Outer Carpathian Variegated Shales – a Potential Red Raw Material in Palaeolithic?

Red and yellow ferruginous raw material played undoubtedly a significant role in prehistory. This article aims at pointing at some, unrevealed by archaeologists, potential raw material that might have been successfully applied in all periods: Carpathian variegated shales.

Red ferruginous raw materials are found in numerous contexts and must have been applied in various fields of human activities, both practical and spiritual. Analysis of inventories from some Upper Palaeolithic sites suggests that prevailing a determined raw material was used: relatively soft (1-2 in the Mohs’ scale), rather compact and concise, more or less fatty under fingers, red or cherry. Questions about provenance appear immediately. Problems, unusual for other raw materials, stem from a very wide distribution and diversity of ferruginous rocks. Variegated shales macroscopically are very similar to other haematite bearing, clayey rocks, present in Poland (especially Lower Triassic formations, easy to find at the ridge of the Świętokrzyskie Mts., in the Tatra Mts. and Upper Silesia) and other Central European countries. They were pointed as a raw material in archaeological context only once: variegated shales from the Ždanice flysch (Czech) were suggested as a sourcing rock for the red artefacts from the Dolní Vestonice Gravettian site (Klima 1963a, fide Vencl 1995).

CARPATHIAN VARIEGATED SHALES – DEFINITION AND RESEARCH METHODS

Variegated shales in Polish geological sources are defined as red and green shales of various ages (Świdziński 1958, fide Franus 2002) from Late Cretaceous through Palaeocene to Eocene. The rock forms long, narrow, parallel belts, concordant to the Carpathian flysch arch, obviously, present
not only in Poland. The rocks are well exposed and can be easily traced, due to their colour, softness and thickness. The label “variegated shales” is related mainly to Carpathian flysch but the name may appear also for other clayey red-greenish rocks from different lithostratigraphical contexts. Variegated shales appeared in sedimentation processes active in the Carpathian part of the Thetis ocean, from Late Cretaceous to Eocene (see also e.g. Stankowski 1996:38n). Sedimentation and diagenesis varied in various parts of the Carpathian Belt and they have been thoroughly explored and reconstructed. Numerous geologists have been dealing with variegated shales (e.g. Kotarba 2003, Franus 2002, Dominik 1977 and many others), mostly in biostratigraphic and industrial aspects. Variegated shales have not been a research subject in prehistoric context.

To work out the problem the following questions should be posed at the beginning. First – do variegated shale possess the features attractive for prehistoric people? Second – are there any specific features that enable to recognise them from other, macroscopically similar, haematite-bearing rocks? Third – do variegated shales from different localities vary and how to notice it?

Table 1. Variegated shales from the Western Carpathian, examined by the authors.

<table>
<thead>
<tr>
<th>Locality</th>
<th>Age, tectonic unit</th>
<th>Bibliography: geological maps and explanations</th>
</tr>
</thead>
<tbody>
<tr>
<td>Istebna, Beskid Śląski</td>
<td>Eocene, Silesian Unit</td>
<td>Burtan 1972</td>
</tr>
<tr>
<td>Przybędza-Radziechowy, Beskid Żywiecki</td>
<td>Eocene, Magura Unit</td>
<td>Burtan et al. 1956</td>
</tr>
<tr>
<td>Sól –Podrachowiec, Beskid Żywiecki</td>
<td>Palaeocene – Eocen, Magura Unit</td>
<td>Ryłko et al. 1990</td>
</tr>
<tr>
<td>Kasina Wielka – Kalety, Beskid Wyspowy</td>
<td>Eocene, Magura Unit</td>
<td>Burtan 1974; Burtan et al. 1976</td>
</tr>
<tr>
<td>Glisne Pass – between Luboń Wielki and Szczebel, Beskid Wyspowy</td>
<td>Eocene, Magura Unit</td>
<td>Burtan et al. 1976</td>
</tr>
<tr>
<td>Sułkowice, Beskid Mały</td>
<td>Palaeocene – Eocen, Silesian Unit</td>
<td>Golonka et al. 1978</td>
</tr>
<tr>
<td>Rożnów, Beskid Sądecki</td>
<td>Palaeocene – Eocen, Magura Unit</td>
<td>Oszczypko et al. 1992</td>
</tr>
</tbody>
</table>

Samples from the Western Carpathian, from the Magura and Silesia Unit were examined (Tab. 1) and the results of chemical analyses of the rocks from the Skole Unit were quoted (Franus 2002). Whenever it was possible,
both the parent rock and the weathering products were researched. The samples were also processed: they were pulverized 15 minutes in a mullite mortar and ground in the same conditions. The products were mixed with water and painted on a palm to assess the adhesivity and durability of the painted layer.

Samples were examined with the use of plane polarized light microscope and X-ray diffractometry.

RESEARCH RESULTS

The research results aimed at answering the three questions posed above. The answer to the first question, concerning a possibility of application of variegated shales as a red raw material in all prehistory and historical periods, is positive. The shales are red, cherry, brownish-red. Processing (pulverising and grinding) changes the colour slightly. Weathered rocks are very soft but not concise; hardness of not weathered rocks differs from ca. 2 to 5 in the Mohs’ scale. They produce very interesting painting layers, durable and of pleasant colour.

The other question concerns the “fingerprints” of variegated shales, in reference to other clayey haematite rich rocks, especially from the Permian and Lower Triassic, widespread in Poland, Czech, Hungary and Germany as well as Terra Rosa deposits. A whole “fingerprint” is composed of several criteria and they are as follows: microstructural features including mineral composition, chemical composition, and size of haematite crystallites. Microstructure of variegated shales under polarized light microscope is monotonous: they are pelitic and aleuripelitic, laminated (Fig. 2, 4), sometimes spotted (Fig. 3). Weathered rock is unlike a parental, with common concentrations of secondary iron ferroxides. Microscopic features observed by other authors (e.g. Franus 2002) are the same. Microphotographs of the the Lower Triassic shales (Fig. 6) and contemporary Terra Rosa (Fig. 5) cast some light on similarities and differences between variegated shales and the rocks macroscopically similar to them (Fig. 1-6).

Another criterion that should be considered is a mineral composition. The results of phase analyses of the shales from the Magura and Silesia Unit are quite uniform (Tab. 2), with the exception of the Glisne Pass sample containing the dolomite.
Figures 1–6. Microphotographs of the Carpathian variegated shales (Fig. 1–4) and other, macroscopically similar rocks (Fig. 5: Contemporary Terra Rosa, Croatia, Fig. 6: haematite bearing mudstone, Świętokrzyskie Mts.) – for comparison of microstructures. PPL, all photographs performed at plane polarised light.

Ryciny 1–6. Mikrofotografie pstrych łupków karpackich (Ryc. 1–4) oraz, dla porównania mikrostruktur, innych, makroskopowo podobnych skał (Ryc. 5: współczesna terra rosa, Chorwacja, Ryc. 6: mułowiec hematytonośny, Góry Świętokrzyskie). Wszystkie fotografie wykonane przy jednym polaryzatorze.
Table 2. Phase composition of the samples and the haematite crystallite size. Numbers in brackets reflect the catalogue numbers of the ICDD database (1995).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Phase composition of variegated shales</th>
<th>Haematite crystallite size measured perpendicularly to (104) planes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kasina Wielka – Kalety, parental rock</td>
<td>Quartz (33-1161), plagioclase (9-466), illite (26-911), chlorite (16-362), haematite (33-664), amorphic phase</td>
<td>Undetermined due to very low peak intensity</td>
</tr>
<tr>
<td>Kasina Wielka – Kalety, weathered rock</td>
<td>Quartz (33-1161), chlorite (16-362), kaolinite (6-221), illite (26-911), haematite (33-664), plagioclase (9-466), mixed-layered illite/smectite I/S, amorphic phase</td>
<td>600Å</td>
</tr>
<tr>
<td>Istebna – Andziolówka</td>
<td>Quartz (33-1161), kaolinite (6-221), chlorite (16-362), illite (26-911), haematite (33-664), plagioclase (9-466), mixed-layered illite/smectite I/S or/and chlorite/illite Ch/I, vermiculite/illite V/I, amorphic phase</td>
<td>530Å</td>
</tr>
<tr>
<td>Glisne Pass</td>
<td>Quartz (33-1161), chlorite (16-362), plagioclase (9-466), illite (26-911), haematite (33-664), dolomite (36-426), calcite (5-586), mixed-layered illite/smectite I/S and/or chlorite/illite Ch/I, vermiculite/illite V/I, amorphic phase</td>
<td>850Å</td>
</tr>
<tr>
<td>Sól – Podrachowiec</td>
<td>Quartz (33-1161), plagioclase (9-466), kaolinite (6-221), illite (26-911), haematite (33-664), chlorite (16-362), mixed-layered illite/smectite I/S and/or chlorite/illite Ch/I, vermiculite/illite V/I, amorphic phase</td>
<td>860Å</td>
</tr>
<tr>
<td>Przybędza weathered shales</td>
<td>Quartz (33-1161), plagioclase (9-466), illite (26-911), kaolinite (6-221), smectite, mixed-layered illite/smectite I/S and/or chlorite/illite Ch/I, vermiculite/illite V/I, amorphic phase</td>
<td>360Å</td>
</tr>
<tr>
<td>Przybędza</td>
<td>Quartz (33-1161), kaolinite (6-221), plagioclase (9-466), haematite (33-664), illite (26-911), mixed-layered illite/smectite I/S and/or chlorite/illite Ch/I, vermiculite/illite V/I, amorphic phase</td>
<td>Undetermined due to very low peak intensity</td>
</tr>
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</table>
The Skole Unit shales have been recognised as containing members of zeolite group (Wieser 1984, fide Franus 2002) and the mineral klinoptilolite was identified by Franus (2002) in the Trójca outcrop. The mineral, an “echo” of volcanic events, was not found in other samples examined by this author. Zeolites are not common in variegated shales of all Carpathian tectonic units.

The next component of the fingerprints set is a size of haematite crystallites. Significance of this parameter for archaeometric research was men-

![Box & Whisker Plot](image)

Figure 7. Crystallite size of haematite in the rocks of different geological origin. Captions: Kudowa – fine grained, hydrothermal haematite (Trąbska, Gaweł 2007), Tatra Mts. – sedimentary rocks (op. cit.), Southern Świętokrzyskie Mts. – Buntsanstein sedimentary rocks (op. cit.), Northern Świętokrzyskie Mts. – Buntsanstein sedimentary rocks (op. cit.), Balaton – Permian sedimentary rocks from the Balaton area, Hungary (Trąbska, Gaweł 2008), contemporary Terra Rosa from various localities (Trąbska, Gaweł 2007).

tioned by Jercher et al. (1998) and Trąbska with Gawel (2007), who solved an important archaeological problem due to its application. Crystallite size of haematite in variegated shales differs slightly from the one of other rocks (Tab. 2 and Fig. 7), though not significantly at the 1,96 significance level. The sample from the Balaton area (Hungary) and the sample of weathered variegated shales were measured only once. Haematite crystallites in the weathering products are smaller than in the parental rocks.

Another criterion is a chemical composition, especially trace elements. When the article was written, still no chemical analyses of the examined samples were performed. However, the analyses of the Skole Unit (Franus 2002) were accessible. They were compared, through multivariate analy-

sis (Fig. 8, 9), with the ferruginous clayey sedimentary rocks data from the Świętokrzyskie Mts. (Trąbska et al. 2008). Separate groups can be distinguished, even within the variegated shales of a one tectonic unit (Fig. 8). Copper, zinc, lead and strontium are probably the most distinctive (Fig. 9).

Another helpful “fingerprint” may come from analysis of Foraminifera assemblages, biostratigraphic markers for the Carpathian flysch units. The problem study has been advanced but limitations appear for archaeological samples: the required sample volume for successful separation of Foraminifera consumes too much material.

Illite and smectite proportion in mixed layered clay minerals of the illite/smectite (I/S) type may provide further information on regional and local features of variegated shales. The method has been worked out and applied to assess an advancement of clayey rocks diagenesis (the higher illite content the more advanced diagenesis; e.g. Środoń, Clauer 2001). A number of them, representing various tectonical units, have been examined (Kotarba
2003) and peculiar features undoubtedly have appeared, e.g. clayey rocks from the Polish part of the Skole Unit are characterized by far lower illite concentration than the Ukrainian ones (op. cit.). Unluckily, the population of examined samples, especially the samples of variegated shales, is still far too low.

CONCLUSIONS

Variegated shales from the Carpathian Mts. may have constituted a raw material for all societies that were interested in its application, including the Palaeolithic ones. The shales are red and cherry, soft, concise and durable as a painted layer. Macroscopically they resemble both a raw material found at several Upper Palaeolithic sites (e.g. Dzierżysław-35, Gönnersdorf, Dolní Vestonice) and a raw material cropping out in Central Europe. Permian and Lower Triassic formations (though not only them) are macroscopically very similar to the Carpathian red shales, although they occur in different locality. An exact description of a sourcing area is a key problem in numerous archaeological researches.

Carpathian variegated shales may be “fingerprinted” when several criteria are examined and compared. Until now, the promising results are yielded by mineralogical analyses, microstructural analyses, haematite crystallite size analyses and chemical analyses (Tab. 1, 2, Fig. 1–9). Variegated shales differ from other red sedimentary rocks macrostructurally (Fig. 1–4. vs. 5–6) and from other red, clayey rocks (Fig. 3). The haematite crystallites size also varies for red rocks of various geological origin and, simultaneously, geographical setting (Tab. 2, Fig. 7). Mineral composition may also be a helpful “fingerprint”, e.g. zeolite group members, identified, up to now, only in the Skole Unit shales (Wieser 1984, fide Franus 2002; Franus 2002) as well as specific features of illite/smectite proportions in various areas of the Carpathian Belt (Kotarba 2003). Comparison of trace elements of the Carpathian variegated shales and the Tertiary siltstones (Fig. 8, 9) allows to recognise the difference between the two. Analyses of the Foraminifera assemblages seem to be less promising for archaeometric purposes due to large volume of a sample necessary for analyses. All the criteria may be useful both in distinguishing the Carpathian shales from other clayey rocks as well as in differentiating them within the Carpathian Belt (Tab. 3).
Table 3. Fingerprints for the Carpathian variegated shales in regional and local extent.
Tabela 3. Cechy charakterystyczne karpackich pstrych łupków w odniesieniu do skali lokalnej i regionalnej.

<table>
<thead>
<tr>
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<th>Carpathian variegated shales vs. red Tertiary siltstones and Terra Rosa</th>
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</thead>
<tbody>
<tr>
<td>Local range</td>
<td>Mineral composition (zeolites, IImite/Smectite ratio)</td>
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<tr>
<td></td>
<td>Chemical composition</td>
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<tr>
<td>Regional range</td>
<td>Chemical composition</td>
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<td></td>
<td>Haematite crystallite size</td>
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<td>Microstructure</td>
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Streszczenie


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