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FERRUGINOUS RAW MATERIAL SOURCES FOR PALAEOLITHIC IN POLAND – PROMISING RESULTS OF PROVENANCE STUDIES

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ABSTRACT

Haematite and haematite bearing rocks is a common raw material in Palaeolithic. Widespread in nature, it occurrs either in isolated oucrops or in privileged litostratigraphic formations (in Central Europe these are Lower Devonian, Lower Permian, Lower Triassic and Upper Triassic rocks). All must have provoked an interest of Palaeolithic people so we have searched for a fingerprint for all. So far provenance studies of ferruginous rocks used to be based on their chemical composition, mineral composition and magnetic properties. We have applied all but another one seems to be promising: haematite crystallite size measured both in natural samples and artefacts. Samples from Poland and other Central Europe countries (Czech, Slovakia, Croatia) have been analysed; they represent various litostratigraphic formations (incl. mentioned above), genetic types and geochronology. Artefacts represent, among others, Aurignacian site (Klissoura, Greece) and Magdalenian site (Dzierżysław, Poland; Hostim, Czech). Systematic measurements of haematite crystallite size point at differences of this parameter depending on the origin and age of a rock (e.g. Lower Triassic haematite rock of residual origin, with its, averagely, 500 angstrem; Precambrian haematite of metamorphic origin with 3000 angstrem and haematite from contemporary terra rosa with ca. 80 angstrem). Large assemblage of examined samples enables us to: a) discuss pros and cons of application of this approach, b) determine, to some degree, a sourcing area for artefacts, c) determine a homogeneity of an assemblage, d) discern intentional powdery remnants from their natural counterparts.

INTRODUCTION

Provenance studies of ferruginous materials and artefacts made of them (haematite, haematite-bearing rocks and ochre) have long been recognised as complex due to the wide abundance of the iron minerals and rocks in the natural environment, the complexity of genetic processes standing behind them and the diversity of their mineralogical and chemical features [13]. Macrofeatures of artefacts can be described easily and then compared with a source material from a data base but a provenance study of the powdered rock or a mineral seems to be impossible. Another problem with the fine grained material concerns the difference between a natural ferruginous powder (e.g. a hardpan, soil iron oxides or Terra Rosa) and a powder introduced originally into an archaeological layer or onto a surface of an artefact. However, it seems that a solution exists: a fingerprint can be searched for in haematite microstructure. Haematite (a mineral itself and a compound in natural mixtures, like haematite-bearing rocks and ochres) has numerous varieties differing in colour and hardness. It results from its micromorphological properties, among them crystallite size. The latter is a consequence of variety of both: natural and human provoked processes, that have been long researched [3]. A crystallite itself can be defined as a microarea that coherently disperses X ray radiation. Crystallite size measurement may contribute to haematite powder artefacts provenance studies (Fig. 1).

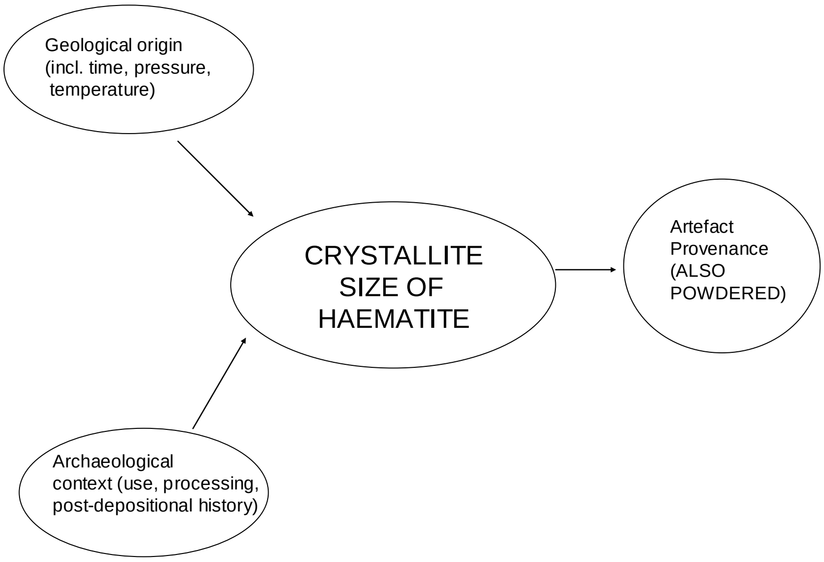

Fig. 1. An ideal schedule of application of haematite crystallite size in provenance studies.

MATERIAL AND METHODS

Material that was examined represented natural haematite-bearing rocks of various origin, geological time and locality (Table 1, Fig. 1) and artefacts made of haematite and haematite-bearing rocks (Table 2).The latter come from the Magdalenian site Dzierżysław-35 (Upper Silesia, Poland) [5] and Klissoura site in Greece, researched by Polish-Greek expedition directed by Prof. B. Ginter, Prof. J. K. Kozłowski and Dr. M. Oumoudelis.

All samples were examined with X-Ray Powder Diffraction methods (details can be found in any handbook of mineralogy or solid state physics, for example see [7]. The XRD patterns were obtained using $Cu_{K\alpha}$ radiation with the Philips APD X'Pert PW 3020 diffractometer with a secondary curved graphite monochromator. Haematite was identified according to the data in ICDD (International Centre for Diffraction Data) catalogue and computer programme XRAYAN [10]. Concentration of haematite in each sample varied. No isomorphic substitutions in haematite structure were found (for more detailed explanation see, for example Bolewski et al. 1993:147-149). Crystallite size, perpendicular to lattice plane (104) (d = 2.70Å), was measured with the Scherrer method, based on a half-width of a 104 analytical peak.

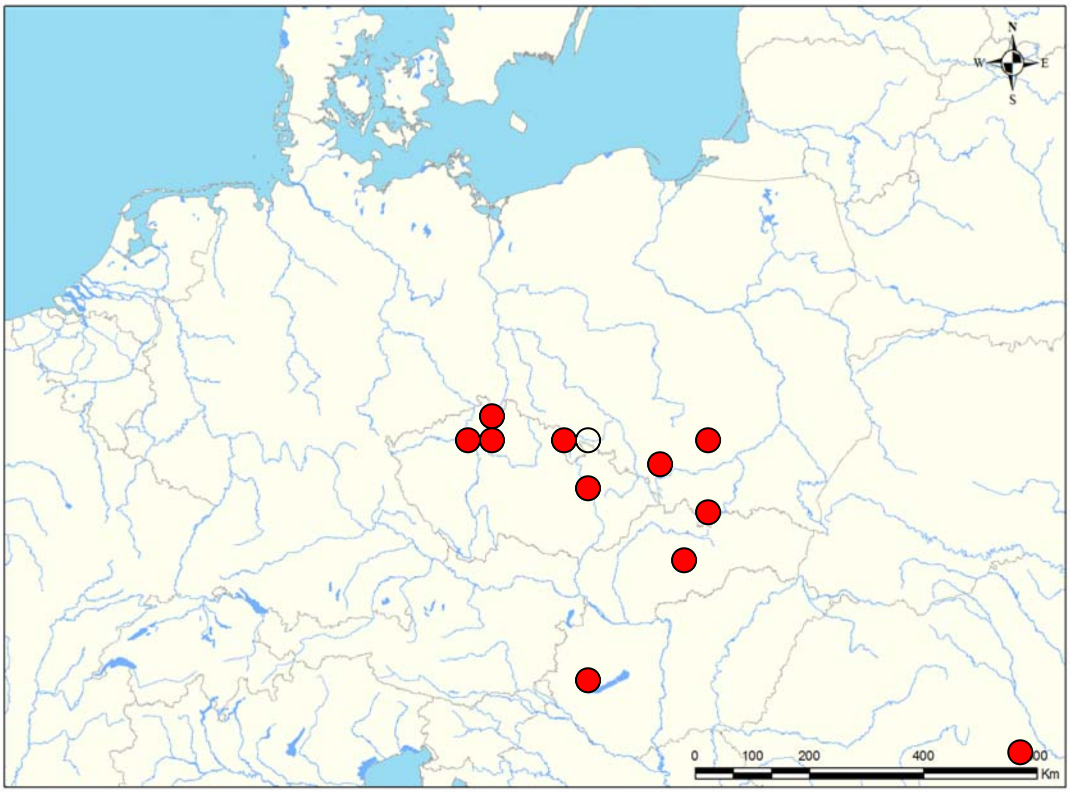

Fig. 2. Localities of geological samples (excl. Croatia amd Greece)
Empty circle stands for the Dzierzysław-35 site.

RESULTS

Measurement results are listed in Tables 1 and 2. All substances are natural mixtures of haematite and other minerals; the presence of the latter may help in provenance studies but does not influence crystallite size that is of our interest.

Sample locality	Geological origin and setting	Age of a rock	Crystallite size
Kudowa (Lower Silesia) Poland	Powdery, light cherry haematite in hydrothermal zone of Kudowa granitoide [8]	Carboniferous	490 Å
	Powdery, light cherry haematite in hydrothermal zone of Kudowa granitoide [8]	Carboniferous	325 Å
	Powdery, light cherry haematite in hydrothermal zone of Kudowa granitoide [8]	Carboniferous	480 Å
Tatra Mts. (Małopolska Province) Poland	Cherry red clay-haematite sedimentary slate [1]	Lower Triassic	680 Å
	Cherry red clay-haematite sedimentary slate [1]	Lower Triassic	570 Å
Chęciny (Świętokrzyskie	Sedimentary or residual haematite silt [6]	Lower Triassic	*320 Å*

Province) Poland			
	Sedimentary or residual haematite silt [6]	Lower Triassic	480 Å
	Sedimentary or residual haematite silt [6]	Lower Triassic	430 Å
	Sedimentary or residual haematite clay [6]	Upper Triassic	*70 Å*
Baranów (Świętokrzyskie Province) Poland	Sedimentary or residual haematite clay [4]	Lower Triassic	430 Å
	Sedimentary or residual haematite clay [4]	Lower Triassic	350 Å
Kopulak quarry (Świętokrzyskie Province) Poland	Sedimentary or residual haematite clay [4]	Lower Triassic	210 Å
	Sedimentary or residual haematite clay [4]	Lower Triassic	350 Å
	Sedimentary or residual haematite clay [4]	Lower Triassic	580 Å
Jaźwica quarry (Świętokrzyskie Province) Poland	Terra Rosa [6]	From Upper Devonian to Eocene	540 Å
	Terra Rosa [6]	From Upper Devonian to Eocene	760 Å
	Terra Rosa [6]	From Upper Devonian to Eocene	600 Å
Polichno (Świętokrzyskie Province) Poland	Sedimentary or residual haematite clay [6]	Upper Triassic	*76 Å*
Laskowa (Świętokrzyskie Province) Poland	Sedimentary or residual haematite clay [6]	Upper Triassic	*69 Å*
Czerwona Góra (Świętokrzyskie Province) Poland	Powdery reddish cherry rock composed of iron oxides and carbonate psamitic and aleuritic grains. Terra rosa is probable here [6]	Upper Permian	1230 Å
Rydno mine area (Świętokrzyskie	Lumps of haematite bearing silt and fine grained sandstone, transported in fluvioglacial	Lower Triassic	430 Å

Province) Poland	sands [6]		
Rydno mine area (Świętokrzyskie Province) Poland	Haematite bearing silt and fine grained sandstone [6]	Lower Triassic	775 Å
Różanka (Świętokrzyskie Province) Poland	Hydrothermal haematite vein [6]	Devonian?	1125 Å
Kasina Wlk. Carpathian Mts, Beskidem Poland	Red flysh siltstone formation	Tertiary, Eocene	600 Å
Klissoura (Greece)	Terra Rosa	Recent	*100 Å*
	Silicified, hard, haematite-bearing rock	Unknown	1230 Å
Croatia, central part	Terra Rosa	Unknown	270 Å
Balaton area Hungary	Haematite bearing fine grained sandstone and siltstone	Upper Permian	215 Å
Tvrdkov (Moravia-Silesia, Czech)	Metamorphic, hard, quartz-haematite-magnetite ore [2]	Precambrian	5420 Å
Bečov, Czech	Naturally burnt silts	Tertiary	1300 Å
Hostim, Czech	Crystalline haematite of the Lahn Dill type [15]	Precambrian	1420 Å
	Weathering products on the surface of the crystalline haematite	Precambrian/recent?	1150 Å
Stadice, Czech	Crystalline haematite, probably scarn [14]	Tertiary?	1100 Å
Soviansko (Slovakia)	Coarse crystallite haematite of hydrothermal origin (150 – 300 o C), a vein fragment [9]	Tertiary	> 6000 Å
Krivyj Rig (Ukraina)	Metamorphic haematite-quartz formation [11]	Precambrian	2050 Å

Table 1. Geological samples (haematite and haematite-bearing rocks).
Results in italics may possess an error due to low amount of haematite in the sample.

Site	Sample	Macroscopic features	Crystallite size
Dzierżysław-35	1996	Dark violet, with tiny sericite producing a shining effect, rather hard. Slaty texture.	468 Å
Dzierżysław-35	4549	Red brown, rather hard. An artefact worked out intentionally.	435 Å
Dzierżysław-35	5097	Red, soft. Pyramidal shape points at a remnant after polishing something?	105 Å
Dzierżysław-35	5173	Red, soft. An artefact probably worked out intentionally. Slaty texture.	620 Å
Dzierżysław-35	5186	Red, soft. An artefact probably worked out intentionally.	310 Å
Dzierżysław-35	5457	Dark, violet, rather hard. Slaty texture.	360 Å
Dzierżysław-35	1370	Silvery, with apparent, long crystalline shapes, hard. Produces a brown cherry strike. An artefact probably worked out intentionally.	3690 Å
Klissoura	Aa3	Dark cherry powder on a surface of a small pebble.	1100 Å

Table 2. Ferruginous artefacts with measured crystallite size.

DISCUSSION AND CONCLUSION

The analytical method that was applied by us requires powdering a sample. Thus, also a material that was powdered intentionally, with features uavailable for macroscopic observation, may be measured. This is the Klissoura sample case (Fig. 3). A small pebble was covered with cherry red powder, that was difficult to discern from dark terra rosa, natural for the environment. An usual phase analysis points, in both cases, at the presence of haematite and prompts practically no solution. Only measurement and comparison of crystallite size of Terra Rosa and the “surface” haematite suggests clearly that two different haematites were examined. First, whose crystallite size equals 100 Å, and the other with 1100 Å crystallites. That is why we are certain that the cherry red powder has nothing to do with natural, recent Terra Rosa haematite and must be of utterly different origin. Large crystallite size of the latter makes us think of intentionally powdered silicified haematite rock from Klissoura (comp. Table 1) or another haematite of magmatic, metamorphic or vein origin (Table 1) used by Aurignacian people (Ginter, pers. comm).

Fig. 3. Klissoura artefact, a pebble covered by haematite powder,
utterly different from neighbouring recent Terra Rosa (See Tabs 1 and 3). Phot. D. Bobak.

It seems that there is no apparent correlation between haematite age and crystallite size. Carboniferous haematite from Kudowa is similar to its younger counterparts, e.g. Lower Triassic. All the same it is worth to consider that haematite itself may be older than a host sedimentary rock, in this case haematite may be older than Lower Triassic. Additionally, if one has a look at this parameter for Terra Rosa haematite then it is clear that a contemporary rock is characterised by a very low crystallite size haematite (Klissoura), compared with older Terra Rosa, at least of Eocene age (Jaźwica quarry) (Table 1).

A genetic factor seems to be important: haematite of metamorphic origin (Tvrdkov, Krivyj Rig), vein origin (Soviansko) and weathering (Terra Rosa outcrops) differs apparently in crystallite sizes (Table 1). Relatively small crystallite size of hydrothermal Kudowa haematite, compared to Soviansko is probably a result of different temperature of hydrothermal processes, supposingly, very low at Kudowa (*vs*. 150 – 300^{o}C at Soviansko). A reason of discrepancy between the (macroscopically similar) Lower and Upper Triassic haematites from the Świętokrzyskie region is actually not known but it may lie in the age: an older than Lower Triassic haematite and exactly Upper Triassic haematite from weathered soils. The described differences should provoke to systematic work on haematite data bases. We have illustrated our observations on the PCA diagram (Fig. 4), exploring raw data.

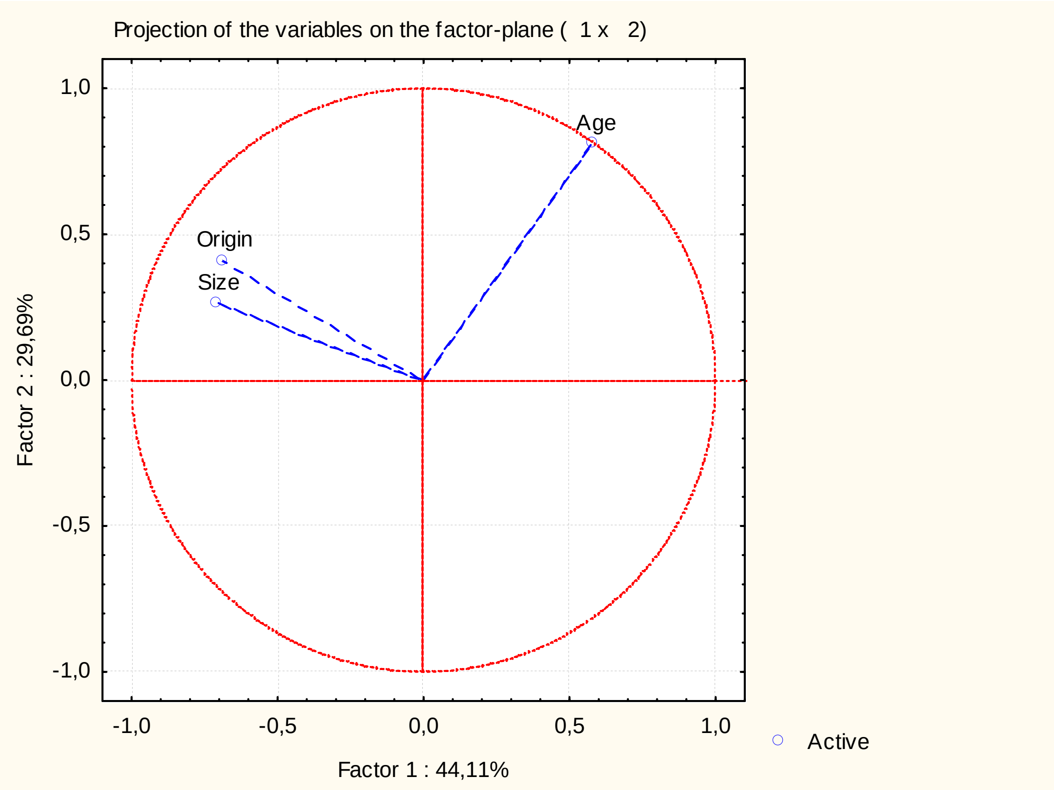

Fig. 4. Exploration of similarity patterns between crystallite size, haematite age and geological origin.

For several artefacts from Dzierzysław-35 site we tried to establish some provenance rule. Obviously, a sample 1370 is different from others with its 3690 Å (Table 2) and its origin must vary (actually, macroscopic observation suggest a Lahn Dill type). The sample 5097 also differs from the rest, though, this time, macroscopically resembles others. But, on the other side, the analysis of natural examples (e.g. a Kopulak quarry) proves that quite wide diversity occurs within a set of samples from the same outcrop. It is the obvious, that a larger amount of analysed samples would enable to construct statistically significant data base. Nevertheless, the differences suggest a multi-source origin of the raw material, in some cases a genetic type of a sourcing outcrop may be pointed at.

Weathering products appearing on a crystalline haematite surface were expected to preserve, more or less, their crystalline size. Actually, they do: Hostim samples are good examples (1420 and 1150 Å).

Discrepancies in haematite crystallite size in samples from the same outcrop may result from: a) natural diversity of the mineral structure, b) low concentration of haematite, c) backgroung fitting in results processing. Whereas the latter factor can be, more or less, eliminated, the two firts remain beyond our control. Nevertheless, we are convinced that further data, both from natural environment and ferruginous artefact would allow to collect a number of statistically significant data. Undoubtedly this approach carries perspectives in analyses of provenace of powdered material.

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