to chemical microanalysis.

Fig. 21. Sample 5a. Incredibly low concentration of a "haematite" powder.

Fig. 21a. Sample 5a. Result of a chemical micro-analysis of a hide surface.
Conclusions

1. Colour and hardness of the used raw material influence, to some degree, final colour effect of processed leather. Satisfying results were achieved both with application of relatively hard “haematite” and very soft natural haematite clay. In the two opposite cases, processing modes had to be modified (Table 3).

2. Expectedly, high amount of used “haematite” powder affected colour intensity (Table 3, Fig. 3: sample 0) and was detected in a chemical microanalysis as enormously (compared to other samples) iron concentration (Figs. 14 and 14a).

3. Intensely processed (scraped) leather softens even after a dozen or so minutes, whereas hair becomes stiffer. The latter is clearly supported by microstructural observation: “haematite” powder usually (though not always) sticks strongly to hair surface and its grains remain comparatively large (Figs. 18, 19). “Haematite” positively facilitated scraping of leather: fat was bound with ferruginous material and the product could have been easily removed with the use of a scraper. Observations of one of us (JT) showed also that haematite clay from the Klucze quarry has cauterising properties that may make the substance useful not only for medical purposes but also in removal damp from hide surface.

4. No apparent differences in usage of “haematite” and limonite were noticed, still microfeatures discrepancies were found: limonite left oval grains, admittedly, rarely observed, but they definitely did not occur in “haematite” processed leather (Fig. 16 vs. other images).

5. “Haematite” and limonite powder left on the processed leather has extremely tiny size (X0 micrometers; Figs. 14–21). Moreover, its grains are definitely scarce, excluding sample 0. Their shapes are prevalingly irregular, lumpy and flaky. Oval powder is found only in a one case and concerns limonite. Thus, practically no shape diversity, due to processing differences applied by us, is observed.

6. Very fine grained “haematite” powder as well as its extremely low concentrations give weak hope of their preservation in a leather post-depositional history. Especially, that ferruginous compounds are closely related with an organic material (leather) that usually contains sulphur. Fine grained ferruginous powder tends to be destabilised and transformed to iron sulphides or other compounds, depending on pH and Eh environmental conditions. Practically no cherry or red powder is expected to be left then (a phenomenon commented widely in pedological literature). Reaction of iron (III) oxides with sulphides ad organic matter was widely reported by mi-
crobiologists and sedimentologists (e.g. Canfield al.1992; Coleman et al. 1993; Crowe et al. 2006).

7. Thus it can be assumed that haematite or ochre powder observed in archaeological sites is supposed to originate rather from unnecessary remnants after skin processing, dispersed around, than from powder dispersed on a hide surface (assuming, according to observations that the hide itself would have utterly disappeared).

8. Experimental research of raw materials application in relation with their microappearance and analysis in post-depositional environment should not be neglected. The authors continue examinations of other aspects of haematite leather processing.

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References


Trąbska J. 2007 Mikrostruktura pyłu hematytowego – wskaźnik użytkowania i pochodzenia (Microstructure of haematite powder – an indicator of mode
of use and provenance). XV Śląskie Spotkania Archeologiczne, Karłów, 16–19.

Trąbska J.
2004 Sprawozdanie z badań mineralogicznych i petrograficznych „ochr” ze stanowiska Dzierżysław 35, Kraków, Not Published.

Wadley L., Williamson B., Lombard M.
2004 Ochre in hafting in Middle Stone Age Stone Africa: a practical role, Antiquity 78, 301.

Woźny J.
2005 Czerwona ochra i ziarna zbóż. Symbolika odrodzenia zmarłych w obrzędach pogrzebowych kultur archaicznych międzymorza bałtycko-pontyjskiego, Bydgoszcz.

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Eksperymentalna obróbka skór z zastosowaniem surowców żelazistych. Makro- i mikrowłaściwości. Wstępne rezultaty

Zastosowanie hematytu, skał hematytonośnych oraz ochr w obróbce skór jest często sygnalizowane w literaturze, choć prace eksperymentalne nie są niestety zbyt rozpowszechnione. Niniejsze, wstępne badania miały na celu pokazanie: a) sposobu pracy przy obróbce skór z udziałem wymienionych surowców (Tabela 1–2), b) własności skór po zastosowaniu tychże surowców, c) mikrostrukturę ziaren hematytów i skał hematytonośnych pozostających na powierzchni skóry po procesie obróbki, d) ocenę możliwości ich zachowania się po depozycji oraz ewentualnego ich zidentyfikowania.