A Danubian Raw Material Exchange Network: a Case Study from Chełmno Land, Poland

Dagmara H. Werra

Autonomous Research Laboratory for Prehistoric Flint Mining, Polish Academy of Sciences, Institute of Archaeology and Ethnology, 105, Solidarności Avenue, PL 00–140 Warszawa
e-mail: werra@iaepan.edu.pl

Rafał Siuda

Institute of Geochemistry, Mineralogy and Petrology, Faculty of Geology, Warsaw University, 93, Żwirki i Wigury, Avenue, PL 02-089 Warszawa
e-mail: rsiuda@uw.edu.pl

Jolanta Małecka-Kukawka

Laboratory of Traceology, Institute of Archaeology, Nicolaus Copernicus University, Toruń, Szosa Bydgoska 44/48, PL 87-100 Toruń
e-mail: jkukawka@uni.torun.pl

Stone raw materials are our best indicators of the range of mutual contacts of the Early farming communities

Lech 1989: 118

Flint supply is one of the best indicators of the range of mutual interregional contacts of prehistoric communities

Lech 1997: 623

Abstract: The paper presents the results of petrographic and geochemical analyses of flint artefacts from Linear Pottery Culture sites from Chełmno Land. The Polish Lowlands are poor in high-quality natural flint resources, which creates an ideal opportunity for research on its distribution. In this paper we present a comparison between macro- and micro-analysis of flint. Twelve flint artifacts were macroscopically analyzed by Jolanta Małecka-Kukawka and Jacek Lech and the results were compared with those determined by electron probe micro analysis (EPMA). The results of the comparisons have revealed that in some cases the 'eye of the researcher' is infallible, but in some other cases the use of petrographic methods is necessary for correct flint source identification.

Keywords: Linear Pottery culture (LPC), 'chocolate' flint, Jurassic-Cracow flint, Chełmno Land, electron probe micro analysis (EPMA)

Introduction

The issue of procurement and distribution of flint by Linear Pottery Culture (LPC) communities has been addressed in Polish literature since the 1960s (Kozłowski ed. 1971). Papers written during that time were concerned with working out a list of tools and determining the importance of flint complexes for the division of cultures and with detecting contacts between Mesolithic and Neolithic societies, using studies on the procurement, processing and distribution of flint (Lech 1988: 276).

The issues of distribution are particularly important in relation to Chełmno Land, which is poor in high-quality natural flint resources, thus creating an ideal opportunity for research on distribution, i.e. the relation between the miner, the processor, and the user. The research conducted since the 1980s showed that this area took part in long-distance goods exchange and that the raw material inventory does not differ from the assemblages elaborated for the LPC in the south of Poland (Małecka-Kukawka 1994; Lech 1997). The accurate identification of those flint rocks that were the objects of exchange in prehistoric societies remains an important question.

Chełmno Land and the state of research on Linear Pottery Culture

Chełmno Land is situated in the east of the Central European Lowland, in a lake region which surrounds the Baltic Sea from the south, enclosing a fragment of the right side of the Vistula river basin. Its borders are demarcated by three rivers: the Osa on the north, the Drwęca on the southeast – two Vistula confluents – and on the west by the Vistula valley (Fig. 1). It is a land with a geomorphologically diversified landscape,

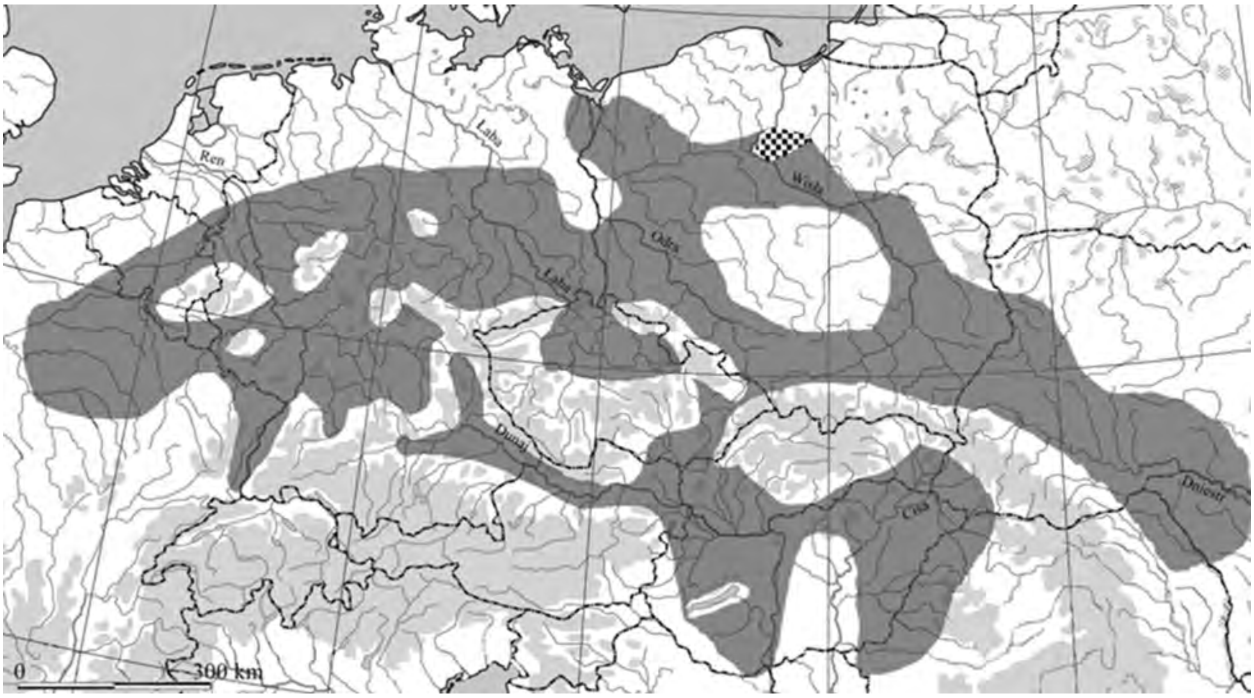

Fig. 1. Chełmno Land (shaded area) and its location within the sphere of Linear Pottery Culture society in Europe. Drawn: D. H. Werra, after Price and Bentley 2005.

different from those settled by the LPC communities of the loess highlands in the south. Its geological form was shaped during the older phases of the last glaciation and presents itself today mainly as flat or wavy moraine highlands composed of early glacial erratics. The area is cut by numerous sub-glacial channels with lakes. Numerous also are the pro-glacial stream valleys and river valleys with sand terraces along the wide floor of the Vistula valley (Galon 1984: 11). Moraine hills do not exceed a height of 150m a.s.l. (Kondracki 1978: 288).

The first known archaeological material belonging to LPC identified in Chełmno Land came from excavations in the area of Grudziądz (Grudziądz district; German: *Graudenz*) and Chełmża, Toruń district (Kossinna 1910: 61; Kozłowski 1924: 53; Kostrzewski 1928: 100). Although no subsequent research relating to the Early Neolithic was conducted in this region for many years, it was believed that this area was peripheral to the wider region of Danubian societies (Kulczycka-Leciejewiczowa 1979: 46).

Only at the end of the 1980s, as a result of excavations at site 43a at Boguszewo, Grudziądz district, were the first dwelling remnants of Danubian communities discovered, and at site 41 at Boguszewo numerous LPC sherds, and much rarer flint artifacts, were also found. The pottery analysis showed (Kirkowski 1990: 12) that the collection could be distinguished by the ornaments, which, according to Anna Kulczycka-Leciejewiczowa (1983a, 1983b, 1987, 2008: 70–81), were characteristic of the oldest LPC phase in the Vistula basin (phase Ia). The early chronology was confirmed by radiocarbon dating: 6420±100 BP (Gd–4427) and 6444±120 BP (Gd–6046), obtained for artefact 24 from site 43b at Boguszewo (Kirkowski 1990: 13; Jadin and Cahen 2003: 660).

During the last two decades of the 20th century, systematic surface collections of archaeological material and archaeological surveys were undertaken in Chełmno Land. This recent research documented 250 settlement points related to LPC communities and, as a consequence, numerous flint products made of so-called ‘imported’ raw materials (Małecka-Kukawka 1994; Kukawka *et al.* 2002: 92 and fig. 2).

The issues

Previous research identified the use of imported raw materials by prehistoric societies living in Chełmno Land and thus their role and importance in the daily lives of prehistoric communities (Lech 1997). What needs further clarification is the issue of the correct identification of the raw materials.

In the Vistula basin we find deposits of several high-quality raw materials, such as ‘chocolate’ flint, Jurassic-Cracow flint, grey white-spotted (Świeciechów) flint, striped flint, and in the eastern zone Volhynian flint. Although each of these raw materials has its very own characteristic features, mistakes in their identification are not uncommon – particularly ‘chocolate’ flint and

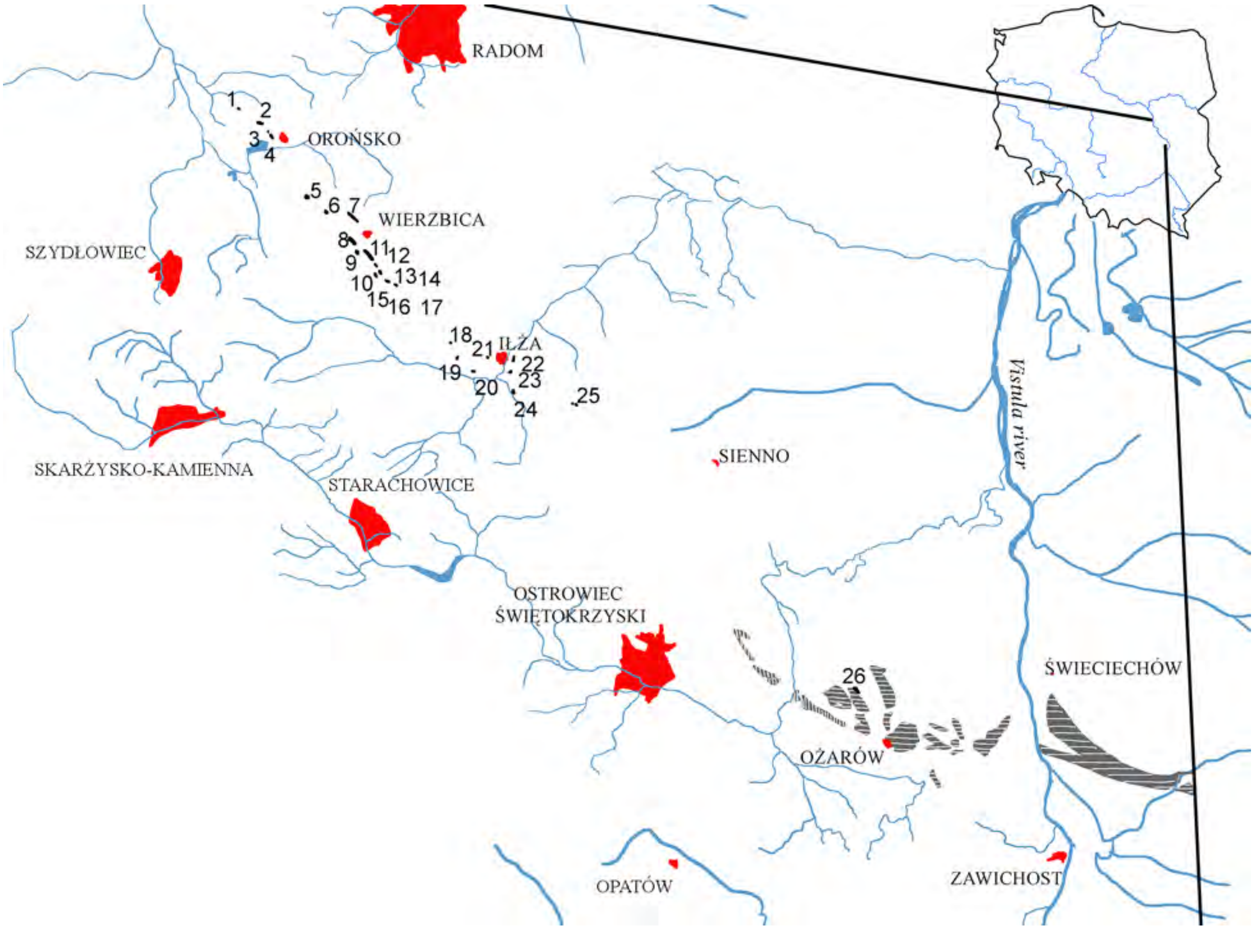

Fig. 2. Occurrence of 'chocolate' flint in pre-Quaternary formations on the northeastern outskirts of the Holy Cross Mountains; 1 – Chronów-Kolonia, Szydłowiec district; 2 – Guzów Szydłowiec district; 3 – Orońsko 'Mały Orońsk' Szydłowiec district; 4 – Orońsko (Orońsk II) Szydłowiec district; 5 – Tomaszów Szydłowiec district; 6 – Rzeczków, Radom district; 7 – Wierzbica quarry, Radom district; 8 – Wierzbica 'Zele', Radom district; 9 –Wierzbica 'Krzemienica', Radom district; 10 – Polany colonies IV, Radom district; 11 – Polany colonies I, Radom district; 12 – Polany colonies II, Radom district; 13 – Polany colonies IIa, Radom district; 14 – Polany III, Radom district; 15 – Polany colonies III, Radom district; 16 – Polany I, Radom district; 17 – Polany II, Radom district; 18 – Pakosław, Radom district; 19 – Seredzice, Radom district; 20 – Seredzice 'Kolonia', Radom district; 21 – Iłża 'Wąwóz Żuchowiec', Radom district; 22 – Iłża 'Krzemieniec' II, Radom district; 23 – Iłża 'Krzemieniec' I, Radom district; 24 – Błaziny Górne, Radom district; 25 – Prędocin, Radom district; 26 – Gliniany 'Wzgórze Kruk', Opatów district.
Drawn: D. H. Werra, after Schild 1971; 1976; Balcer 1976; Budziszewski 2008, 2015.

Jurassic flint, which are often mistaken for one another. In his 1971 publication, Romuald Schild showed the main locations of occurrences of 'chocolate' flint and divided this raw material into eleven groups. On this occasion he also pointed to its similarity to Jurassic-Cracow flint, in particular, his remarks concerned the allocated group IX (Schild 1971: 14). Almost forty years later Janusz Budziszewski emphasized the necessity of elaborating methods for describing raw materials in terms of petrographic categories, as well as for identifying its different types (Budziszewski 2008: 95).

In answer to the acknowledged necessity of filling the knowledge gap in identification of flint rocks in 2012, we started a scientific project entitled: Zróżnicowanie górno jurajskich krzemieni 'czekoladowych' ze środkowej Polski z punktu widzenia możliwości identyfikacji w badaniach archeologicznych[1] (Differentiation of Upper Jurassic 'chocolate' flint from Central Poland – possibilities of identification in archaeological research).

The basic goal of the project was to work out a method or methods of distinguishing flint rocks and to apply the results obtained to research on its archaeological distribution. Initial emphasis was put on specifying the description of 'chocolate' flint diagnostic features. Presently we know of twenty-six sites where this raw material occurs. They form a complex consisting of the largest number of prehistoric mining fields in Poland (Fig. 2). Despite the fact that research on the occurrence

[1] The project was financed by the National Center for Science (DEC-2011/03/N/HS3/03973).

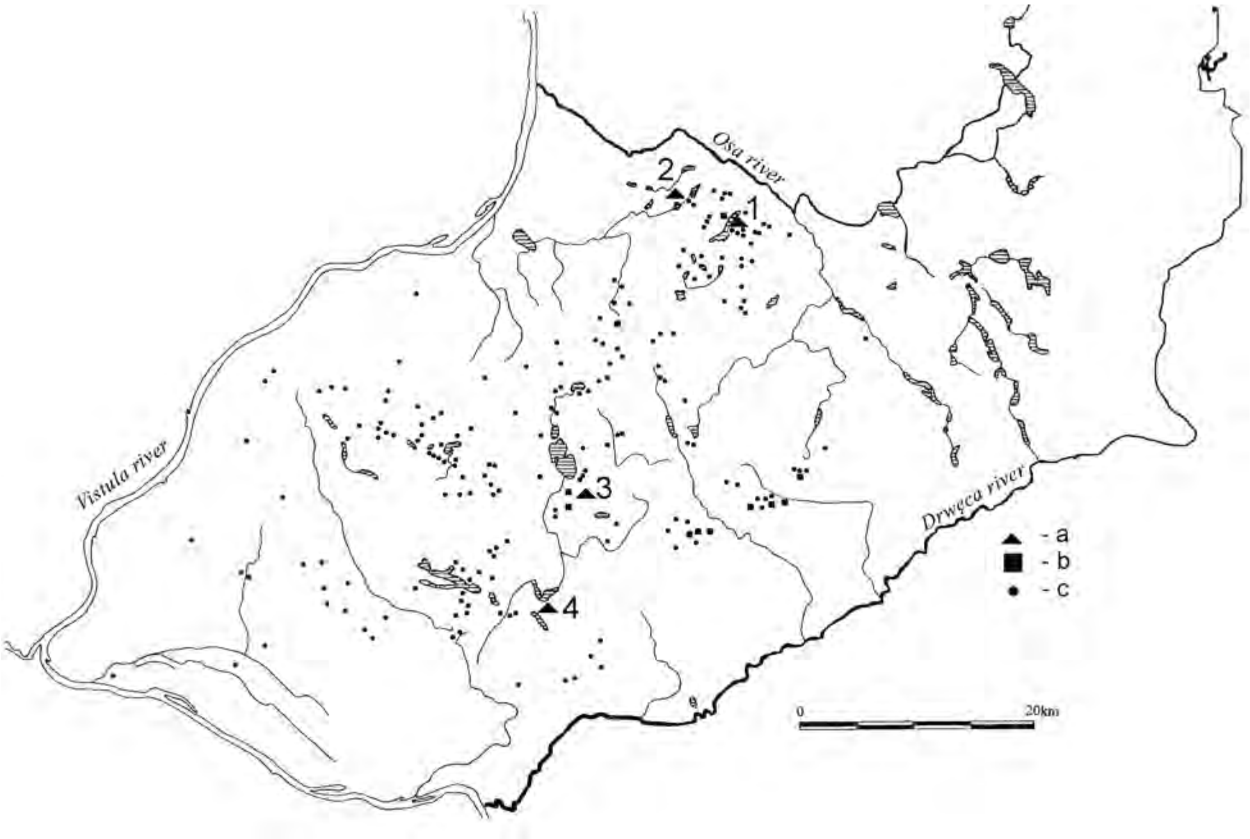

Fig. 3. Sites of Linear Pottery Culture society in Chełmno Land: a – sites presented in text: 1 – Boguszewo; 2 – Annowo; 3 – Ryńsk; 4 – Nowy Dwór; b – aggregation of Linear Pottery Culture society sites; c – singular sites of Linear Pottery Culture society. Drawn: D. H. Werra, after Kukawka *et al.* 2002, with changes.

and geological nature of 'chocolate' flint has been conducted for over ninety years, there are important gaps in knowledge of both topics. Among basic problems we can name: determining the number of levels of occurrence of this raw material in the limestone bedrock; determining their stratigraphic contexts; and the geological dating of these layers. We concentrated in this project on presenting the differentiation of raw material based on mineralogical categories, as well as its characteristic features in comparison to other flint rocks.

One of the methods used was the micro-area chemical composition analysis of minerals. During the examination of geological samples the mineral compositions of various types of flint from different areas of Poland were analyzed, resulting in the precise recognition of subordinate minerals present in flint concrections (Werra and Siuda 2015). The results obtained pointed to the importance of apatite and other phosphates in the identification of flint provenance. For example, a distinctive feature of the 'chocolate' flint occurring in the Jurassic rocks of the northern and north-eastern Mesozoic border of the Holy Cross Mountains is the presence of carbonate fluorapatite, devoid of admixtures of rare earth elements (REE). Simultaneously it was observed that the presence of REE-enriched phosphates is characteristic of the Jurassic flints from the Cracow area. These observations confirmed the elevated content of REE in the Jurassic-Cracow flint from Sąspów, Cracow district – as already discovered in 1976 by Jacek Lech (Lech 1980: 217).

The positive results from the analyses performed on geological samples allowed the beginning of the next stage of investigations – an attempt to identify the archaeological material by examining the chemical composition of minerals in micro-scale on the basis of macroscopic identification. Chosen for this procedure were 12 flint artifacts from four Chełmno Land sites related to the activities of LPC societies (Fig. 3 and 4).

The research method

Identification of subordinate minerals occurring in the flint material under examination was based on the micro-area chemical composition analyses. For this purpose, uncovered and polished microscope thin sections were made from flint samples. The chemical analyses were conducted with the use of an electron

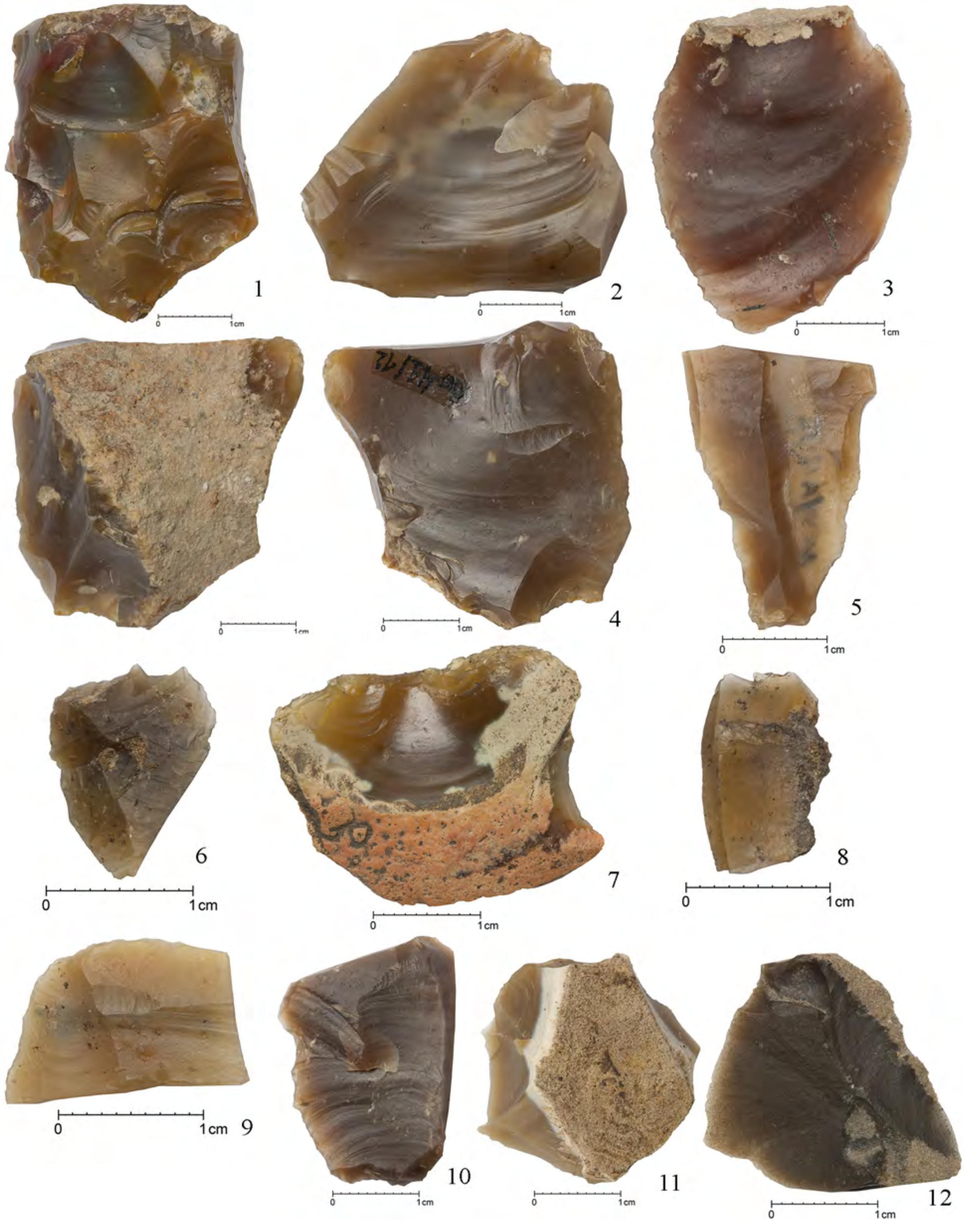

Fig. 4. Photographs of analyzed flints. Numbers are compatible with the numbers in Table 4: 1 – Nowy Dwór, site 9, Golub-Dobrzyń district, object A12, 1st mechanical layer; 2 – Nowy Dwór, site 9, Golub-Dobrzyń district – heap; 3 – Nowy Dwór, site 9, Golub-Dobrzyń district, object A 46 1 mechanical layer; 4 – Boguszewo, site 41, Grudziądz district; 5 – Nowy Dwór, site 9, Golub-Dobrzyń district, trench 24B, 1 mechanical layer; 6 – Nowy Dwór, stan 9, Golub-Dobrzyń district, object A6, 1 mechanical layer; 7 – Ryńsk, site 42, Wąbrzeźno district; 8 – Annowo, site 7, Grudziądz district; 9 – Nowy Dwór, site 9, Golub-Dobrzyń district, object A6, 2 mechanical layer; 10 – Nowy Dwór, site 9, Golub-Dobrzyń district, object A46, 1 mechanical layer; 11 – Nowy dwór, site 9, Golub-Dobrzyń district, object A12, 2 mechanical layer; 12 – Nowy dwór, site 9, Golub-Dobrzyń district, object A12, 2 mechanical layer. Photo: M. Osiadacz.

microprobe, CAMECA SX–100 model, at the Inter-Institute Analytical Complex for Minerals and Synthetic Substances (University of Warsaw). The accelerating voltage was 15kV, and the current was 10nA. The electron beam diameter was set according to the size of the analyzed inclusions and varied from 5 to 10μm.

Micro-area chemical analysis occurs through an excitement of X-rays in a sample by using an electron beam, with electrons emitted by glowing tungsten filament and accelerated in an electrostatic field. Before touching the material under analysis, the x-ray beam is shaped by a set of electromagnetic lenses to focus on the smallest cross section possible (usually few μm). The X-rays excited in the sample are separated by a spectrometer before reaching a detector and then subjected to analysis. Qualitative and quantitative determinations of chemical elements are then determined based on comparisons with standard data obtained using identical excitation conditions.

Minerals

Based on the micro-area analyses and BSE (back-scattered electrons) images, a few subordinate minerals were identified (Tab. 1). In most cases it is impossible to determine the mineral type precisely because of the small size of the analyzed mineral aggregates. The accurate identification is also sometimes hindered by the strong hydration of these aggregates and their high porosity. This unfavourably influences the quantification of the particular elements, leading to a drop in the analytical total to below 100 wt. % of element oxides. Deficient chemical analyses of apatites are also due to the presence of carbonate ions, which typically occur in the so-called 'bone' apatite constituting the skeleton elements of organisms. Due to the analytical problems, the empirical formulas calculated for the apatite based on the micro-area analyses are only tentative. The calculations were based on the ideal amount of calcium, considering the obtained Ca concentrations as the ones being least affected.

Pyrite

This mineral usually occurs in the form of euhedral cubic crystals, up to a few μm in size. The pyrite crystals create pseudomorphoses after organic remnants or framboidal aggregates (Fig. 5A). Irregular pyrite aggregates are sometimes encountered, inter-grown with hematite and aluminium phosphates.

Hematite

Hematite is one of the most commonly occurring minerals. Its aggregates are usually found in the form of very fine segregations, up to 5 μm in diameter, randomly dispersed in the flinty rock matrix. They occur in most of the analyzed flint samples (Fig. 5B). From time to time hematite create pseudomorphoses

Table 1. Comparison of presence of subordinate minerals in analyzed flint.

Sample No.	apatite	pyrite	barite	feldspar K	ilmenite	rutile	leucoxene	hematite	goethite	phosphate Al(Pb)	phosphate REE	Phosphate Al.
1								xx				
2	x		xxx					xxxx		x		
3								xx				
4								xx				
5								xx				
6							x	xx				
7		xx										
8		xx						xxx	xx			xx
9								xx				
10	xxx		xxxx									
11					xxx	xx		xxxx			xx	xx
12	xxx	xx	xxxx	x				xx	xx			

x – singular grain
xx – grains rarely encountered
xxx – grains often encountered
xxxx – grains very often encountered

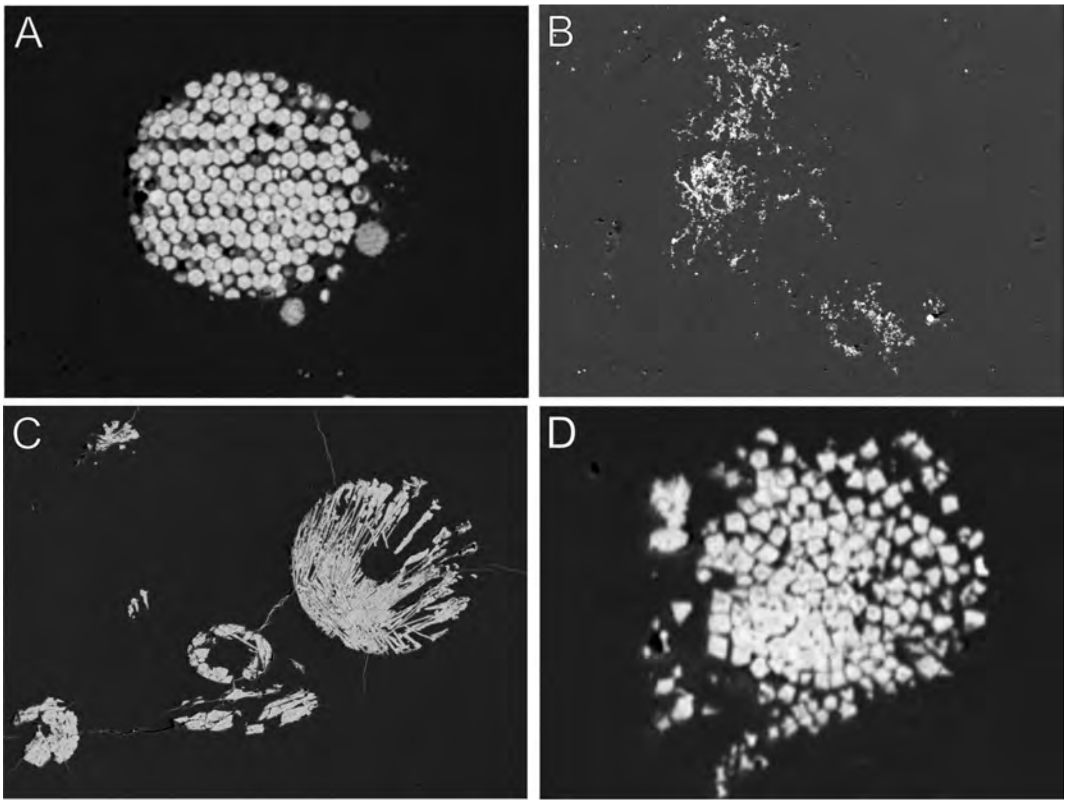

Fig. 5. A – framboidal pyrite aggregate; B – hematite inclusions; C – tabular crystals of hematite in voids after crinoids; D – pseudomorphose of hematite after framboidal pyrite Photo: R. Siuda.

after organic remains. These are usually composed of fine-crystalline hematite, forming homogenous fillings of skeleton elements of microfossils with undetermined taxonomic affiliation. Very rarely pseudomorphoses comprising tabular hematite crystals are encountered; the tabular crystals reach 50µm in length. In this case the hematite crystal fills voids after skeleton elements of *Echinodermata* (Fig. 5C). Pseudomorphoses of hematite of framboidal pyrite are relatively scarce (Fig. 5D). Hematite also appears in the form of very fine segregations within aggregates of phosphate minerals.

Ilmenite

This mineral forms very small grains, up to 10 or so µm in size. They are characterized by a strong curvature of the edges, indicative of detrital ilmenite, which is allogenic in origin (Fig. 6A). Ilmenite identification was based on EDS analysis (Fig. 6B).

Rutile

This mineral occurs as elongated grains, up to 30µm in size (Fig. 6C). Due to the small size of rutile aggregates their identification was based on EDS analysis only (Fig. 6D).

Iron oxyhydroxides (goethite)

Strongly hydrated phases rich in Fe (most likely goethite) form irregular aggregates, up to 10 or so µm in size. They are usually accompanied by pseudomorphosed efflorescent framboidal pyrite (Fig. 6E). Sometimes one can observe thin veinlets filled by Fe oxyhydroxides. Unlike hematite, during WDS analyses the Fe oxyhydroxides are very unstable and quickly decompose under the electron beam, consequently conducting the correct chemical analysis of these phases was impossible.

Baryte

Baryte usually occurs in the form of tiny (up to 20µm in size) spherical or oval aggregates built of thin-tabular crystals. They are usually randomly set within the flinty matrix. Occasional fragments with more frequent barite aggregates are observed (Fig. 6F).

K feldspar

A mineral of the K feldspar composition was identified in a single sample, where it occurs as grains reaching 40µm in size.

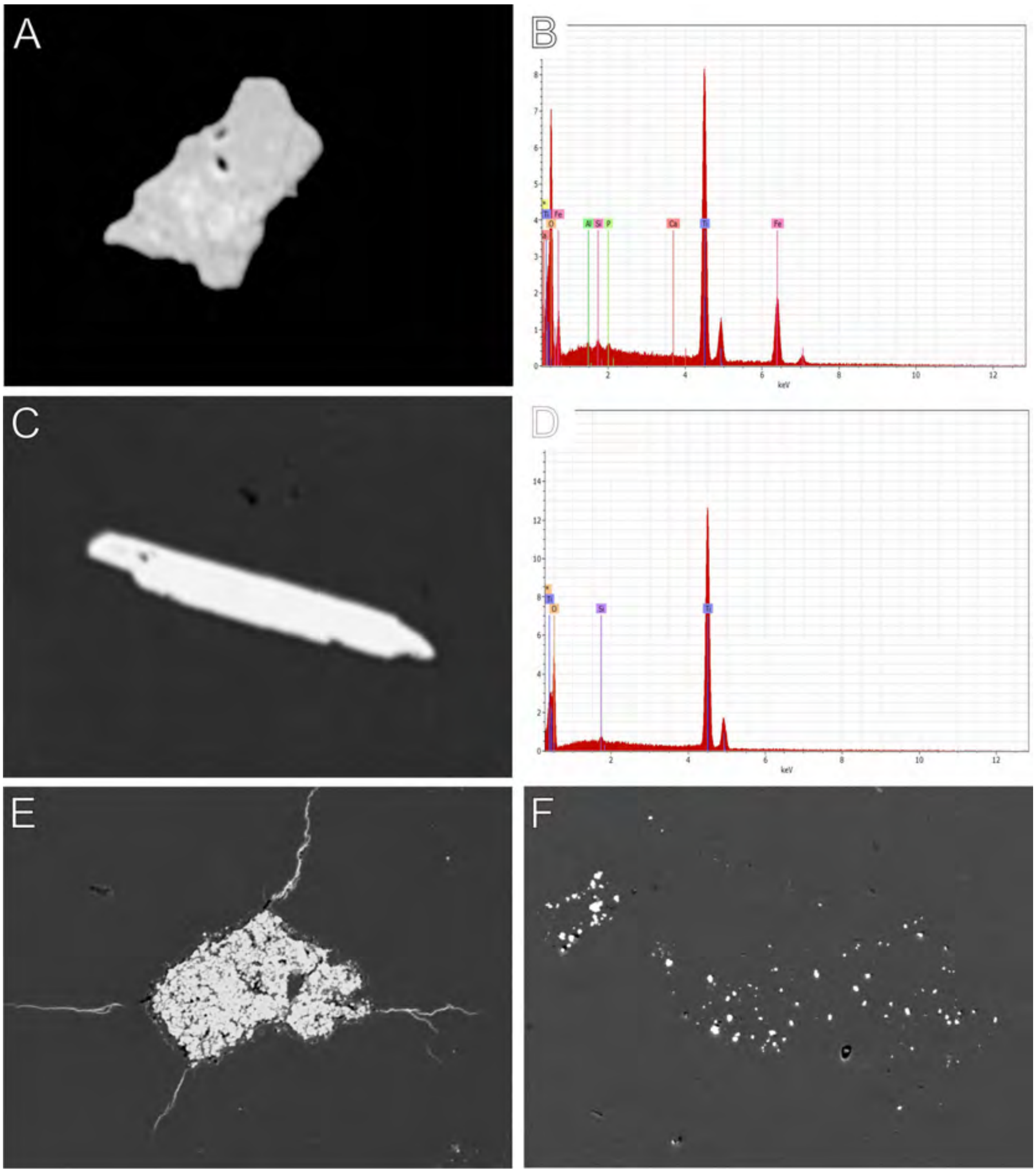

Fig. 6. A – ilmenite grain; B – EDS spectra of ilmenite; C – rutile grain; D – EDS spectra of rutile; E – iron oxyhydroxide after pyrite; F – small inclusions of barite. Photo: R. Siuda

Apatite

Apatite is a rare constituent in the flints under consideration here, and when present they usually form elongated aggregates, up to 100μm in length and distinguished by the presence of numerous, very tiny cracks, set perpendicularly to the aggregate elongation (Fig. 7A). They may also show high porosity. Single segregations of pyrite or barite are encountered in such apatite aggregates (Fig. 7B). Very rarely found are irregular apatite accumulations. All morphological types of apatite represent fragments of skeleton elements coming from microfossils of undetermined taxonomic affiliation.

During the current research, the chemical composition of apatite was determined from samples 10 and 12 (Ta. 2). Apatite from the first sample occurred as a single, very small grain of an irregular shape (Fig. 7C). It is characterized by an elevated amount of yttrium, lanthanum, and cerium, accounting for a total of *c.* 2.5 wt.% REE_2O_3. Apatite from flint no. 12 occurred in the form of elongated lath-like crystals randomly spaced in the flinty rock matrix (Fig. 7A, B). This type of apatite does not contain REE elements. Both analyzed apatites show a distinct deficiency of the phosphate anion in the tetrahedral site. It is probably compensated by the presence of carbonate ion.

Table 2. Chemical analysis of apatite.

	Sample No 10										Sample No 12	
CaO	51.71	52.83	50.60	50.32	52.13	50.55	50.37	49.43	49.72	52.29	51.20	50.25
FeO	0.41	0.67	1.22	5.18	1.86	0.35	0.33	0.28	0.12	0.34	0.22	0.35
Na_2O	1.58	0.41	2.29	0.45	0.42	0.74	0.74	1.05	1.18	0.87	0.53	0.49
SrO	0.17	0.17	0.17	0.16	0.16	0.10	0.16	0.21	0.16	0.22	0.11	0.11
MgO	0.15	0.13	0.13	0.13	0.15	0.37	0.32	0.41	0.38	0.44	0.00	0.00
MnO	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Al_2O_3	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	0,32	0,43
Y_2O_3	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	0,13	0,14
La_2O_3	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	0,00	0,10
Ce_2O_3	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	0,11	0,00
P_2O_5	34.72	33.91	29.11	32.22	33.54	36.03	34.88	37.21	37.05	36.82	33.00	33.26
SO_3	1.09	1.02	1.15	1.29	1.37	1.39	1.35	1.08	1.22	1.10	1.07	1.19
SiO_2	1.05	1.00	0.62	0.33	0.26	0.13	0.20	0.14	0.11	0.36	1.31	2.06
CO_2*	0.37	0.49	0.90	0.70	0.58	0.24	0.34	0.12	0.23	0.38	0.00	0.00
F	2.96	2.73	2.54	3.26	3.04	3.22	2.94	3.04	2.21	2.26	1.94	2.76
total	**94.21**	**93.35**	**88.73**	**94.02**	**93.49**	**93.10**	**91.61**	**92.96**	**92.38**	**95.06**	**89.94**	**91.12**
O=F	-1,25	-1,15	-1,07	-1,37	-1,28	-1.35	-1.24	-1.28	-0.93	-0.95	-0.82	-1.16
total	**92.96**	**92.20**	**87.66**	**92.65**	**92.21**	**91,75**	**90,37**	**91,68**	**91,45**	**94,11**	**89,12**	**89,96**
Ca^{2+}	4.69	4.86	4.52	4.54	4.77	4.79	4.80	4.73	4.73	4.77	4.85	4.83
Fe^{2+}	0.03	0.05	0.08	0.36	0.13	0.03	0.02	0.02	0.01	0.02	0.02	0.03
Na^{+}	0.26	0.07	0.37	0.07	0.07	0.13	0.13	0.18	0.20	0.14	0.09	0.08
Sr^{2+}	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Mg^{2+}	0.02	0.02	0.02	0.02	0.02	0.05	0.04	0.05	0.05	0.06	0.00	0.00
Mn^{2+}	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Al^{3+}	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	0.03	0.05
Y^{3+}	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	0.00	0.00
La^{3+}	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	0.00	0.00
Ce^{3+}	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	0.00	0.00
PO_4^{3-}	2.49	2.46	2.05	2.30	2.43	2.70	2.63	2.81	2.78	2.65	2.47	2.53
SO_4^{2-}	0.07	0.07	0.07	0.08	0.09	0.09	0.09	0.07	0.08	0.07	0.07	0.08
SiO_4^{4-}	0.09	0.09	0.05	0.03	0.02	0.01	0.02	0.01	0.01	0.03	0.12	0.18
CO_3^{2-}	0.50	0.66	1.22	0.95	0.79	0.32	0.46	0.16	0.31	0.51	0.00	0.00
F^{-}	0.79	0.74	0.67	0.87	0.82	0.90	0.83	0.86	0.62	0.61	0.54	0.78

Unidentified Al, REE and Pb phosphates

Single aggregates of Al, REE and Pb phosphates were encountered in three samples of the flints we studied. In sample no. 8 a single, elongated aggregate of aluminum phosphate was found, *c.* 100μm long (Fig. 7D). In the analyzed mineral the amount of aluminum varies from 27.44 to 32.43 wt.% Al_2O_3 (Tab. 3). This element is accompanied by calcium (from 4.64 to 5.87 wt.% CaO) and rare earth elements. Total REE concentration varies in the range from 6.92 to 8.18 wt.% REE_2O_3. The observed elevated amounts of iron, barium and sulphur should be connected with the occurrence of tiny inclusions of pyrite, hematite, and barite.

Aluminium phosphate was also detected in sample no. 2. Here it occurs as a single grain, *c.* 15 μm in size (Fig. 7E). The amount of aluminium in this mineral fluctuates from 29.39 to 30.30 wt.% Al_2O_3 (Tab. 3). This element is associated with small amounts of calcium

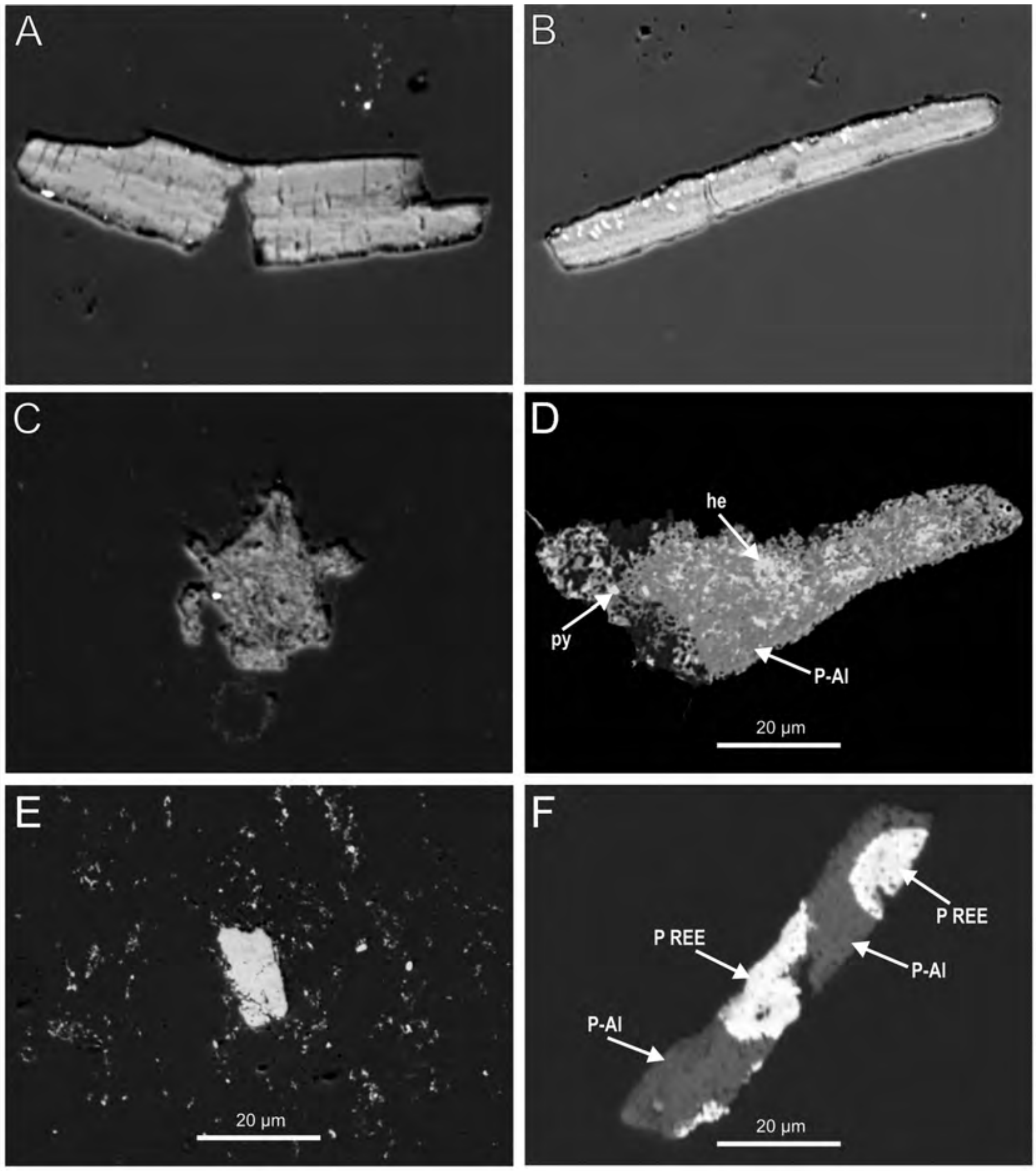

Fig. 7. A – elongated apatite aggregate (sample no 12); B – apatite aggregate (grey) with small inclusions of pyrite and barite (white) (sample no 12); C – irregular aggregate of apatite (sample no 10); D – unidentified Al phosphate (P–Al) with inclusions of pyrite (py) and hematite (he) (sample no 8); E – unidentified Al phosphate (sample no 2); F – aggregate of Al phosphate (P-Al) and REE phosphate (P REE; sample no 11). Photo: R. Siuda.

(from 5.42 to 5.98 wt.% CaO) and rare earth elements. The total amount of the REE changes from 2.54 to 2.87 wt.% REE_2O_3. A characteristic feature of the analyzed mineral is the presence of lead, in amounts varying from 5.94 to 6.43 wt.% PbO.

Al- and REE-containing phosphates were also found in sample no. 11. In this sample the presence of a polymineral, an elongated aggregate reaching 70µm in size, was detected (Fig. 7F). The aggregate is composed of an older aluminium phosphate in the process of being replaced by a younger REE phosphate. The amount of Al in the first phosphate changes from 23.06 to 32.43 wt.% Al_2O_3, and that of phosphorus from 26.47 to 27.48 wt.% P_2O_5. An elevated concentration of rare earth elements is also observed, varying from 8.00 to 10.11 wt.% REE_2O_3 (Tab. 3). Mutual ratios of these elements may indicate that the analyzed phase is compositionally close to florencite-Ce. The younger phase is represented by REE phosphate. Total REE amounts in this phase vary from 37.42 to 44.05 wt.% REE_2O_3 (Tab. 3). Among these elements the main role is played by cerium. The amount of aluminium is small and varies from 1.10 to 4.17 wt.% Al_2O_3. Noteworthy is a similar level of calcium

Table 3. Chemical analysis of unidentified phosphates Al, Al (Pb) and REE.

% wag.	Sample No 8			Sample No 2			Sample No 11					
	Al phosphate			Al (Pb) phosphate			Al phosphate			REE phosphate		
Al^2O^3	27.44	29.16	28.28	30.30	29.39	29.52	32.43	31.38	30.15	2.22	4.17	1.10
CaO	4.66	5.30	4.64	5.42	5.81	5.98	5.87	5.56	4.90	4.95	6.38	5.50
PbO	0.00	0.00	0.00	5.94	6.15	6.43	0.00	0.00	0.00	0.00	0.00	0.00
FeO	7.72	2.34	7.22	1.37	1.30	1.52	0.71	0.52	7.44	5.23	4.78	13.17
SrO	1.87	1.84	1.95	4.82	5.12	5.07	2.06	1.88	2.03	0.21	0.35	0.00
BaO	4.02	4.45	5.14	0.98	1.06	1.58	3.70	4.23	5.30	0.38	0.66	0.07
Ce^2O^3	4.31	5.17	4.27	1.16	1.17	1.31	4.88	5.18	4.41	18.22	21.00	19.07
Pr^2O^3	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.06	0.00	1.81	1.57	1.62
La^2O^3	2.75	3.01	2.65	1.42	1.38	1.43	3.59	3.52	2.43	8.00	10.40	10.31
Nd^2O^3	0.00	0.00	0.00	0.00	0.00	0.00	0.90	1.29	1.00	7.17	8.38	7.59
Sm^2O^3	0.00	0.00	0.00	0.00	0.00	0.00	0.17	0.00	0.00	1.04	0.99	0.96
Y^2O^3	0.00	0.00	0.00	0.00	0.00	0.14	0.00	0.00	0.00	1.18	1.72	1.60
P^2O^5	25.84	27.83	25.09	25.97	25.58	26.53	27.35	27.48	26.47	25.01	30.43	24.23
SiO^2	1.04	2.88	1.21	1.45	2.79	0.42	5.58	4.71	4.81	23.27	0.72	3.74
SO^3	2.54	1.39	1.96	2.67	3.07	3.51	0.18	0.18	0.14	0.18	0.32	0.14
F^-	0.00	0.30	0.25	1.09	0.70	0.60	0.52	0.71	0.63	0.29	0.18	0.20
total	82.19	83.66	82.67	82.59	83.51	84.02	87.95	86.71	89.72	99.15	92.02	89.28
O=F	0.00	-0.14	-0.11	-0.48	-0.32	-0.26	-0.22	-0.30	-0.27	-0.13	0.00	-0.10
total	82.19	83.52	82.55	82.11	83.19	83.76	87.73	86.41	89.45	99.01	92.02	89.18

concentration in both phosphates: it only changes from 4.90 to 6.38 wt.% CaO. Concentrations of iron and silicon determined by some analyses are likely due to the presence of subtle inclusions of hematite and quartz (chalcedony).

Origin of flints in the light of the analysis of the subordinate minerals

Flints are sedimentary rocks of a unique character. Their monomineral character and lack of significant amounts of accessory or subordinate minerals means that the determination of the provenance of flinty material based on mineralogical research is exceedingly difficult. However, research on mineral compositions of different flint types from various areas of Poland conducted by the authors allowed us to recognize in detail the subordinate minerals occurring in flint concretions (Werra and Siuda 2015), and the research carried out here shows that apatite and other phosphate minerals may be used for flint identification.

Phosphates present in the analyzed flints can be divided into two types. The first of these is represented by carbonate-fluorapatite, which is the building material of skeleton elements in organisms (these are most probably fish bone fragments). The second type is composed of phosphates containing elements from the group of rare earth elements. The occurrence of carbonate-fluorapatite inclusions was observed exclusively in ‘chocolate’ flint originating from the Jurassic carbonate rocks that constitute the N and NE borders of the Holy Cross Mountains. On this basis we can propose that this mineral is a diagnostic feature for this type of flint. The significance of phosphates containing REE for the purpose of identification is much more restricted; their presence was recognized exclusively in flint originating from the region around Cracow, and even there they are absent in the samples taken from Wołowice, Cracow district. Nearly 40 years ago Jacek Lech pointed out the high level of REE presence in Jurassic Cracow flint (Sąspów; Lech 1980: 217), and we now know that the presence of hematite may be an indicator as to the flint’s original location (Přichystal 2013). Admittedly, this mineral occurs in various types of flint, but it is particularly abundant only in samples originating from the Cracow area.

The results of the micro-area analyses were compared with the macroscopic results. The latter were performed by Jolanta Małecka-Kukawka from the Nicolaus Copernicus University at Toruń, in consultation with various researchers of flint rocks (cf. Małecka-Kukawka 2001). The last determination of raw materials was performed in 2003 for samples taken from the site at Nowy Dwór, Golub-Dobrzyń

Table 4. Macroscopic analysis results compared to microscopic results.

Site	Description	Jacek Lech – 2015	Jolanta Małecka-Kukawka – 2003	Micro-area analysis results
1 – Nowy Dwór, site 9, Golub-Dobrzyń district, object A12, 1st mechanical layer	Flake removed from a flaking surface of a flake core (technical) with an initial splintered piece exploitation	Jurassic-Cracow flint	undefined	The presence of hematite may suggest Jurassic-Cracow flint or Baltic erratic flint
2 – Nowy Dwór, site 9, Golub-Dobrzyń district, heap	Flake with negative flake scars on the dorsal surface	Jurassic-Cracow flint	Jurassic, area around Cracow	The presence of hematite and of phosphates enriched with REE may suggest Jurassic-Cracow flint
3 – Nowy Dwór, site 9, Golub-Dobrzyń district, object A 46 1 mechanical layer	Flake with negative flake scars and unprepared butt	Jurassic-Cracow flint	Raw material – Jurassic-Cracow flint; but cortex like in‘chocolate’ flint	The presence of hematite may suggest Jurassic-Cracow flint or Baltic erratic flint
4 – Boguszewo, site 41, Grudziądz district	Partially initial flake	Jurassic-Cracow flint	Jurassic-Cracow flint	The presence of hematite may suggest Jurassic-Cracow flint or Baltic erratic flint. The absence of apatite excludes ‘chocolate’ flint
5 – Nowy Dwór, site 9, Golub-Dobrzyń district, trench 24B, 1 mechanical layer	Flake butt fragment, scar	Jurassic-Cracow flint	undefined	The presence of hematite may suggest Jurassic-Cracow flint or Baltic erratic flint
6 – Nowy Dwór, stan 9, Golub-Dobrzyń district, object A6, 1 mechanical layer	Flake scar	Baltic erratic flint, lightly burned	undefined	The presence of hematite may suggest Jurassic-Cracow flint or Baltic erratic flint
7 – Ryńsk, site 42, Wąbrzeźno district	Partially initial flake	Jurassic-Cracow flint	undefined	undefined
8 – Annowo, site 7, Grudziądz district	chip	Possible Jurassic-Cracow or ‘chocolate’ flint with emphasis on ‘chocolate’ flint	undefined	The presence of hematite and phosphates enriched with REE may suggest Jurassic-Cracow flint
9 – Nowy Dwór, site 9, Golub-Dobrzyń district, object A6, 2 mechanical layer	chip with scars	Possible Jurassic-Cracow flint or Baltic erratic flint, with certainty of no ‘chocolate’ flint	undefined	The presence of hematite may suggest Jurassic-Cracow flint or Baltic erratic flint
10 – Nowy Dwór, site 9, Golub-Dobrzyń district, object A46, 1 mechanical layer	Flake with negative flake scars on the dorsal surface	Jurassic-Cracow flint	Jurassic-Cracow flint	The presence of apatite without REE points to ‘chocolate’ flint
11 – Nowy dwór, site 9, Golub-Dobrzyń district, object A12, 2 mechanical layer	Partially initial flake	‘chocolate’ flint	‘chocolate’ flint – light colour	The presence of hematite and phosphates enriched with REE may suggest Jurassic-Cracow flint
12 – Nowy dwór, site 9, Golub-Dobrzyń district, object A12, 2 mechanical layer	Flake with negative flake scars on the dorsal surface	‘chocolate’ flint – from outcrops from central part of ‘chocolate’ flint stream	‘chocolate’ flint – dark colour variety	The presence of apatite without REE points to ‘chocolate’ flint

district. Some samples contained material which could not be clearly determined in terms of the presence of subordinate ingredients (due either to the small size of samples or the lack of cortex, etc.). At the same time, they showed features that allowed us to eliminate their local (erratic) origin. Such samples, among others from the sites at Ryńsk, Wąbrzeźno district, and Annowo, Grudziądz district (cf. Małecka-Kukawka 2001: 38, 42), as well as at Nowy Dwór (Małecka-Kukawka 2009: 170–171), were declared as undefined, with an indication of their south-Polish origin. Examples of such specimens, considered as undefined, were chosen for chemical constituents analysis. The specimens were chosen from several sites and were unambiguously identified by Małecka-Kukawka, as well as other scientists consulting in this material examination. These are samples 2 (Nowy Dwór), 4 (Boguszewo), 10, 11, and 12 (Nowy Dwór). In addition, a renewed determination of the sources of these raw materials was carried out by Jacek Lech in 2015 before submitting the specimens to chemical analysis. Table 4 shows the results of the macroscopic analyses compared to the microscopic results.

As comments on the effectiveness of the presented method we may draw the following conclusions:

1. Samples 1, 3, 5, 6, and 9 were identified by Małecka-Kukawka as undefined, and by Lech in 2015 as Jurassic-Cracow flint: the micro-area analysis confirmed with a high probability that these samples are made of Jurassic-Cracow flint.
2. Samples 2 and 4 were unambiguously determined by Małecka-Kukawka and Lech as Jurassic-Cracow flint: the micro-area analysis confirms the correctness of the macroscopic results.
3. Sample 12 was also unambiguously determined by both Małecka-Kukawka and Lech as 'chocolate' flint: the micro-area analysis confirms the correctness of the macroscopic results.
4. Sample 10 was unambiguously determined by both scientists as Jurassic-Cracow flint: according to the micro-area analysis it is 'chocolate' flint.
5. Sample 11 was unambiguously determined by both scientists as 'chocolate' flint: but according to the micro-area analysis it is not 'chocolate' flint.

The results presented in points 1, 2 and 3 above confirm the concordance of traditional, macroscopic raw material determinations with the method of chemical ingredients analysis and point to the usefulness of the latter in settling certain doubts (e.g. samples 1, 3, 5, 6, 9).

Equally interesting are the discrepancies in the determination of raw materials while using the 'traditional' (samples 10 and 11) and chemical methods. The differences in macroscopic identification and micro-area identification may result from the features of the material, its small size, and the lack of all diagnostic features. The so-called 'chocolate' flint on the Cracow-Częstochowa Upland (Krajcarz and Krajcarz 2009; Krajcarz *et al.* 2012; Cyrek 2013: 23) also contains macroscopic features that are close to those of the 'chocolate' flint from the north-eastern borders of the Holy Cross Mountains.

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