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FERRUGINOUS RAW MATERIAL SOURCES FOR PALAEOLITHIC IN POLAND (CENTRAL EUROPE) – PROVENANCE STUDIES: OCCURRENCE, LITOSTRATIGRAPHY AND APPLICATION

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ABSTRACT

The problem of ferruginous raw material provenance is complex and involves numerous methods and approaches [1,5,6]. Analysis of the chemical composition, with the usage of the statistical methods and geochemical interpretation has been widely used in the study of almost all provenance problems. We have decided to apply this mode of analysis to samples from the selected litostratigraphic levels with haematite bearing rocks. There has long been known, that haematite bearing rocks, though widespread in nature, are specifically bound to certain litostratigraphic levels. They appeared in the past geological periods due to favourable climatic conditions ruling in certain areas, i.e. arid and/or arid and hot regime. For the area of Central Europe some litostratigraphic levels are privileged and these are mainly: Lower Devonian ("Old Red"), Lower Permian, Upper Permian, Lower Triassic, upper part of Lower Triassic, Upper Triassic, Tertiary (mostly Eocene). The range of these formations, available now on a surface, can be traced on any geological map [3,4]. We have concentrated on the area of the Świętokrzyskie Mts., from where an Upper Palaeolithic haematite mine complex (Rydno) was found [7]. Haematite bearing rocks occur here in all mentioned formations except Lower Permian. Their territorial range and petrographic character (Fig. 2, 3) are various but the Lower Triassic rocks (deposits of haematite rich sandstones, silts and clays) seem to be most interesting due to their macroscopic appearance (colour and softness; Fig. 2; comp. with Fig. 4). Extremely abundant ferruginous material found in the Dzierżysław-35 site [2] in Upper Silesia (Poland) provoked us to search for its source. The distance from the site to the Świętokrzyskie Mts. is not so long: only about 150 km and there are not (and most probably there were not in the past) any significant geomorphological obstacles. Was this region an object of interst to the Magdalenians? We have tried to answer this question.

MATERIALS AND METHODS

Natural ferruginous samples and artefacts (locality presented on the map; Figs. 1, 2, 3) were chemically and statistically analysed. All samples were collected on surface except a one that comes from shallow (1 m depth) drilled material. The mentioned exceptional sample was found in a shallow (ca. 1 m) drilling. Archaeological material is represented by artefacts from the Magdalenian Dzierżysław 35 site (Upper Silesia, Poland; Fig. 4). Their codes cover the numbers from 12 to 30, standing for the following artefacts: 1760p, 2062p, 2507p, 2511p, 2587p, 2695p, 2724p, 2866p, 3198p, 3341p, X7t, DZ35t, 1760t, 3622t, 3384t, 5097t, 5173t, 5358t. Letters "p" and "t" symbolise the method of chemical analysis that was applied: either PIXE (Particle Induced X-Ray Emission) or TXRF (Total Reflection X-Ray Fluorescence; a reason for applying the two methods and a part of the data (chemical analyses of the artefacts) are available in another place [9]. Chemical analyses of the samples from the Świętokrzyskie Mts. were performed with the EDXRF method and are listed in the Appendix. Macroscopically the "archaeological" assemblage is more or less homogeneous, representing haematite silt or clay, with parallel texture, with 1 or 2 Mohs hardness, resembling natural material from the Świętokrzyskie Mts. Statistical analyses (Principal Component Analysis, Kohonen self organizing network and k-means cluster analysis) were conducted on the data from the chemical analyses. The latter was performed for the artefacts 2062, 2511, DZ35, 3384, 5358.

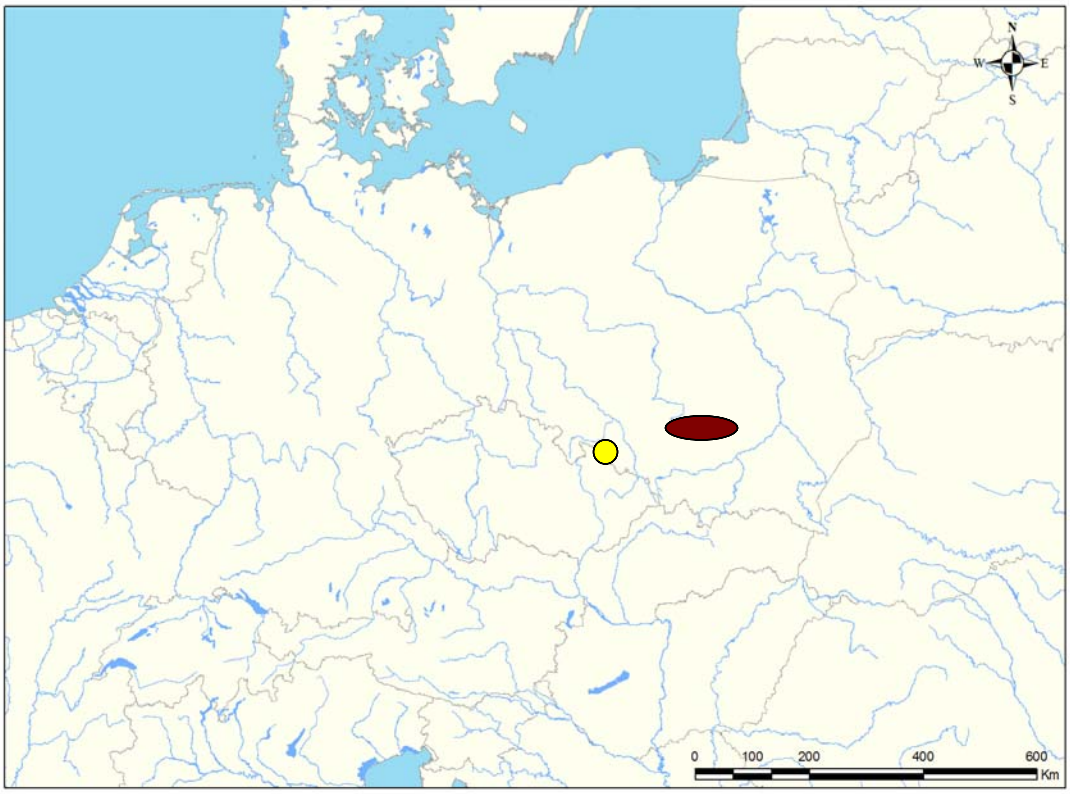

Fig. 1. A map of Poland (and adjacent states) with areas of Świętokrzyskie Mts. samples locality (horizontal ellipse) and artefacts locality (Dzierżysław-35 site, Upper Silesia).

Fig 2. Haematite silt and clay, Lower Triassic. Świętokrzyskie Mts, central Poland.

Fig. 3. Czerwona Góra quarry, Świętokrzyskie Mts. Red deposits of Upper Permian, probably with later terra rosa imposed.

Fig. 4. An artefact from the Dzierżysław-35 Magdalenian site, Upper Silesia, Poland. Haematite silt. Original size. Phot. by M. Frołow.

RESULTS AND DISCUSSION

All chemical analyses were processed with the use of several statistical methods. Let PCA analysis be first to comment. First component in the correlation matrix attains reasonable 31,78% value. Distribution of samples in the Factor 1 vs. Factor 2 plane (Fig. 5) points clearly at the following facts: a) "natural" samples and some artefacts cluster in the left half of the diagram (according to the Factor 1 axis, more statistically significant than the Factor 2 axis), b) all samples from the Świętokrzyskie Mts. are clustered in a 4th quarter, being separated in respect to the artefacts, c) artefacts are dispersed in the 1st, 2nd and 3rd quarters and do not create apparent clusters. Results of the PCA analysis suggest that some artefacts (situated in the left part of the diagram) may come from the Świętokrzyskie region area. But another method of statistical analysis, self organising Kohonen network (Fig. 6), stressed and confirmed that the "natural" samples are separated in the respect to the artefacts. The number of four red points was accepted arbitrarily, as the most efficient in this kind of data processing, the number of triangles represent the number of variables (here: elements) used for analysis. Again, among four groups (red ellipses), a group of the Świętokrzyskie Mts. samples is separated from the others (artefacts). Artefacts, again, are dispersed without clear regularities within the three other groups, maybe with the exclusion of the four artefacts, seen as separated here and, to some degree, in the PCA (samples 23, 24, 26, 27; Fig. 5), though the sample 24 should be interpreted as an outlier. Principal Component Analysis is also a useful tool to analyze the geochemical patterns. Certain elements tend to occur together, certain not and they may be correlated in a stronger or weaker way. This information usually cast some light on a raw material provenance. Each geochemical pattern can point at a specific sourcing area (e.g. weathering zone of a Ni-Cr-Fe formation). The PCA diagram (Fig. 7) points at some regularities of this type: Fe, Mn and Pb (right cluster) are negatively correlated with Cr, Ni, Ti, Ga and Sr (left cluster). Ca, Rb, Cu, Zn (middle cluster) are not correlated with the two former. In "natural" samples Cr, Ti, Ni, K, Ga and Sr concentrate. As for the artefacts, they are gathered in the 1st, 2nd and the 3rd quarters and do not create apparent clusters. Nevertheless, some suggestions on geochemical differentiation can be put forward and two groups may be separated. In the first Fe, Mn and Pb dominate, whereas in the second Cu, Zn with Ca, Sr and Rb prevail (Fig. 7). PIXE analyses of the five randomly selected samples belonging to the set of artefacts (13, 15, 23, 26, 30; comp. Fig. 5) were processed in another statystical approach with the use of k-means cluster analysis (Fig. 8). The elements gathered at the left side are negatively correlated with the ones at the right position. Thus, iron (and cobalt) have, geochemically, nothing in common with silica and alumina, pointing that haematite, not ochre (a natural mixture of iron hydroxides, clay minerals, quartz and others), is a dominant iron bearing phase. Then, no substitution of titanium should be expected in the haematite lattice: it also has its place in an opposite position to iron, what eliminates a group of Ti-rich haematite sources. A close position of Fe and Cr requires performing further analyses and interpreting the (probably not casual) observation.

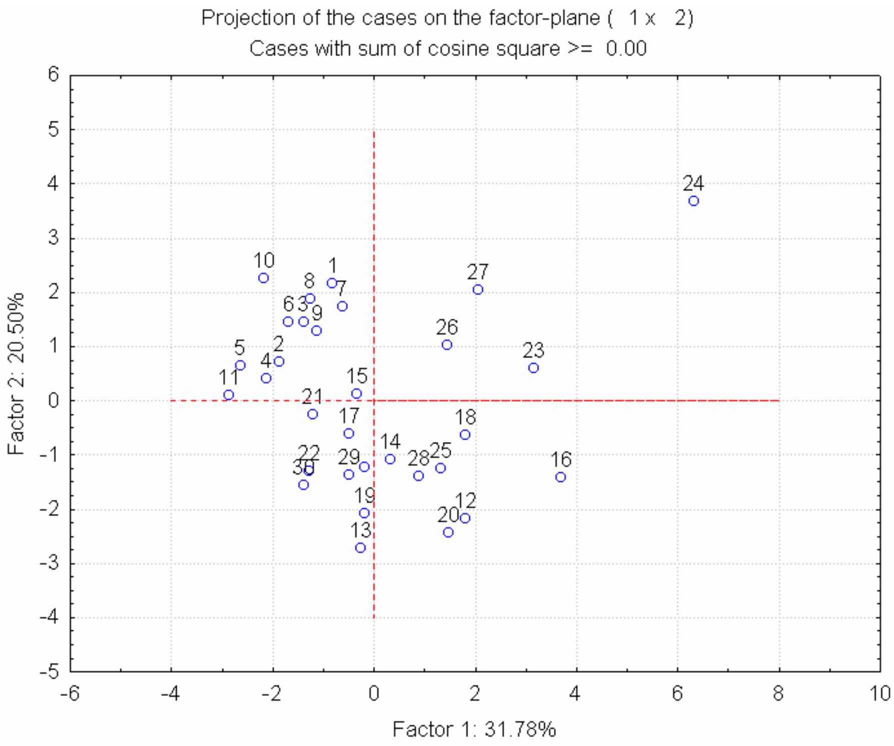

Fig. 5. PCA analysis of natural samples (no. 1-11) and ferruginous artefacts (no. 12-30).

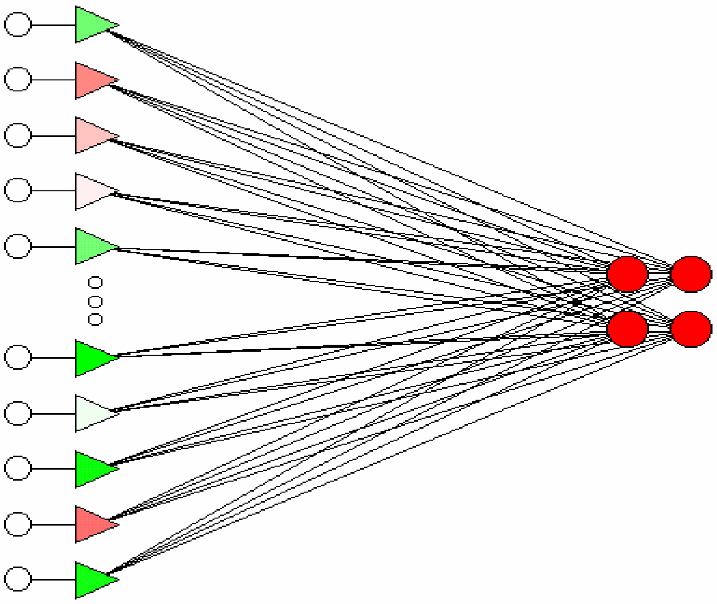

Fig. 6. Diagram of Kohonen network applied for organizing the samples 1 – 30. Samples from the Świętokrzyskie Mts. are separated from artefacts.

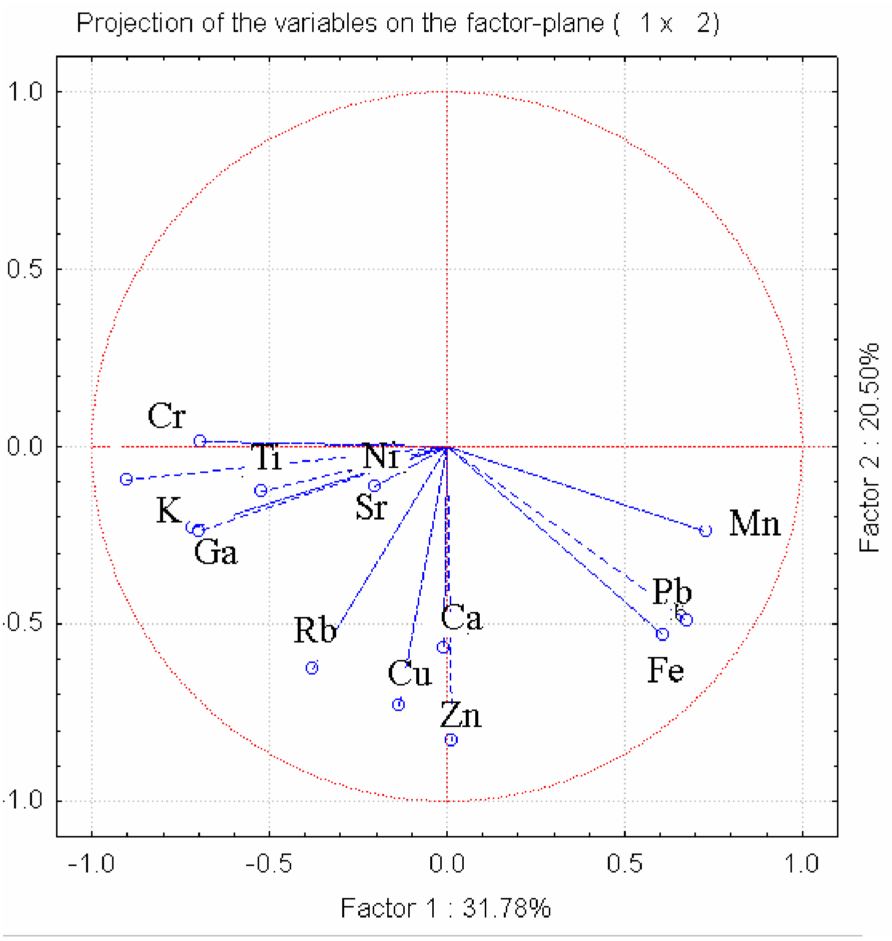

Fig. 7. PCA diagrams: analysis of correlation of geochemical data.

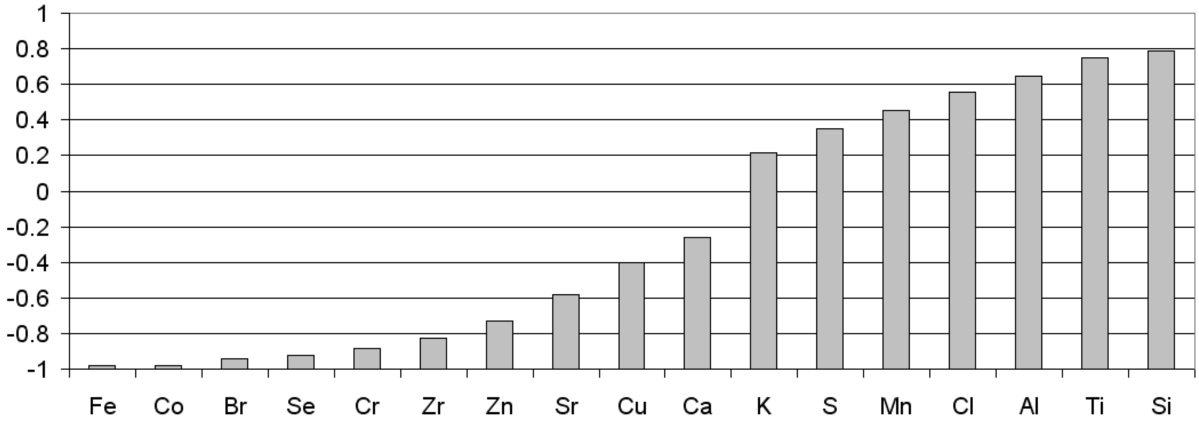

Fig. 8. K-means cluster analysis of PIXE chemical analyses results of five selected artefacts (no. 13, 15, 23, 26 and 30; Fig. 6).

CONCLUSIONS

1. Certain litostratigraphic areas in Central Europe and Poland seem to be very perspective in provenance studies of sourcing regions for ferruginous materials (Lower Devonian, Lower Permian, Upper Permian, Lower Triassic, upper part of Lower Triassic, Upper Triassic, Tertiary - mostly Eocene; comp. Figs. 1-3).
2. In the search for source of ferruginous raw material used by the Magdalenian inhabitants of the place that we call now the Dzierżysław-35 site in Upper Silesia, the Świętokrzyskie

Mts. area was considered by us as extremely worth to explore due to at least three reasons: a) widespread, easily accessible haematite-bearing rocks of various lithological formations, b) raw material macroscopically resembling, to some degree, artefacts from the Dzierżysław 35 site (haematite silts and clays; Figs. 2,3,4), c) Upper Palaeolithic Rydno haematite mine occurrence in the northern part of the area [7]. Field, petrographic, geochemical and statistical analyses, based on examination of ten samples from the outcrops and twenty artefacts let us draw a conclusion that the Świętokrzyskie Mts. haematite bearing clays and silts, though widely explored by Rydno communities, were, most probably, not the objects of interest to the Magdalenians settled in the Upper Silesia. They have their own geochemical pattern, with Cr, Ti, Ni, K, Ga and Sr dominance (Fig. 7).

3. The artefacts assemblage is not homogeneous, if geological origin of raw material is considered. The 20 examined samples can be cautiously divided into two groups, where Cu, Zn, Rb, Cs dominate in a one of them, while Fe, Pb and Mn concentrate in the other. Still, it should be kept in mind that the presence of the Cu, Zn, Pb in the two groups might point at a common source bearing a character of a weathered hydrothermal veins or scarns.
4. Five artefacts analysed with the k-means method show a pattern with Fe and Cr co-ocurring. This suggests a common source: a weathering zone enriched in these elements. Unluckily, the limited number of samples does not authorise us to put forward any crucial conclusion. Additionally, in these artefacts iron is bound in haematite, not in ochre, and it is a Ti-poor haematite: this excludes Fe-Ti iron ores as a source area for haematite. This complex set of fingerprints may appear very useful if detailed field survey and detailed geochemical study of suspected source areas is going to be continued. More samples should be analysed to make the image clearer. Then also a joint geochemical – statistical analyses and planigraphy should point at certain rules.

APPENDIX

Results of EDXRF chemical analysis of the samples from the Świętokrzyskie Mts [ppm]. Measurement incertainity in brackets.

Locality	Sample code	K [%]	Ca	Ti	V	Cr	Mn	Fe [%]	Ni	Cu	Zn	Ga	As	Rb	Sr	Y	Pb
Gleba	1	0,97 (0,03)	3503 (167)	3043 (188)	152 (9)	92 (9)	453 (29)	1,87 (0,14)	22,4 (3,2)	14,5 (1,5)	9,6 (2,1)	12,3 (0,5)	12,6 (0,8)	75,2 (7,1)	135,1 (9,5)	21,8 (0,9)	44 (7)
Wierzbno	2	1,62 (0,13)	331 (63)	4455 (70)	156 (15)	174 (4)	491 (17)	5,35 (0,25)	52,8 (3,4)	17,6 (2,9)	96,1 (4,6)	23,9 (0,1)	32 (4)	138 (6)	79,0 (0,3)	22,9 (0,9)	51 (12)
Polichno	3	1,55 (0,09)	2063 (118)	3860 (156)	107 (10)	119 (3)	322 (13)	3,94 (0,32)	28 (2,9)	16,9 (0,6)	21,8 (2,2)	16,6 (1,3)	7,7 (3,4)	101,6 (3,8)	39,3 (1,1)	14,6 (1,5)	40 (7)
Chęciny	4	2,06 (0,01)	1955 (109)	3990 (318)	165 (3)	107 (6)	202 (6)	2,96 (0,05)	34,4 (2,1)	54,3 (4,1)	41,2 (3,2)	17,5 (1,3)	13,2 (1,3)	115,4 (3,8)	92,8 (5,2)	15,5 (1,1)	43 (3)
Chęciny	5	2,08 (0,35)	1675 (2173)	4841 (786)	309 (47)	223 (2)	462 (56)	4,77 (0,30)	38,6 (7,9)	22,1 (0,3)	44,3 (3,4)	24 (1)	29,3 (4,7)	143 (8)	96 (6)	27 (1)	21 (7)
Chęciny	6	1,79 (0,19)	1792 (117)	4107 (172)	249 (18)	122 (11)	318 (28)	3,37 (0,09)	22,7 (1,5)	12,2 (1,1)	24,5 (3,1)	17,4 (1,1)	35,3 (1,1)	107 (3)	98 (3)	16,6 (1,7)	46 (5)
Chęciny	7	1,26 (0,08)	1327 (55)	2542 (58)	133 (1)	109 (8)	360 (31)	2,33 (0,08)	17,4 (2,9)	14,5 (1,8)	22,8 (1,3)	16 (2)	14,3 (5,2)	88,7 (3,2)	71,5 (1,8)	13,9 (0,8)	82 (7)
Czerwona Góra	8	1,82 (0,09)	774 (43)	2715 (126)	129 (18)	93 (9)	272 (10)	2,59 (0,25)	26,1 (2,5)	12,9 (0,8)	20,1 (2,6)	18,4 (2,9)	15,7 (4,8)	116 (10)	56,9 (4,9)	17,9 (2,7)	49 (7)
Baranów	9	0,61 (0,05)	260 (46)	4273 (582)	131 (23)	374 (89)	3527 (134)	20,17 (1,04)	75,3 (2,6)	41 (4)	23,8 (0,6)	20 (3)	113 (13)	98 (5)	91,3 (3)	11,4 (1,3)	<LLD
Baranów	10	1,41 (0,17)	531 (109)	5260 (564)	302 (35)	192 (23)	297 (73)	4,78 (0,36)	20,2 (1,2)	12,2 (2,2)	<LLD	24,0 (3,3)	18,9 (3,3)	107 (9)	216 (15)	29,6 (2,9)	44 (7)
Baranów	11	1,98 (0,03)	1177 (117)	5328 (336)	228 (14)	199 (12)	312 (13)	5,07 (0,16)	119 (2)	14,2 (1,5)	115 (3)	27 (3)	19,2 (4,1)	166 (4)	188 (1,2)	44 (3)	43 (9)
Limit of Detection		0,069	141	138	83,6	49,3	33,5	0,01	12,4	9,7	1,9	6,6	5,1	4,3	4,3	4,7	7,2

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