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

Introduction

Leather processing is supposed to have been one of the commonest activities 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 arose during the observation of microstructural variability of paintings, differing in chronology and techniques, which were performed with the red ferruginous colourants (Trąbska 2007). It can be assumed that red colouring observed in ar-

archaeological 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.

Table 1
Features of "haematite" samples used in experiments

Tabela 1
„Hematyt” wykorzystany w eksperymentach: cechy makroskopowe i skład fazowy

Sample 723 – violet colour, with reddish shade, rather hard. Phase composition: haematite, quartz, kaolinite, illite (Trąbska 2004)	Sample 5462 – light pink colour, soft.
Sample 2274 – violet colour, with reddish shade, rather hard.	Sample 6463 – orange-yellow colour, soft.
Sample 2695 – red-orange colour, rather hard. Phase composition: goethite, haematite, quartz, anortite (Trąbska 2004)	Sample 6782 – violet colour, with sericite shine, rather hard.
Sample 3832 – orange-yellow colour, rather hard.	Sample 7196 – violet with reddish hue, rather hard.
Sample 5189 – yellow limonite, rather hard.	Natural haematite clay from the Klucze quarry (Upper Silesia Province, Table 2, Fig. 1)
Contemporary artists' haematite powder.	

Table 2
Photographs of selected raw materials used in experiments

Tabela 2
Fotografie wybranych surowców wykorzystanych w eksperymentach

<p>Fig. 1 Natural "haematite" from the Klucze quarry</p> 	<p>Fig. 2 Sample 6463</p> 
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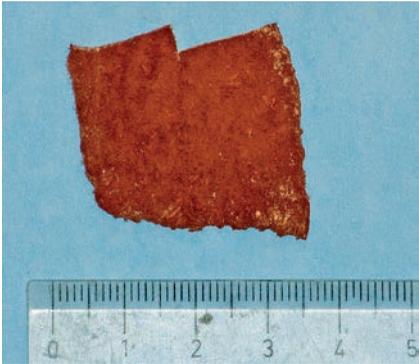
Experimental work

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-

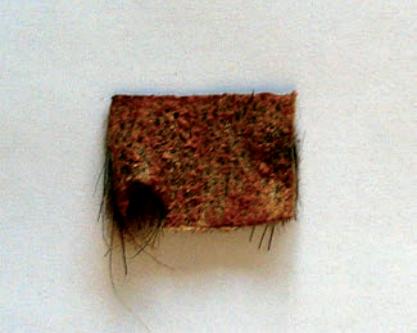
tite” lumps were so hard (sample 723) that required an intensive scraping to produce a powder.

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

Rezultaty obróbki skór „hematytem”. Fot. D. Bobak

Sample	Mode of processing	“Haematite” sample	Photography of a processed hide fragment
1	2	3	4
0	“Haematite” powder scraped on a leather surface, that was then scraped with the flint tool (scraper)	3832	Fig. 3 
1		Commercial pigment	Fig. 4 
1a		2274	Fig. 5 

1	2	3	4
2	<p>"Haematite" powder scraped on a leather surface, that was then scraped with the flint tool (scraper)</p>	2695	<p>Fig. 6</p> 
2a	<p>"Haematite" powder scraped on a leather surface, that was then scraped with the flint tool (scraper)</p>	6782	<p>Fig. 7</p> 
3	<p>Limonite powder scraped on a leather surface, that was then scraped with the flint tool (scraper)</p>	5189	<p>Fig. 8</p> 

1	2	3	4
3a	"Haematite" powder (made of a very hard specimen) scraped on hair	7196	<p data-bbox="738 297 794 321">Fig. 9</p> 
4	"Haematite" powder scraped on a leather surface, that was then scraped with the flint tool (scraper)	5462	<p data-bbox="738 874 808 898">Fig. 10</p> 
4a		5462	<p data-bbox="738 1267 808 1291">Fig. 11</p> 

1	2	3	4
5	Leathered covered with natural haematite clay	"natural haematite": haematite clay	<p data-bbox="725 301 790 325">Fig. 12</p> 
5a	Very hard "haematite" powder, intensely scraped on a leather surface, that was then scraped with the flint tool (scraper)	723	<p data-bbox="725 763 790 787">Fig. 13</p> 

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.

Ryc. 14. Próbką 0. Mikrostruktura powierzchni skóry opracowanej za pomocą „hematytu”. Strzałka pokazuje skupienia „hematytu”. Surowiec żelazisty obecny jest na powierzchni skóry w postaci płatkowych wystąpień, tak drobnych, że dopiero analiza chemiczna umożliwia ich zlokalizowanie.

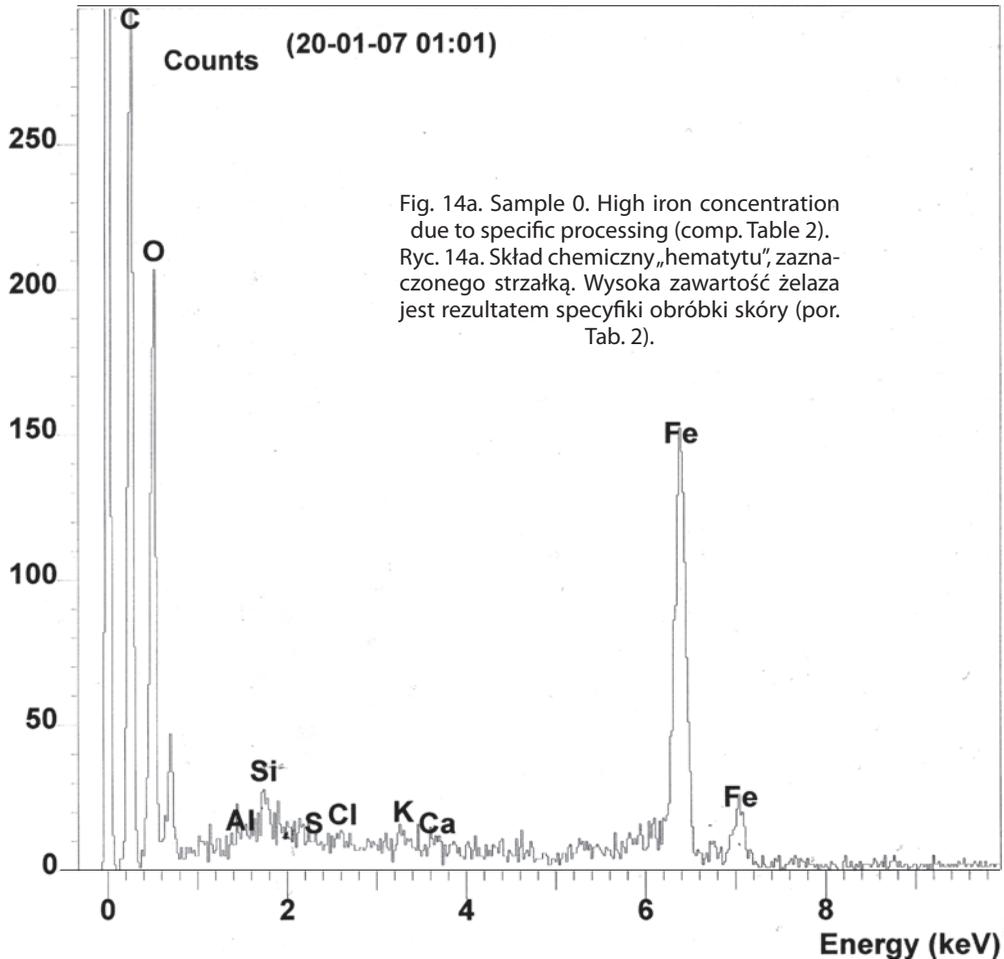
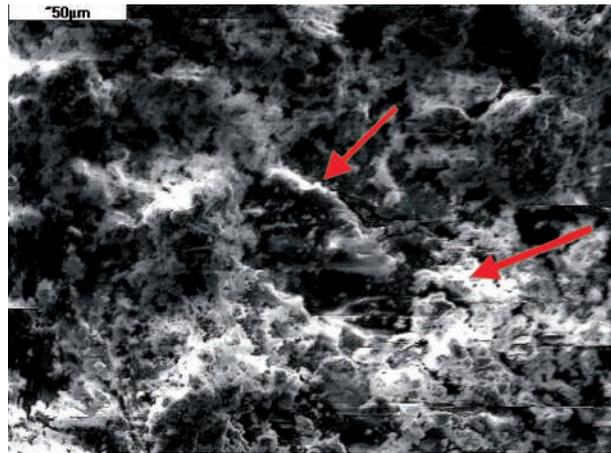


Fig. 14a. Sample 0. High iron concentration due to specific processing (comp. Table 2). Ryc. 14a. Skład chemiczny „hematytu”, zaznaczonego strzałką. Wysoka zawartość żelaza jest rezultatem specyfiki obróbki skóry (por. Tab. 2).

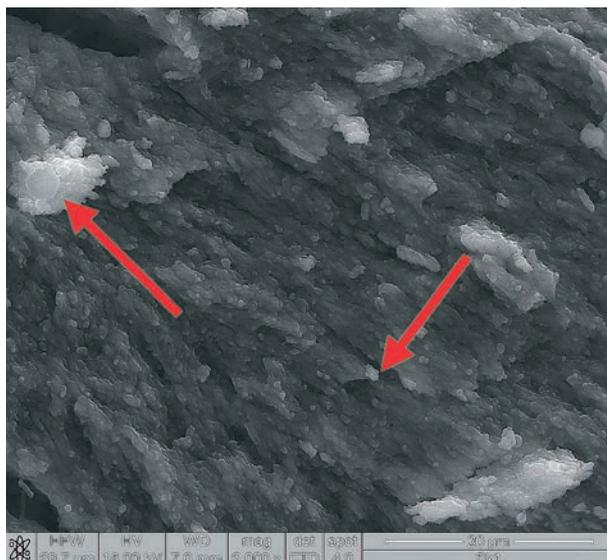


Fig. 15. Sample 1. Tiny “haematite” particles, occasionally aggregating in larger lumps, pointed by arrows.
Ryc. 15. Próbką 1. Drobne cząstki „hematytu”, czasem tworzące wyraźne skupienia, wskazane przez strzałkę.

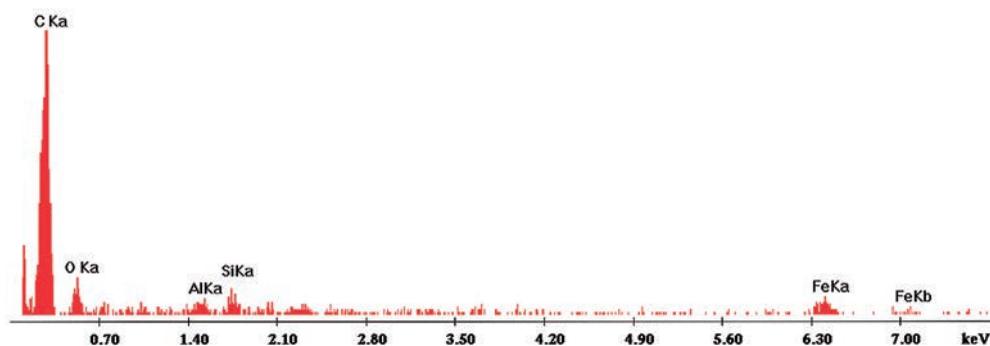
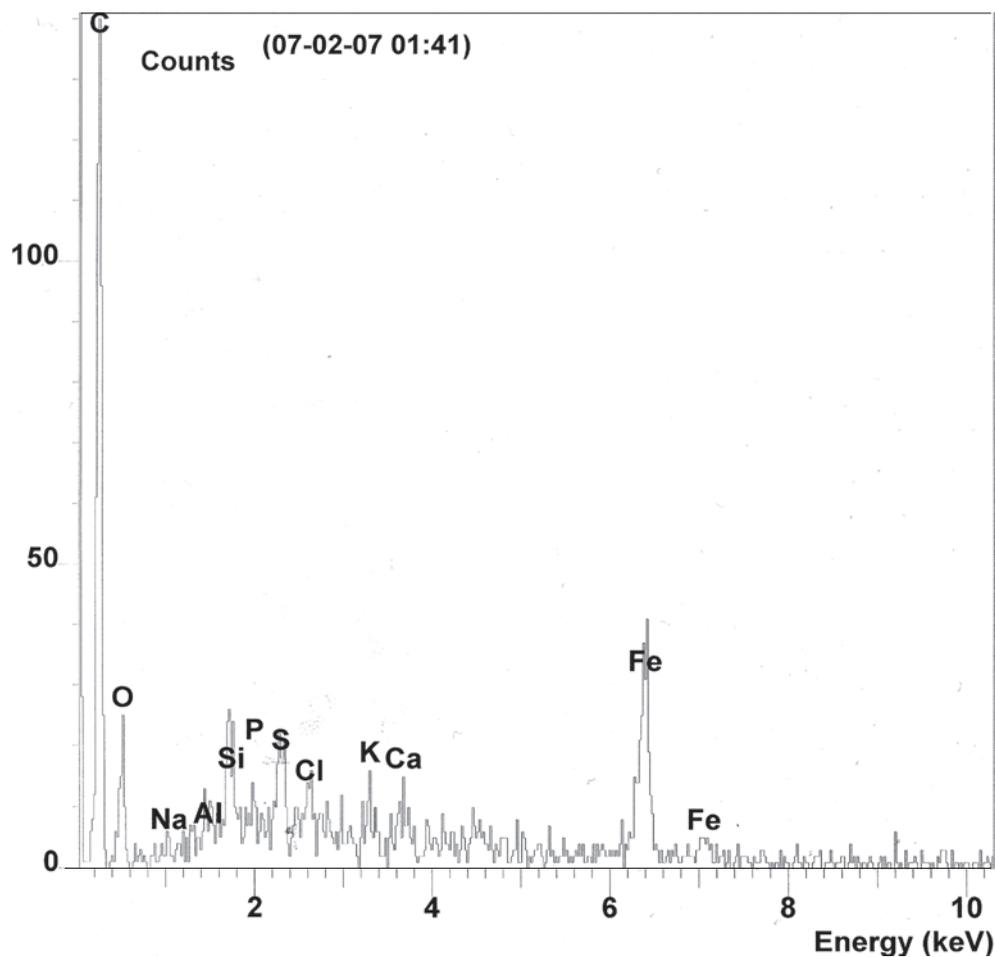
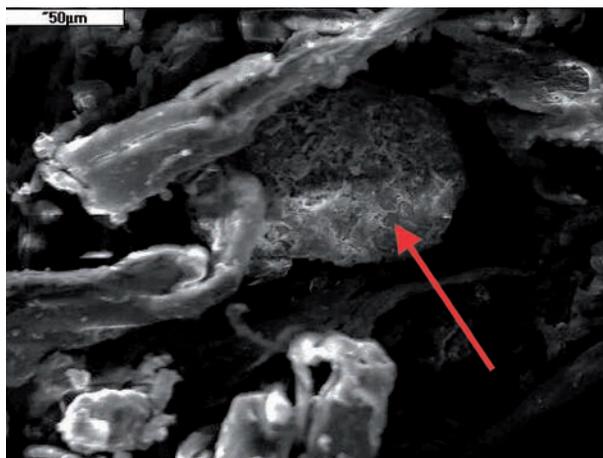


Fig. 15a. Very low concentration of iron and other “haematite” elements: typical composition of a processed leather surface.

Ryc. 15a. Bardzo niska koncentracja żelaza i innych pierwiastków wchodzących w skład „hematytu”: typowy skład chemiczny powierzchni oprowadzonej skóry.

Fig. 16. Sample 1a. An oval grain of a limonite powder: a unique image in the examined set of samples.

Ryc. 16. Próbkę 1a. Owalne ziarno sproszkowanego limonitu: unikalna morfologia w badanym zespole.



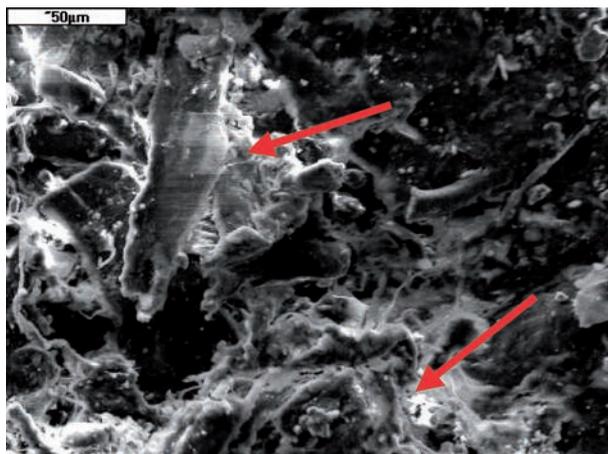


Fig. 17. Sample 2. Iron compounds have here shape of fine lumps, recognisable only due to chemical analysis.

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

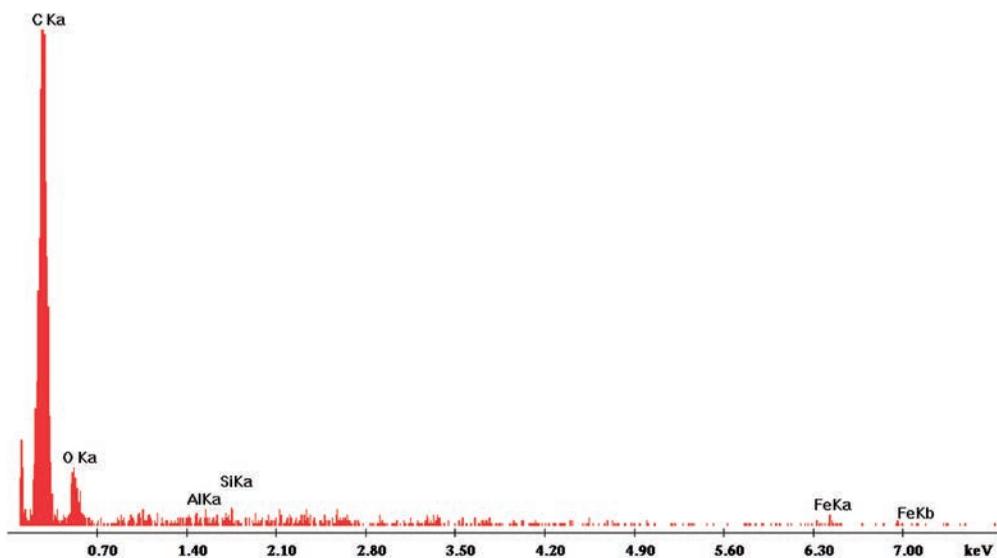
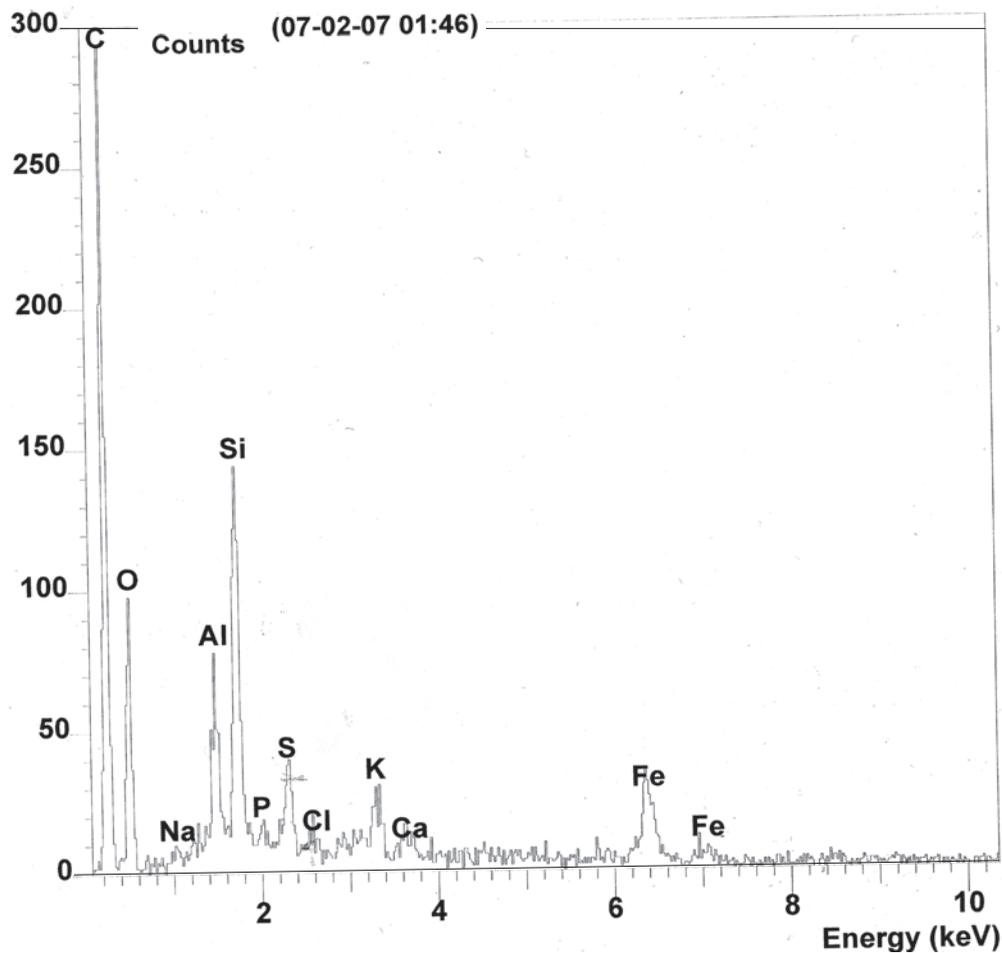
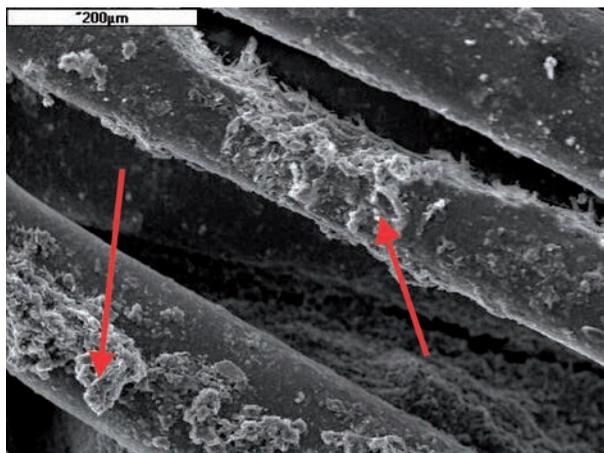


Fig. 17a. Sample 2 and 2a. The results of a chemical microanalysis is representative for the two samples and, again, point at very low concentration of iron.

Ryc. 17a. Próbką 2 i 2a. Rezultat analizy chemicznej jest jednakowy dla obu próbek. Ponownie wskazuje on na bardzo niską koncentrację żelaza.

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

Ryc. 18. Próbką 3a. Związki żelaza widoczne są wyraźnie w postaci grudek na powierzchni włosów, silnie do niej przylegając.



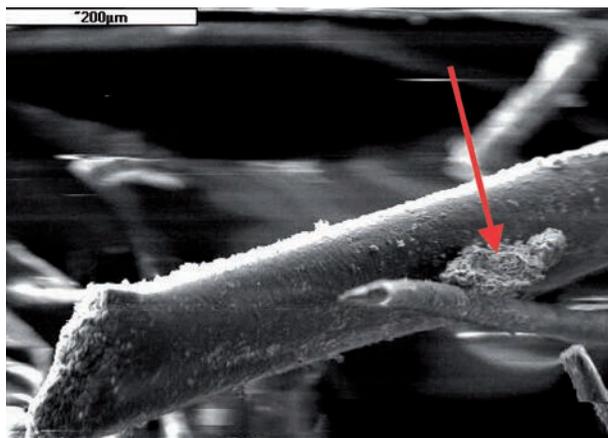


Fig. 19. Sample 4. Irregular lumps of iron compounds located loosely in hide corners. This particle rapidly disappeared from the microscope observation field.

Ryc. 19. Próbką 4. Nieregularne grudki surowca żelazistego usytuowane luźno w zagłębieniach włosów: cząstka zaznaczona strzałką zniknęła szybko z pola obrazu mikroskopowego.

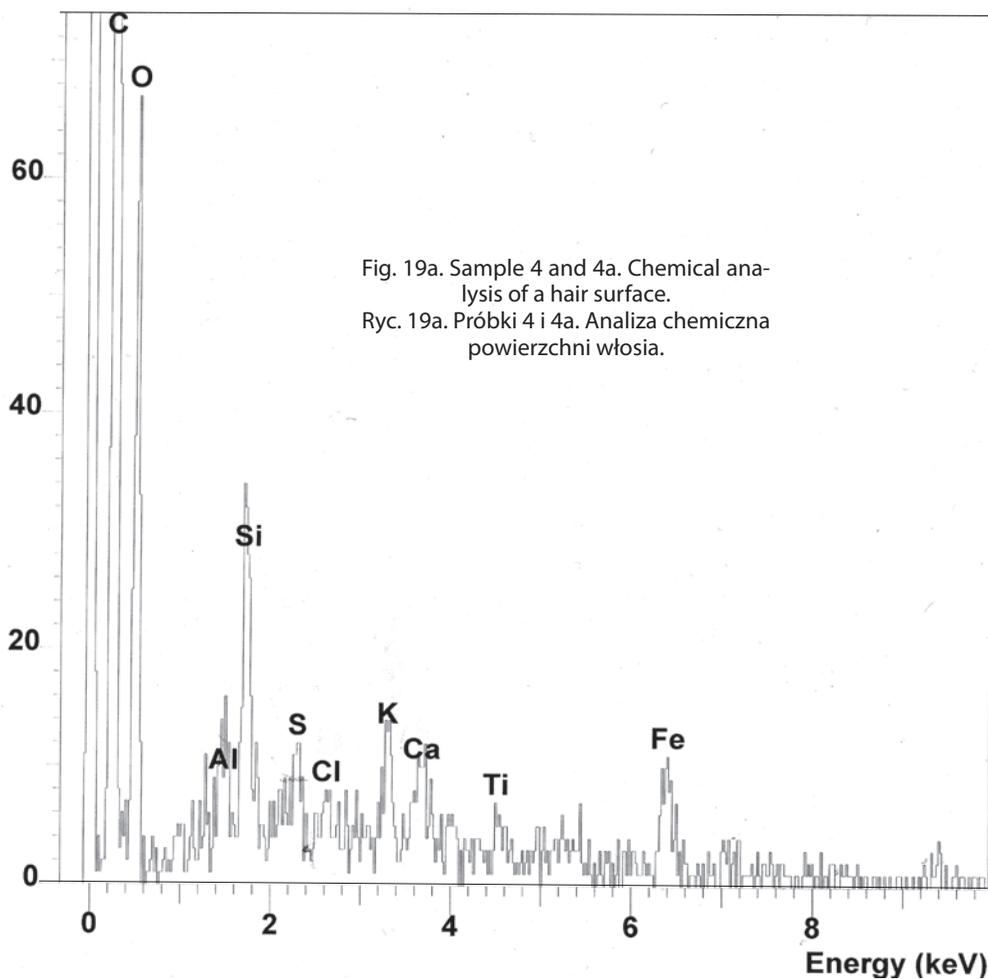
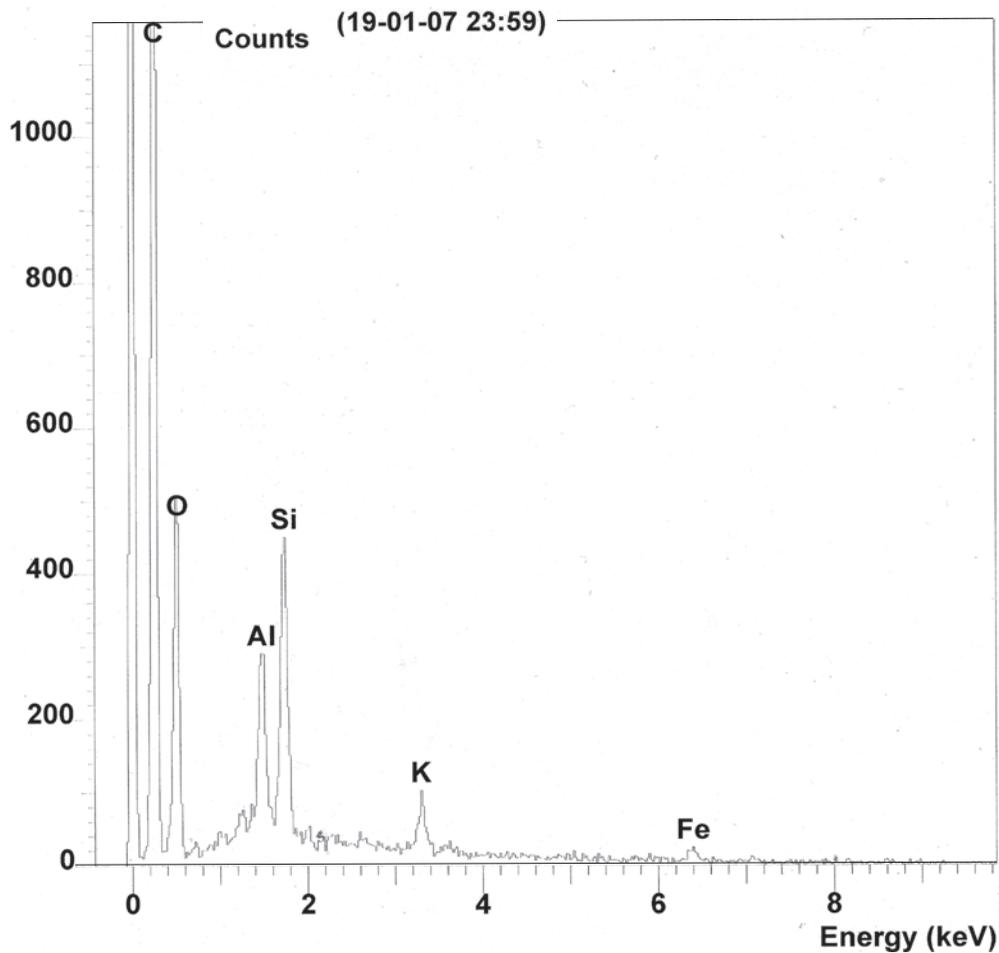
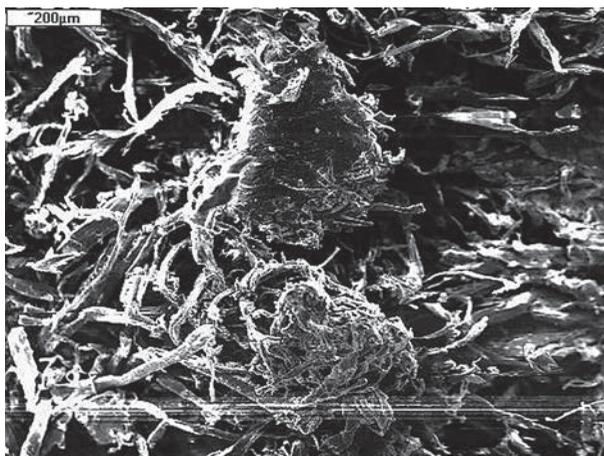


Fig. 20. Sample 5. Very low concentration of "haematite" powder. Only single particles can be identified due to chemical microanalysis.

Ryc. 20. Próbką 5. Bardzo niska koncentracja proszku „hematytu”. Pojedynczo występujące cząstki można zidentyfikować tylko za pomocą analizy mikrochemicznej.



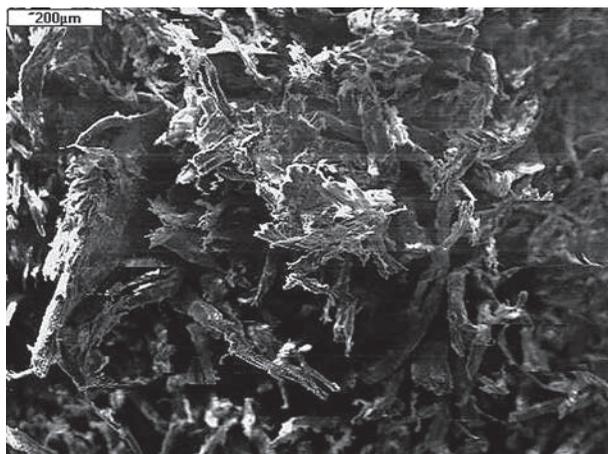


Fig. 21. Sample 5a. Incredibly low concentration of a "haematite" powder.
Ryc. 21. Próbkka 5a. Niezwykle niska koncentracja proszku „hematytowego” na powierzchni skóry.

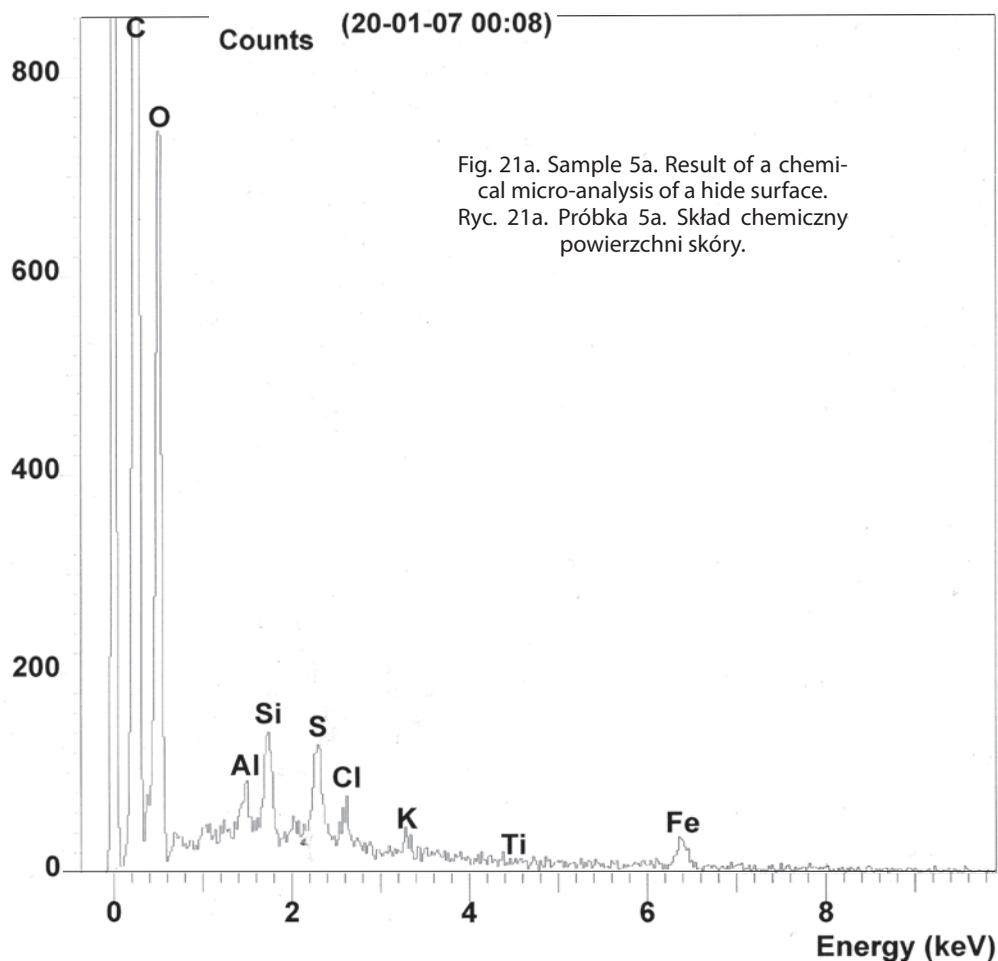


Fig. 21a. Sample 5a. Result of a chemical micro-analysis of a hide surface.
Ryc. 21a. Próbkka 5a. Skład chemiczny powierzchni skóry.

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

Zastosowanie hematytu, skał hematytowych 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 hematytowych pozostających na powierzchni skóry po procesie obróbki, d) ocenę możliwości ich zachowania się po depozycji oraz ewentualnego ich zidentyfikowania.

Surowce żelaziste (tutaj: skały hematytowe oraz limonit) zabarwiają wyraźnie skóry. Skóry ulegają także zmiękczeniu, z wyjątkiem włosów, które przejawia tendencje do bycia bardziej sztywnym (Tabela 3). Obserwacje ich powierzchni pod dużym powiększeniem pokazują, że ilość pozostającego proszku jest bardzo niewielka. Kształt mikrocząstek proszku z użytego surowca przedstawia prawie wszędzie nieregularne grudki i płatki. W jednym tylko przypadku, mianowicie tam, gdzie użyto limonitu, kształt jest wyraźnie różny (owalne skupienia). Wielkość ziaren proszku pozostającego na skórze jest bardzo niewielka (ryc. 14–21) i nie rokuje możliwości zachowania się go w obecności substancji organicznej.