Archaeologia Polona, vol. 54: 2016, 99–114
PL ISSN 0066-5924

On The Chemical Composition of 'Chocolate' Flint from Central Poland

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The paper presents the initial results of energy-dispersive x-ray fluorescence (EDXRF) spectrometric analysis of 'chocolate' flint from outcrops located on the northeastern slopes of the Świętokrzyskie (Holy Cross) Mountains in central Poland. EDXRF analysis shows that the composition of certain major and minor elements allow us to distinguish between and among some varieties of 'chocolate' flint. EDXRF analysis also was undertaken on other flints know from Poland (Jurassic-Cracow; Gray-white spotted; Striped Flint), providing a geochemical baseline for instrumental identification of these flints in archaeological sites.

KEY-WORD: 'chocolate' flint, EDXRF, Central Poland, flint identification

INTRODUCTION

In the years following World War I, Stefan Krukowski (1920, 1922) published two important articles emphasizing the relevance of the study of flint raw materials to research on prehistoric 'mining, transport and trade'. In the first of these he wrote that it:

> '[…] jest cel … zwrócić … uwagę naszych prehistoryków, wspomaganych przez petrografów i geologów, na doniosłość tych zagadnień [górnictwo, transport i handel] nie tylko dla cywilizacji neolitycznych wogóle, lecz szczególniej dla morfologii wyrobów z krzemienia, jakoteż łączności między współistniejącemi i nastepującemi po sobie kulturami.'

> '[…] the goal is ... to call ... the attention of our prehistorians, assisted by petrolographists and geologists, on the importance of these issues [mining, transport and trade], not only for the Neolithic civilization in general, but especially for the morphology of the products of flint, and also to communication between the coexistence and succession of the cultures.' (Krukowski 1920: 185; additions and translation by DHW).

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'Chocolate' flint held an important place in Krukowski's research. As early as 1922 he and Jan Samsonowicz discovered the first 'chocolate flint' outcrops located on the northeastern slopes of the Świętokrzyskie (Holy Cross) Mountains in central Poland (Krukowski 1922, 1923; Samsonowicz 1923).

Since Krukowski's work, a considerable amount of research on 'chocolate' flint has been undertaken over the past several decades (e.g., Schild 1971, 1976, 1987, 1995a, 1995b, 1997; Kaczanowska and Lech 1977; Schild *et al.*, 1977; 1985; 1997; Chmielewska 1980, 1988; Lech 1984, 1995, 1997; Lech 1987, 1990; Herbich 1993; Herbich and Lech 1995; Cyrek 1995; Bednarz and Budziszewski 1997; Małecka-Kukawka 1997; Sulgostowska 1997; Bednarz 2001; Borkowski *et al.*, 2008; Budziszewski 2008; Přichystal 2009, 2013). This research was pivotal to demonstrating that 'chocolate' flint was the most important raw material used by prehistoric communities from Paleolithic through Late Bronze Age times (Lech 1984; Sulgostowska 2005) from the north-east margin of the Świętokrzyskie (Holy Cross) Mountains to as far away as the Carpathian Mountains. In fact, it is has recently been identified as being present in the flint assemblages at archaeological sites in Belarus, the Czech Republic, Hungary, Latvia, Lithuania, Slovakia, and the Ukraine (Schild 1976; Budziszewski 2008; Sulgostowska 2008; Kozłowski 2013; Bíro 2014: 61).

BACKGROUND

Following Krukowski's (1920) pioneering description of the macroscopic characteristics of 'chocolate' flint there have been several other attempts to characterize it (e.g. Budziszewski 2008: 33). In perhaps the best known of these, Romuald Schild (1971: 7–17, 1976: 149) used macroscopic and microscopic criteria to identify 11 groups of 'chocolate' flint using material collected from 16 geological extraction points on the north-east rim of the Świętokrzyskie (Holy Cross) Mountains. He took into account the macroscopic properties of color, luster, composition, texture, structure, shape and size of nodule, and type of cortex (Schild 1976: 149), as well as microscopic characteristics revealed by a petrographic analysis of thin sections using laser light (Schild 1971: 6).

On the basis of these examinations Schild (1976: 149) wrote that of the 11 groups he identified 'three groups are of importance being the most common and possibility also the most popular in prehistory'. The first group is dark brown (10 YR 2/2) in color, waxy, usually not banded or occasionally microbanded rarely with a black central part (10 YR 2/1). This group occurs in central and eastern portion of 'chocolate' flint strip (Group I; see Fig. 1 and Table 1). The second group is dark grayish brown (10 YR 2/1) and brown (10 YR 4/3) in color. The nodules are waxy and transparent, not usually banded, and rarely irregularly laminated. This group occurs in the western portion of the strip (Group VI and VII; see Fig. 1). The last (third) group is typically black in the central portion of the nodule (10 YR 2/1) and very dark gray to dark brown (10 YR 3/1 – 10 YR 3/3), rarely dark grayish brown (10 YR 4/2), in the remaining mass. This variety is not banded, but dull to dull waxy and weakly transparent. This group occurs in the central part of the strip (Group X; see Fig. 1; Schild 1971: 7–17, 1976: 149). Schild (1971) also identified a Group IX, which is similar to Group VI. Group IX raw materials are brown in color (10 YR 4/3), sometimes gray-brown (10 YR 4/2), sometimes with gray spots. This flint, which occurs at Orońsko (Szydłowiec district;

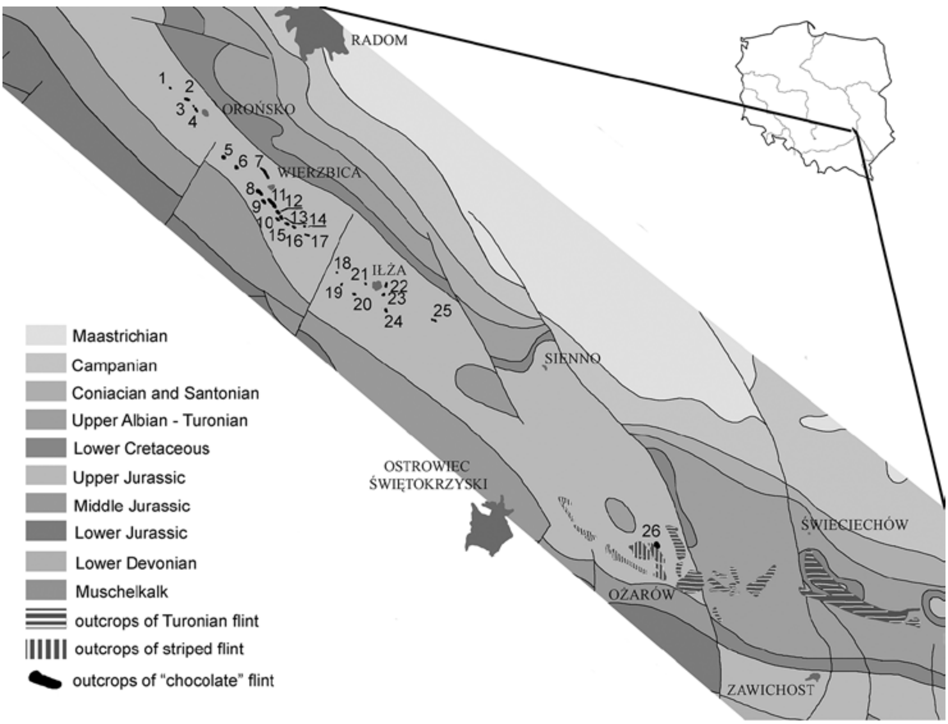

Fig. 1. 'Chocolate' flint locations in pre-Quaternary formations on the northeastern outskirts of the Holy Cross Mountains; 1 – Chronów-Kolonia, Szydłowiec dist.; 2 – Guzów Szydłowiec dist.; 3 – Orońsko 'Mały Orońsk' Szydłowiec dist.; **4 – Orońsko (Orońsk II) Szydłowiec dist.**; **5 – Tomaszów Szydłowiec dist.**; 6 – Rzeczków, Radom dist.; **7 – Wierzbica quarry, Radom dist.**; **8 – Wierzbica 'Zele', Radom dist.**; 9 – Wierzbica 'Krzemienica', Radom dist.; 10 – Polany kolonie IV, Radom dist.; 11 – Polany kolonie I, Radom dist.; 12 – Polany kolonie II, Radom dist.; 13 – Polany kolonie IIa, Radom dist.; 14 – Polany III, Radom dist.; 15 – Polany kolonie III, Radom dist.; 16 – Polany I, Radom dist.; 17 – Polany II, Radom dist.; 18 – Pakosław, Radom dist.; 19 – Seredzice, Radom dist.; 20 – Seredzice 'Kolonia', Radom dist.; 21 – Iłża 'Wąwóz Żuchowiec', Radom dist.; 22 – Iłża 'Krzemieniec' II, Radom dist.; 23 – Iłża 'Krzemieniec' I, Radom dist.; 24 – Błaziny Górne, Radom dist.; **25 – Prędocin, Radom dist.**; 26 – Gliniany 'Wzgórze Kruk', Opatów dist. (Schild 1971, 1976; Balcer 1976; Dadlez *et al.*, 2000; Budziszewski 2008; Budziszewski *et al.*, 2015; sites listed in boldface print are discussed in the text). Graphic design: D.H. Werra.

Table 1. Characteristics of the eleven groups of 'chocolate' flint distinguished by Schild (1971: 7–17)

Group	Colour	Trans-parency	Compo-sition	Luster	Shape and Size of Nodule	Type of Cortex	Occurrence
I	Dark brown (10 YR 2/2); black central part (10 YR 2/1)	good and medium	petite and medium	waxy	flat, diam-eter tens cm	Thin, up to 1 mm; rough or smooth	Chronów-Kolonia, Wierzbica 'Zele'; Polany I, Polany II, Polany kolonie II, Polany kolonie III, Iłża, Prędocin
II	Black (10 YR 2/1), thin rim dark brown (10 YR 2/2)	Medium and bad	Medium and thick	waxy	Round nod-ules, from few up to tens cm	Rough, some-times more than 5 mm	Iłża
III	Dark brown (10 YR 3/2)	good and medium	petite and medium	waxy	Flat and round	Thin and smooth	Wierzbica 'Zele', Polany I, Polany kolonie I and II, Prędocin
IV	Dark, red-brown (5 YR 3/2), with bald spots (%YR 2/1)	medium	thick	dull	Round, up to tens cm diameter	Up to 1mm very rough	Polany Kolonie II
V	Dark-gray-brown (10 YR 3/2) and dark-brown (10 YR 2/2), with gray spots	From good to bad	petite	Waxy, waxy-dull, dull	Big nod-ules maybe tablets	Thin, less than 1 mm	Chronów-Kolonia, Guzów, Wierzbica 'Zele', Polany Kolonia I, II and III
VI	Dark-gray-brown or brown (10 YR 4/2 – 10 YR 4/3)	good	petite	waxy	Big nodules and tablets	Thin, less than 1 mm	Orońsko, Tomaszów
VII	Dark-gray-brown (10 YR 4/2) and dark reddish-gray spots	Good and medium	Petite and medium	Dull-waxy and waxy	Big, irregular tablets	Thin	Guzów, Orońsko
VIII	Dark-gray-brown (10 YR 4/2) or dark-yellow-brown with gray, brown and black bands	Good and medium	petite	waxy	Tablets	Thin, less than 1 mm	Tomaszów

IX	Brown (10 YR 4/3) or dark-gray-brown (10 Yr 4/2)	Petite – with gray spots	good	waxy	Unknown	Rough 1–2 mm, under the cortex white rim	Orońsko
X	Black (10 YR 2/1), dark-gray (10 YR 3/1), dark-gray-brown (10 YR 3/2), dark-brown (10 YR 3/3) or dark-gray-brown (10 YR 4/2)	bad	thick	dull	Irregular nodules and tablets	Thin and thick	Guzów, Wierzbica 'Zele', Polany I, III, Polany kolonie I and III
XI	Dark-gray-brown (10 YR 4/2)	Medium and bad	Petite and medium	dull	Big, irregular tablets	Thin up to 1mm and smooth or thick 5 mm and rough	Tomaszów

Schild 1971: 14), can look very similar to Jurassic-Cracow flint.

However, attempts to distinguish these different flint varieties using macroscopic characteristics were not particularly successful. In fact Schild (1976: 150) concluded that 'the study of thin sections makes the recognition of the exact source almost impossible' although he held out hope that 'the use of other scientific techniques might help the identification of the exact source'.

THE PRESENT PROJECT

Almost forty years after those words were written a new project about 'chocolate' flint was undertaken by the Institute of Archeology and Ethnology Polish Academy of Science in cooperation with Geochemical Research Laboratory (USA)[1]. In recent studies (Hughes *et al.*, 2011, Hughes *et al.*, 2012, Högberg *et al.*, 2013) non-destructive energy-dispersive X-ray fluorescence (EDXRF) analysis was applied to the problem of drawing chemical distinctions between and among various types of Scandinavian flint and flints from Lithuania and Belarus. EDXRF results showed that using this method chemical differences between certain flints can be identified, so we applied this same method to a pilot study of 'chocolate' flint from Poland. The main goal was to see if it was possible to identify chemical differences among 'chocolate' flint from different outcrops, but we also investigated differences among other regional flint types in the Vistula River basin (*e.g.* Turonian flint; grey white-spotted – Świeciechów; striped, Jurassic-Cracow) and, on the eastern fringes of the region, Volhynian flint.

[1] The analysis were funded by the National Science Centre in Poland (PRELUDIUM 2; UMO-2011/03/N/HS3/03973).

From a geological standpoint, the siliceous rocks used by prehistoric communities occur in late Jurassic deposits – the highest Oxfordian limestone and Lower Kimmeridgian – but precise determination of the relative stratigraphic position of the 'chocolate' flint is difficult due to the lack of a clear chrono-stratigraphic division between of the rocks occurring in the area. The problem is exacerbated because of the lack of a clearly defined boundary between Oxford and Kimmeridgian in different parts of Europe. Samsonowicz (1934) wrote that 'chocolate' flint usually occurs in one thin level, in a stable stratigraphic position, but Pożaryski (1948) later argued that 'chocolate' flints are continuously distributed but can occur in thick deposits for several meters. Subsequent geological research appeared to support Pożaryski's view, but more recent studies (Dembowska 1953; Wyrwicki 1969) are more consonant with Samsonowicz's earlier findings. Although most geologists working in this area assign 'chocolate' flints to the upper part of Upper Oxford (Malinowska and Dembowska 1973; Dąbrowska 1983) others (e.g. Kutek 1983; Gutowski 2004) assigns 'chocolate' flint to the lower Kimmeridgian, and some other researchers believe that this flint occurs in both of these levels (Wyrwicka 1969; Migaszewski *et al.*, 2006). Archaeological research shows that prehistoric exploitations points for 'chocolate' flint are visible in one line and level around 6 m thick but it is still unclear whether 'chocolate' flints were created at one, discrete, level or whether they occur in several stratigraphic horizons (Budziszewski 2008: 45). To say the least, the dating issue is still far from settled and must await more detailed geological and archaeological study.

SAMPLE SELECTION

For the present study we selected 37 samples from four distinct archaeologically documented prehistoric 'chocolate' flint mines from Upper Oxfordian (ca. 157–164 Ma) and possibly Kimmeridgian (ca. 152–157 Ma) geological deposits in the Holy Cross Mountains. These include: Orońsko (n= 8; loc. 4 in Fig. 1), Tomaszów (Szydłowiec district; n= 9; loc. 5 in Fig. 1), Wierzbica (Radom district; n= 11; locs. 7–8 in Fig. 1), and Prędocin (Radom district; n= 9; loc. 25 in Fig. 1). From these sites we analyzed flint from the three main visual groups identified by Schild (1976). Prędocin represents Schild's (1976) group I, Orońsko and Tomaszów represent group II, and Wierzbica 'Zele' the last – III group (Table 1). Geographically they include the main locale in the north-west part of 'chocolate' flint belt (group II), the middle (group III) and the south-east part (Prędocin).

STUDY RESULTS AND DISCUSSION

Figure 1 shows the locations of the samples collected for this study, and Table 2 presents chemical data for the analyzed flint samples. All specimens were analyzed using non-destructive EDXRF using laboratory analysis conditions and instrumentation described in an earlier study (Hughes *et al.*, 2012). Samples chosen for analysis were cleaved from parent nodules collected during surface studies made during 2012–2014. Flints from Orońsko and Tomaszów were collected from the surface of the sites. In the case of Wierzbica, fresh raw material was collected directly from the flint layers exposed in the walls of the quarry and Wierzbica 'Zele' samples were selected from a deep shaft excavated in the 1980's. The specimens were cut into 30 cm squares using diamond saw blade (VC–50 2001 LECO Corp.) together with VC Cutting Oil and a 100 water cooled diamond saw blade manufactured by the Dedra company. The surface of flint samples so produced were not polished in any way. Prior to EDXRF analysis the sample surfaces were cleaned with distilled water to remove any noticeable surface contaminants. As discussed previously (Hughes *et al.*, 2012: 786), care was taken to avoid targeting the X-ray beam onto calcareous or fossil inclusions. Otherwise, the only other analysis requirement was that each sample be relatively flat, ≥ 15–20 mm in diameter, and have a minimum surface size of ≥ 2–3 mm.

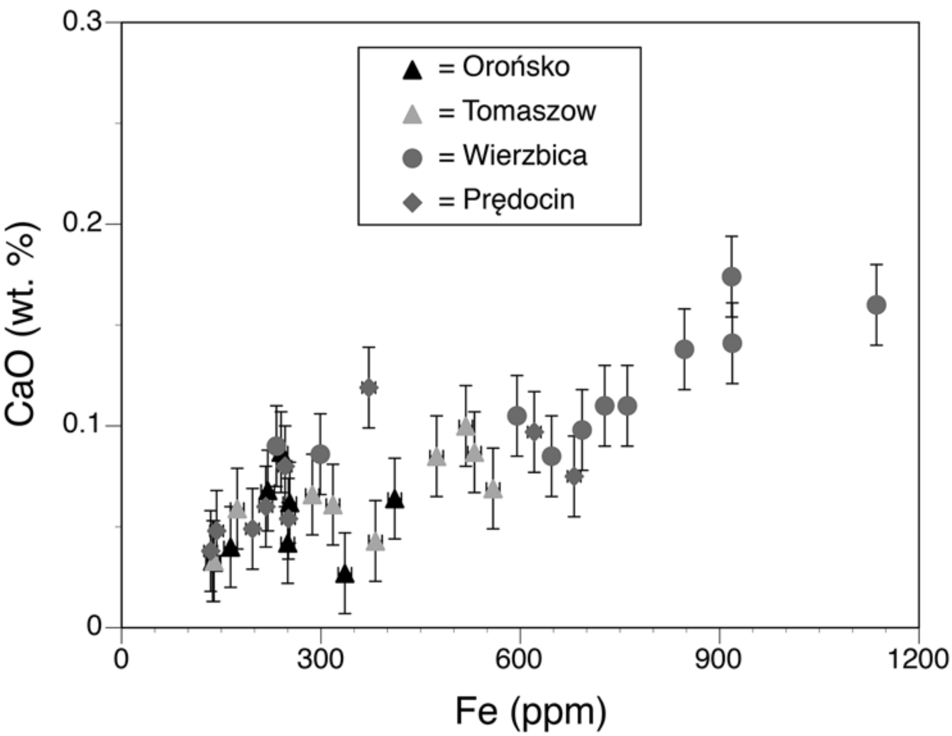

Fig. 2. The composition of Ca vs. Fe in geological specimens of 'chocolate' flint from the northeastern slopes of the Świętokrzyskie (Holy Cross) Mountains in central Poland. Error bars delimit 95% probability estimates for elemental composition. Graphic design: R.E. Hughes.

Table 2. The Chemical Composition of 'Chocolate' Flint from Poland

Locality	Lab I.D. #	Major and Minor Elements								
		Al_2O_3 (wt. %)	SiO_2 (wt. %)	SO_3 (wt. %)	Cl (ppm)	K_2O (wt. %)	CaO (wt. %)	Ti (ppm)	Mn (ppm)	Fe (ppm)
Orońsko psy się gryzły, Szydłowiec dist.	ORO-1	0	99,69	0,022	11	0,042	0,087	37	1	240
Orońsko 'Truskawki', Szydłowiec dist.	ORO-2	0,000	99,61	0,016	171	0,065	0,068	38	2	220
Orońsko 'Truskawki', Szydłowiec dist.	ORO-4	0,129	99,64	0,013	0	0,095	0,027	105	6	336
Orońsko 'Przy bramie', Szydłowiec dist.	ORO-5	0,000	99,67	0,023	17	0,036	0,033	26	1	137
Orońsko 'Przy bramie', Szydłowiec dist.	ORO-6	0,173	99,52	0	0	0,053	0,064	58	4	411
Orońsko 'Truskawki', Szydłowiec dist.	ORO-7	0	99,55	0,02	0	0,046	0,042	26	1	250
Orońsko 'Truskawki', Szydłowiec dist.	ORO-8	0	99,36	0,023	509	0,123	0,062	38	0	253
Orońsko szkółka, Szydłowiec dist.	ORO-10	0	99,66	0,017	0	0,031	0,04	64	3	164
Tomaszów, Szydłowiec dist.	TOM-1	0,000	99,53	0,009	226	0,091	0,087	46	0	531
Tomaszów, Szydłowiec dist.	TOM-2	0,000	99,56	0,002	0	0,06	0,069	66	3	559
Tomaszów, Szydłowiec dist.	TOM-3	0,000	99,49	0,029	400	0,101	0,085	62	3	474
Tomaszów, Szydłowiec dist.	TOM-4	0,000	99,37	0,013	247	0,075	0,059	57	3	174
Tomaszów, Szydłowiec dist.	TOM-5	0	99,49	0	0	0,037	0,066	51	2	287
Tomaszów, Szydłowiec dist.	TOM-6	0,000	99,37	0,031	187	0,1	0,1	183	5	518
Tomaszów, Szydłowiec dist.	TOM-7	0,124	99,50	0,022	104	0,083	0,043	66	4	382
Tomaszów, Szydłowiec dist.	TOM-8	0	99,43	0,021	0	0,052	0,061	57	1	318
Tomaszów, Szydłowiec dist.	TOM-9	0	99,50	0,021	0	0,04	0,03	36	1	115
Wierzbica Kamieniolom, tablica, Radom dist.	WiK-1 (run 2)	0,000	99,54	0,021	0	0,061	0,086	52	2	299
Wierzbica Kamieniolom, layer 1, Radom dist.	WiK-2 (run 2)	0,085	98,99	0,024	577	0,088	0,09	55	3	233
Wierzbica 'Zele' brown, Radom dist.	WZ1-B	0,067	99,15	0,028	737	0,083	0,141	105	3	919

Wierzbica 'Zele' brown, Radom dist.	WZ1-B1 (run 1)	0,000	99,32	0,02	308	0,074	0,138	93	2	847
Wierzbica 'Zele' black, Radom dist.	WZ2-C (run 2)	0,000	99,53	0,036	58	0,044	0,105	68	3	595
Wierzbica 'Zele' brown, Radom dist.	WZ3-B	0,000	99,49	0,027	58	0,031	0,11	66	1	727
Wierzbica 'Zele' brown, Radom dist.	WZ3-B1 (run 2)	0,000	99,43	0	0	0,051	0,085	95	0	647
Wierzbica 'Zele' black, Radom dist.	WZ3-C	0,000	99,50	0,021	0	0,045	0,101	104	5	573
Wierzbica 'Zele' black, Radom dist.	WZ3-C1 (run 2)	0,000	99,48	0,035	92	0,055	0,098	83	2	693
Wierzbica 'Zele', Radom dist.	WZp-1 (run 2)	0,039	99,18	0,028	566	0,077	0,174	114	5	918
Wierzbica 'Zele', Radom dist.	WZp-2	0,051	99,59	0,027	102	0,057	0,113	80	2	706
Prędocin, Radom dist.	PRE-1	1,260	98,35	0,025	194	0,128	0,097	130	117	621
Prędocin, Radom dist.	PRE-2	0,123	99,27	0,023	199	0,126	0,119	83	9	372
Prędocin, Radom dist.	PRE-3	0,000	99,77	0,012	0	0,043	0,06	48	1	217
Prędocin, Radom dist.	PRE-4	0,000	99,29	0,021	327	0,089	0,08	49	1	246
Prędocin, Radom dist.	PRE-6	0,000	99,54	0,015	0	0,03	0,038	23	2	134
Prędocin, Radom dist.	PRE-7	0,000	99,52	0,021	99	0,051	0,054	38	2	251
Prędocin, Radom dist.	PRE-8	0,000	99,50	0,021	0	0,058	0,048	37	3	143
Prędocin, Radom dist.	PRE-9	0,149	99,21	0	264	0,164	0,075	65	4	681
Prędocin, Radom dist.	PRE-10	0,000	99,38	0,018	0	0,03	0,049	31	1	197
JCh-1 measured (average of 9 analyses)		0,435	98,61	0,003	0	0,220	0,038	196	127	2754
S.D. (9 analyses)		0,139	0,27	0,001		0,006	0,004	10,52	5	36,6
CV% (9 analyses)		32,000	< 1	44,3		2,73	9,7	5,4	4	1,3
JCh-1 (recommended)		0,734	97,81	nr	14	0,221	0,045	189	134	2490

Recommended values for JCh-1 from Imai et al. (1996). nr = not reported. S.D. = standard deviation; CV% = coefficient of variation.
Detection limits for each element follow Hughes *et al.*, 2012: 781

Figure 2 plots the composition of Ca vs. Fe in the 'chocolate' flint geological specimens listed in Table 1. These aggregate data give a good overall picture of the Ca/Fe variability within the deposits, but there is a hint that finer scale discrimination might be possible. Note, in particular, the cluster of Fe values at around 300 ppm, separated by around 300 ppm from others of higher Fe composition (see Fig. 3 and 4). Significantly, the two samples with the lowest Fe composition from Wierzbica (labeled as tablica and Level 1 in Table 2) were freshly chipped from the modern quarry wall, while the others were undifferentiated by depth and selected from the Wierzbica 'Zele' archaeological mine. Taken together, these data suggest that we may be able to make finer chemical distinctions within some 'chocolate' flint deposits by separating the samples by geological strata (or at least on the basis of superposition in the deposits). This could be difficult to accomplish at some of the mines, but might be very possible at others (like Krzemionki Opatowskie flint mine, Ostrowiec Świętokrzyski district, see below).

Based on an admittedly small sample, we were not completely successful at discriminating between Jurassic-Cracow flint analyzed from Sąspów, Bębło (Kraków district), Jurassic

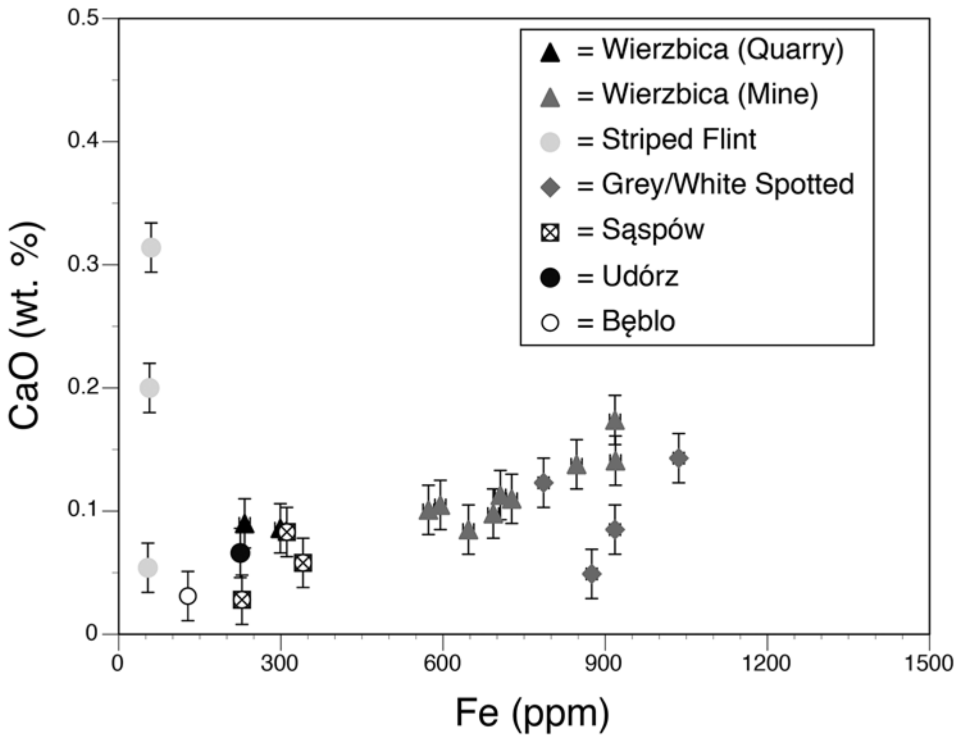

Fig. 3. The composition of Ca vs. Fe in geological samples of 'chocolate' flint compared with Gray-white spotted, Jurassic-Cracow and Striped Flint. Error bars delimit 95% probability estimates for elemental composition. Graphic design: R.E. Hughes.

flint from Udórz (Zawiercie district), and 'chocolate' flint, which several researchers (e.g., Krajcarz and Krajcarz 2009; Krajcarz *et al.*, 2012) have noted is very similar visually to 'chocolate' flint. With the exception of 'chocolate' flint from Tomaszów, Figure 3 does show, however, that overlap in Ca/Fe composition between Jurassic-Cracow and 'chocolate' flints occurs only in the lowest range of Fe compositions. Therefore, with a larger sample, we may be able to eliminate attributing visually similar brown flint artifacts to a Jurassic-Cracow flint 'source' if they contain Fe in concentration ≥ 600 ppm. This remains to be demonstrated, and will require additional analysis to confirm or refute.

Although it wasn't the specific focus of our project, we did collect and analyze flint from other localities for comparative purposes. One of the most dramatic chemical contrasts identified in these comparisons occurs with what has been referred to as Striped Flint, which is best known from occurrences at Krzemionki Opatowskie and Borownia (Ostrowiec Świętokrzyski district; see Fig. 1). This variety of flint is relatively depleted in iron compared with the other flints examined, and it contains no measurable amount of potassium (K). As Fig. 3 shows, Ca/Fe data were not adequate to distinguish between

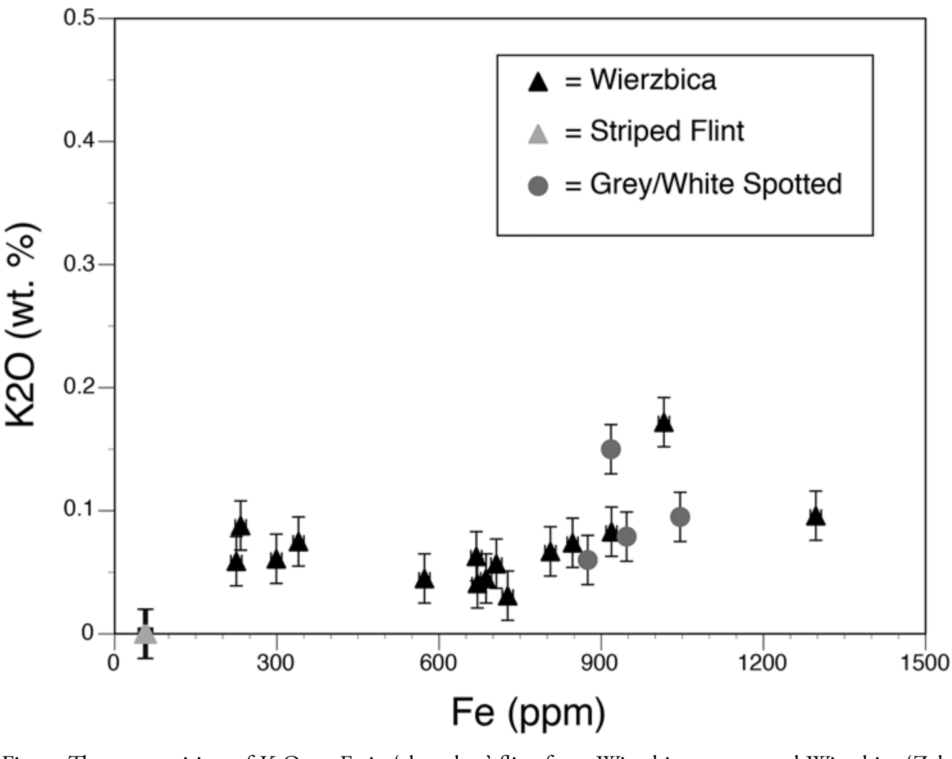

Fig. 4. The composition of K_2O vs. Fe in 'chocolate' flint from Wierzbica quarry and Wierzbica 'Zele' mine compared with geological samples of Gray-white spotted and Striped Flint. Error bars delimit 95% probability estimates for elemental composition. Graphic design: R.E. Hughes.

Gray-White spotted flint and 'chocolate' flint, but K vs. Fe data did effect a separation between them (see Fig. 4). We suspect that the reason for this is that the white spots in spotted flint contain large amounts of calcium, as do some varieties of Scandinavian flint. These spots (calcium-rich domains) are often so close together in gray-white spotted flint that it was rarely possible to direct the x-ray beam to a 'pure' surface, and the result was that these Ca-rich domains inflated the average concentration of Ca. This same inclusion problem exists, at more tractable scale, in flint from Krzemionki Opatowskie, but the Ca/Fe contrast with 'chocolate' flint makes it less of a problem.

More generally, as was the case in previous studies (Hughes *et al.*, 2011, 2012), the present work illustrates some of the advantages and disadvantages of non-destructive EDXRF for the characterization of flint. The advantages are that EDXRF is fast, relatively inexpensive, completely non-destructive, fully quantitative, and sensitive to a large number of elements that occur in flint and other rocks. The disadvantages are that it cannot measure minute concentrations of rare earth elements (like neutron activation [NAA] and inductively coupled plasma mass spectrometry [ICPMS] can) and it isn't as precise for certain elements as NAA and ICPMS. However, NAA and ICPMS are time-consuming, and they both require sacrificing some portion of the sample for analysis, which may not be problematic from a geological standpoint, but it certainly *is* a drawback when analyzing irreplaceable archaeological artifacts.

SUMMARY COMMENTS

As discussed above, one of the goals of the present project was to investigate the degree to which the visual and petrological classifications advanced by Schild (1976, 1987) corresponded with the geochemical data we generated here for a sample of 'chocolate' flint. Based on the major and minor elements we analyzed here, we were unable to distinguish between Schild's groups I and II flint. However, it may be possible to distinguish flints from Wierzbica 'Zele' mine. As discussed previously, we identified a distinction in Fe content between flint analyzed from the Wierzbica ('Zele') *mine* and the Wierzbica *quarry.* Microprobe and petrographic analysis (R. Siuda unpublished data) revealed a large number of small pyrite inclusions inside flint from the Wierzbica ('Zele') *mine*, while flint examined from the Wierzbica quarry contained very few pyrite inclusions. This fact helps explain the lower Fe content in the flint from the Wierzbica quarry and may assist in chemical and macroscopic identification. Based on these findings there may be a correspondence between Schild's (1976) group III flint and the Wierzbica ('Zele') *mine*.

In summary, the major and minor element data generate here were important in providing baseline information for the range of chemical composition within and among different 'chocolate' flint localities in the Świętokrzyskie (Holy Cross) Mountains of central Poland. In addition, based on the data presented here, Ca/Fe contrasts were identified between 'chocolate' flint and striped flint analyzed from Borownia and Wojciechówka (Opatów district; listed as Striped-Flint in Figs. 3 and 4), and K vs. Fe composition data documented a separation between Gray-White spotted flint (Świeciechów flint) and 'chocolate' flint (Fig. 4). Unfortunately based on a small sample of Jurassic-Cracow flint from Sąspów, Udórz, and Bębło we were not completely successful at discriminating between this flint and 'chocolate' flint. However a possible separation in Ca/Fe composition provides a starting point for future investigations (Fig. 3).

We are encouraged that *non-destructive* chemical signatures could be identified among different visual varieties of flint, and reckon that these contrasts should be of utility when applied to archaeological artifacts. Overall, the chemical profiles identified for 'chocolate' and some other flint in Poland flint provide a solid foundation for future research and for refinement of chemical signatures.

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