DETERMINING THE SUITABILITY OF PORTABLE-XRF FOR THE CHARACTERIZATION OF FLINT ARTIFACTS AND RAW MATERIALS FROM THE LOWER DANUBE BASIN

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Keywords: *flint, raw material, Eneolithic, portable XRF, Lower Danube Basin.*

Cuvinte cheie: *silex, materie primă, eneolitic, XRF portabil, bazinul Dunării de Jos.*

Abstract: *This article provides a preliminary evaluation of the suitability of portable X-ray fluorescence (pXRF) for determining the chemical composition of flint artifacts and geological samples from the Lower Danube Basin. The artifacts analyzed in this study originate from Eneolithic settlements from southern Romania and northeastern Bulgaria. Geological samples of flint were collected from primary and secondary deposits from northern Bulgaria, in the Ludgorie region and Nikopol region, and from the northern bank of the Danube, near Ciuperceni - Teleorman county. This study determines that materials from the Ludgorie and Nikopol regions can be distinguished from one another based on their concentrations of strontium (Sr) and zirconium (Zr). However, Nikopol and Ciuperceni could not be distinguished from one another based on the elements analyzed in this study.*

Rezumat: *Acest articol oferă o evaluare preliminară a caracterului adecvat al spectometrului portabil prin fluorescență de raze X (pXRF) pentru determinarea compoziției chimice a artefactelor litice și a probelor geologice din bazinul inferior al Dunării. Artefactele analizate în acest studiu provin din așezări eneolitice din sudul României și din nord-estul Bulgariei. Eșantioane geologice provin din depozite primare și secundare din nordul Bulgariei, din regiunea Ludgorie și din zona orașului Nikopol și de pe malul nordic al Dunării, zona din vecinătatea localității Ciuperceni (județul Teleorman). Acest studiu indică faptul că silicolitele din regiunile Ludgorie și Nikopol pot fi distinse între ele pe baza concentrațiilor lor de stronțiu (Sr) și zirconiu (Zr). Probele provenite din depozitele geologice de la Nikopol și Ciuperceni nu au putut fi deosebite între ele pe baza elementelor analizate în acest studiu.*

Introduction.

The objective of this paper is to provide an initial evaluation of the suitability of portable X-ray fluorescence (pXRF) for the analysis of flint artifacts and raw materials from the Lower Danube Basin, in southern Romania, and northern Bulgaria.

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Materials from this region are commonly known as Balkan flint. These high quality raw materials were widely used during the Neolithic and Eneolithic periods. However, due to their widespread use, archaeologists have dubbed this as the "Balkan flint problem", given the difficulty of determining the provenance of artifacts made of these materials. An important role in this issue and in the identification of possible geological sources from Bulgaria have Maria Gurova and Chavdar Nachev[1].

Some previous research concerning the "Balkan flint problem" has sought to resolve this issue by using benchmark geochemical methods of analysis[2]. Although, methods such as laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS), electron probe micro analysis (EPMA), and thin-sectioning are semi-destructive, if not wholly destructive to individual specimens and artifacts. Furthermore, these techniques are not portable, require considerable time for sample preparation, and are generally more expensive. Therefore, this study aims to contribute to the characterization and provenance of Balkan flints via pXRF, a non-destructive, cost-effective, and rapid method of geochemical analysis.

The lithic artifacts we analyzed in this study date to the Eneolithic period (c. 5000-3800 BC), and were derived from several archaeological sites: Vitănești *Măgurice* located in Teleorman county, Romania, Goljamo Delčevo located in Varna region, Bulgaria, and Stanovets located in the Shumen region, Bulgaria. The artifacts from the Vitănești *Măgurice* site were collected from the Gumelniţa B1 layer[3]. The artifacts from Goljamo Delčevo were collected from the Karanovo VI layer[4]. The analyzed material from the Stanovets site is associated with the Karanovo V cultural layer. Additional lithic artifacts used in this study were collected from several prehistoric flint-knapping sites in the Ludgorie region. These materials were collected from surface lithic scatters found at the Ravno, Ceakmaka, and Ciukata sources.

Lithic provenance is based on the idea that an artifact and its geological source of origin will have a similar, if not identical, geochemical composition. In order to determine the geological provenance of the artifacts analyzed in this study, reference samples were collected from flint deposits in the Ludgorie and Nikopol regions, as well as from the Ciuperceni deposit foundin Romania (Fig. 1). The samples used in this study to represent the Ludgorie region are derived from the Tetovo, Kriva-Reka, Ravno, Ceakmaka and Ciukata deposits. Due to logistical restrictions, geological samples were only collected from just one primary source deposit in the Nikopol region. Samples representing the three different macroscopic types were collected and analyzed from Ciuperceni area.

Tetovo is a primary deposit of siliceous rock that occurs in Aptian (Lower Cretaceous) age limestones (Fig. 2). The deposits from Kriva-Reka, Ravno (Ravno a and b - two different macroscopic types), Ceakmaka and Ciukata (Ciukata a, b - two different macroscopic types) are secondary alluvial-proluvial deposits found in

[1] Gurova *et alii* 2016; Andreeva *et alii* 2014; Gurova 2009; Gurova 2008; Nachev 2009a; Nachev 2009b; Gurova, Nachev 2008; Nachev, Nachev 1988.
[2] Gurova *et alii* 2016; Bonsal *et alii* 2010; Andreeva *et alii* 2014.
[3]For chronology see Andreescu *et alii* 2003.
[4]For the Goljamo Delčevo tell cronology see Todorova *et alii* 1975.

carbonate sands[5]. At Nikopol, siliceous inclusions are found in Upper Cretaceous (Campanian) chalks (Fig. 3). The siliceous rocks from Ciuperceni (Ciuperceni a, b, c - three macroscopically different types) (Fig. 7) are found in secondary alluvial deposits.

Flint from the Tetovo, Kriva-Reka, Ceakmaka, Ciukata and Ravno deposits typically range in colour from brown, to beige yellow. Their cortex also varies in thickness from approximately 5 mm to 15 mm (Fig. 4, 5). Macroscopic assessments of these source materials are insufficient to accurately attribute artifacts to individual groups given the degree of visual variability within these geological deposits. This degree of variation is consistent with the majority of the flint raw materials located in the northern and northeastern regions of Bulgaria. As a result, geochemical analyses are needed to reliably determine the provenance of individual artifacts in this region.

Flint raw materials from Nikopol generally have irregular shapes and range in size from approximately 15 cm to 40 cm. The cortex surrounding these materials can be extremely thin, and is typically a light brownish-gray colour of the flint (Fig. 6). Ciuperceni is located approximately 3 km to the northeast from Nikopol, north of the Danube. The shape of individual cobbles found at Ciuperceni is typically irregular with a thin cortex, and the flint is light gray in colour (Fig. 7). Interestingly, the Ciuperceni A type (Fig.7a) has macroscopic characteristics very similar to those at Nikopol[6]. This makes these two sources difficult to differentiate from one another without microscopic or geochemical analyses.

Methods

A Bruker AXS Tracer III-SD X-ray fluorescence spectrometer was used for all pXRF analyses in this study. All pXRF analyses were completed at the Department of Anthropology, University of Alberta, in Edmonton. An effort was made to analyze geological samples on freshly fractured surfaces, with little-to-no cortex, and on areas possessing the flattest surface. This was an attempt to reduce the potential impacts of chemical weathering as well as X-ray scattering due to uneven, or irregular surfaces, on individual specimens.

In the past decade, pXRF has been widely used for obsidian provenance. Under certain conditions, pXRF can be comparable to a variety of benchmark geochemical techniques such as instrumental neutron activation analysis (INAA), and inductively coupled plasma mass spectrometry (ICP-MS)[7]. Furthermore, pXRF has been used to determine the provenance of non-volcanic artifacts and materials[8]. However, the suitability of pXRF for the analysis of flint artifacts needs to be evaluated individually given the possibility of broad intra-source variability within a given source deposit.

The Bruker AXS Tracer III-SD is equipped with a rhodium (Rh) X-ray tube and a silicon drift detector (SDD) with a measured resolution of 148 eV FWHM for 5.9 keV

[5] Nacev 2009.
[6] Hila 2015, p. 71.
[7] Lynch *et alii* 2016; Frahm 2013; Frahm, Doonan 2013; Phillips, Speakman 2009; Craig *et alii* 2007; Millhauser *et alii* 2011; Shackley 2012; Shepard *et alii* 2010; Liritzis, Zacharias 2011; Tykot 2010; Tykot 2016.
[8] Kristensen *et alii* 2016; Seosaimhín 2014; Conrey *et alii* 2014; Goodale *et alii* 2012; Hila 2015; Niță *et alii* 2015.

X-rays. Operating conditions were 40 kV and 30μA beam current, with filtration of the primary X-rays by apolymetallic filter (0.3047 mm Al, 0.0254 mm Ti,0.1523 mm Cu). Artifacts and geological samples were analyzed for 180 seconds, and when possible, on three distinct locations to account for intra-sample variability. The results for each sample is the average of the three analyses.

Nine elements were quantified: Mn, Fe, Zn, Ga, Rb, Sr, Y, Zr, and Nb. These elements were measured using their Ka X-ray emissions. Intensities were calculated as ratios to the Rh Compton peak and converted to parts per-million (ppm) using the Bruker AXS proprietary obsidian calibration. This calibration has been proven to be effective for the characterization of non-volcanic lithic materials and artifacts[9]. Reference samples from the National Institute of Standards and Technology (NIST) were used to evaluate the instrument's precision and accuracy over the course of the analyses. These standards are NIST 278 –obsidian, and NIST 2710a - Montana soil. All ppm results have been rounded to the nearest whole number where possible (Tables 1 and 2).

Results

The results of the analyses of the NIST reference standards display generally good agreement with the recommended values for the trace element Rb, Sr and Zr (Tables 3 and 4). However, the results for Mn and Fe show generally poor agreement (≥ 10% relative percent difference [RPD]). This discrepancy is attributed to the matrix effect of analyzing powered samples opposed to solid, ground and polished, morphologically flat samples[10]. As a higher RPD is noted for Mn and Fe in NIST 278 when compared to NIST 2710a, the pXRF device used for this study is still considered to have a reasonable level of precision and accuracy for these elements based on the agreement of the results for NIST 2710a with the recommended NIST values. It is possible that the NIST 278 sample lost some of its volume or compaction during its use which increased the matrix effects within this sample. Regardless, these results demonstrate the importance of continually monitoring a device's precision and accuracy by comparing results to the recommended values of well characterized reference standards.

Given the observed overlap in concentrations of major elements between the multiple geological deposits examined, trace elements Rb, Y, Sr and Zr are determined to be the most suitable to distinguish individual deposits and artifacts. In particular, Sr and Zr are found to be the most effective in providing separation between the analyzed materials.

To interpret the results of the pXRF we used the GAUSS MURAP program developed at the University of Missouri Research Reactor facility. For this study 2D bivariate plot diagrams proved useful in providing visual representations of the data, as well as for assessing the overall chemical similarity of individual deposits. The ellipses are calculated and set at a constant Mahalanobis distance by the group's centroid. In this

[9] Kristensen *et alii* 2016; Speakman *et alii* 2011.
[10] Lynch *et alii* 2016.

study all ellipses are drawn at a 95% confidence interval which accounts for two standard deviations.

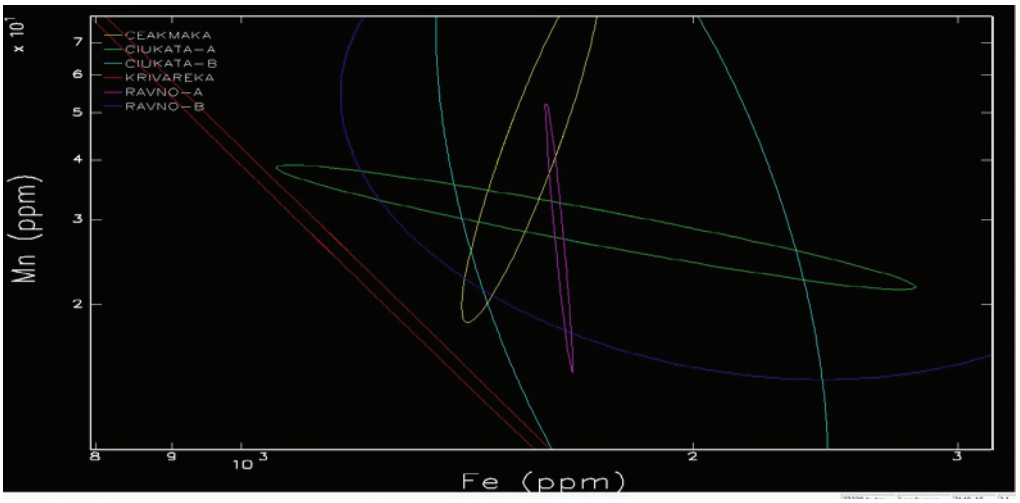

Figure 8. Bivariate plot of the samples from the Ludgorie region using Fe and Mn.

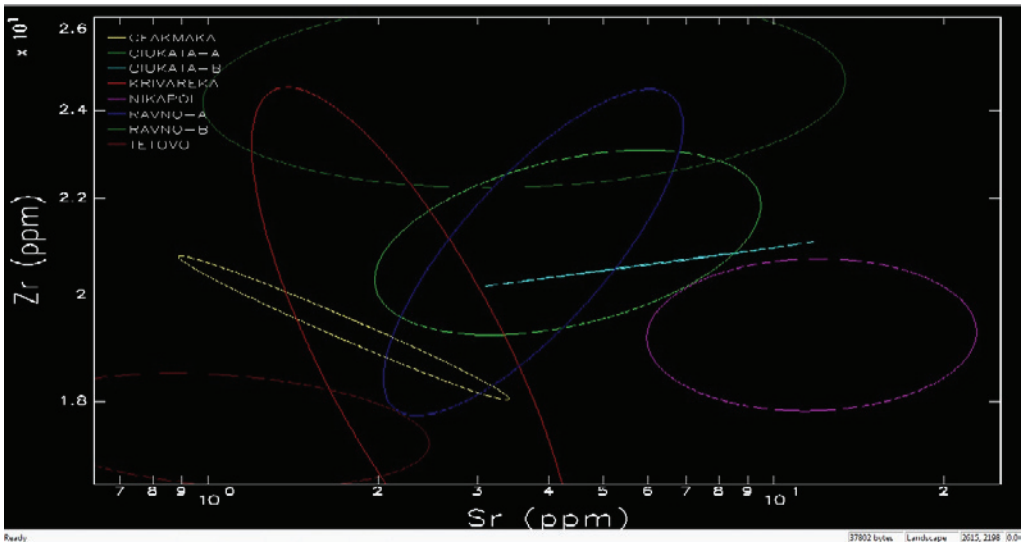

Figure 9. Bivariate plot of the samples from the Ludgorie region and Nikopol using Sr and Zr.

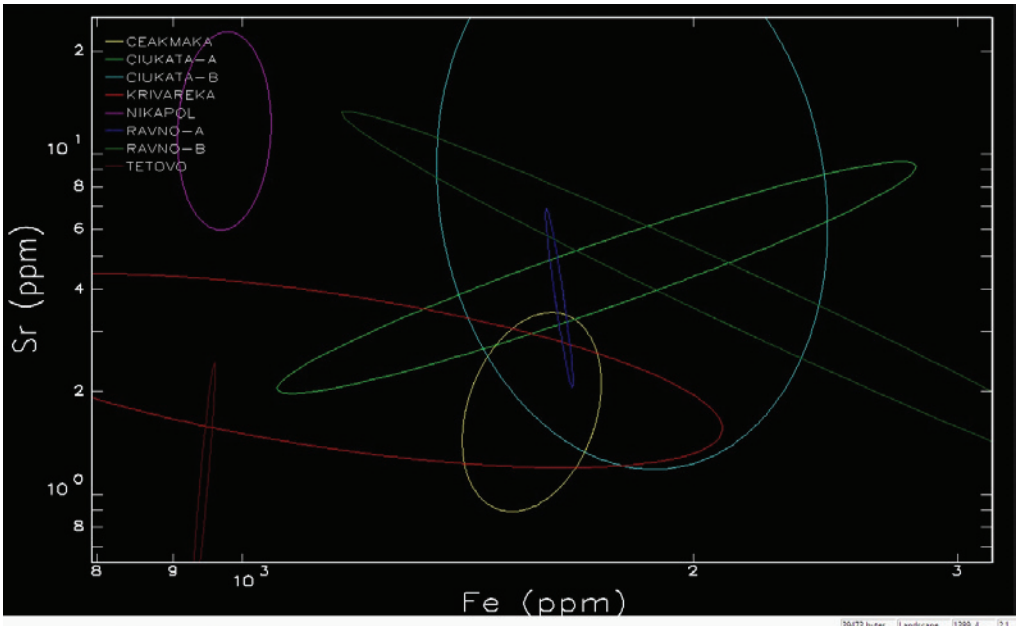

Figure 10. Bivariate plot of the samples from the Ludgorie region and Nikopol using Fe and Sr.

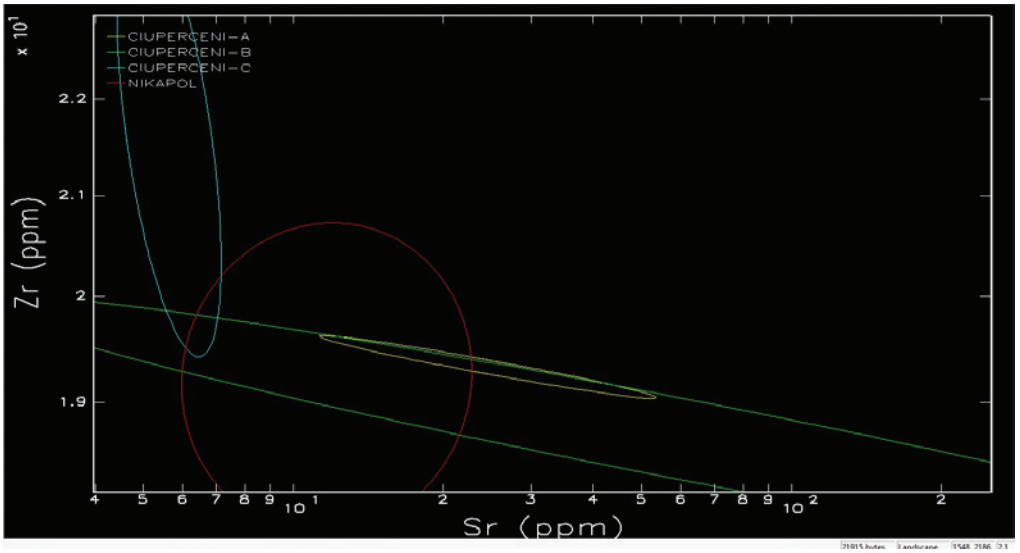

Figure 11. Bivariate plot of the samples from the Nikopol and Ciuperceni using Sr and Zr.

Based on the elements quantified in this study, it is not possible to differentiate the individual sources from the Ludgorie region given their overlapping concentrations. The concentrations of Mn and Fe show potential for separating the northern and central sources of the Ludgorie region from the southern portion of the region; that is the Ravno, Ceakmaka and Ciukata deposits from the Kriva-Reka (Fig.8). However, these results may only be limited to the samples analyzed in this study, and may be the result of the irregular Mn and Fe results seen in the analyses of the reference standards. Future analyses should determine if a clear chemical distinction can be made between deposits in the northern and southern of portions of the Ludgorie region, and, if the concentrations of Fe and Mn are related to distinct geological groups.

Based on our results we can distinguish samples from the Ludgorie region and those from Nikopol and Ciuperceni. This was achieved through a comparison of the concentrations of Sr and Zr (Fig.9 -10). However, the Nikopol and Ciuperceni materials could not be entirely distinguished from one another as these sources display similar concentrations of Sr (Fig. 11). This is particularly interesting given that that the Ciuperceni deposits are located approximately 3 km north of Nikopol.

Distinguishing Artifact Groups

To aid in the identification of individual groups among the analyzed artifacts we used hierarchical cluster analysis and bivariate plots. For the artifacts from Goljamo Delčevo (Fig. 12), three chemically distinct groups are observed. However, four distinct groups of flint were identified according to the macroscopic characteristics of these artifacts[11].

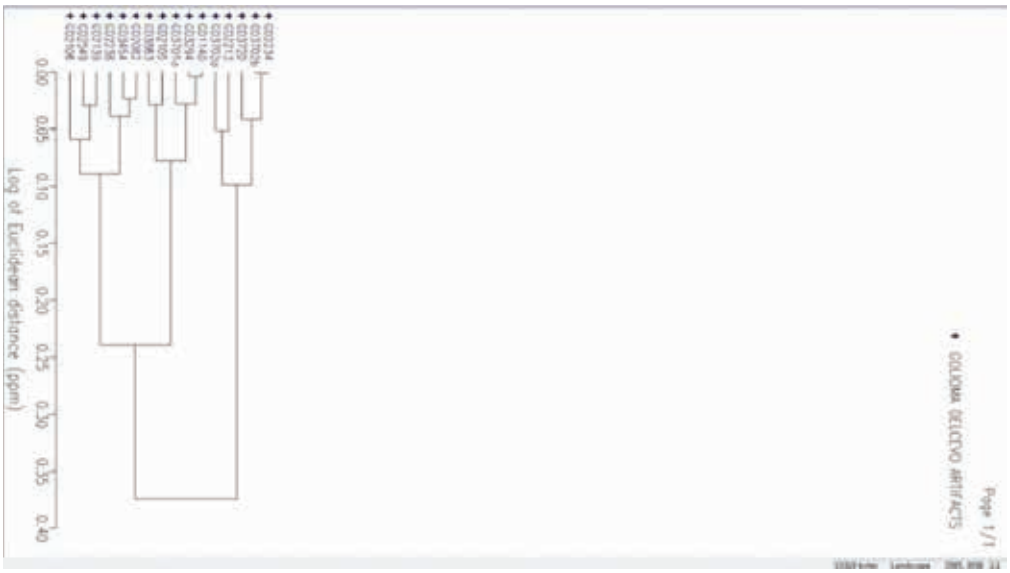

Figure 12. Cluster analysis applied to the Goljamo Delčevo artifacts.

[11]Todorova *et alii* 1975.

At least four groups have been identified for the artifacts from Vitănești. One distinct group is represented by a single artifact which in our opinion indicates the use of raw materials derived from an alluvial deposit (Figure 13).

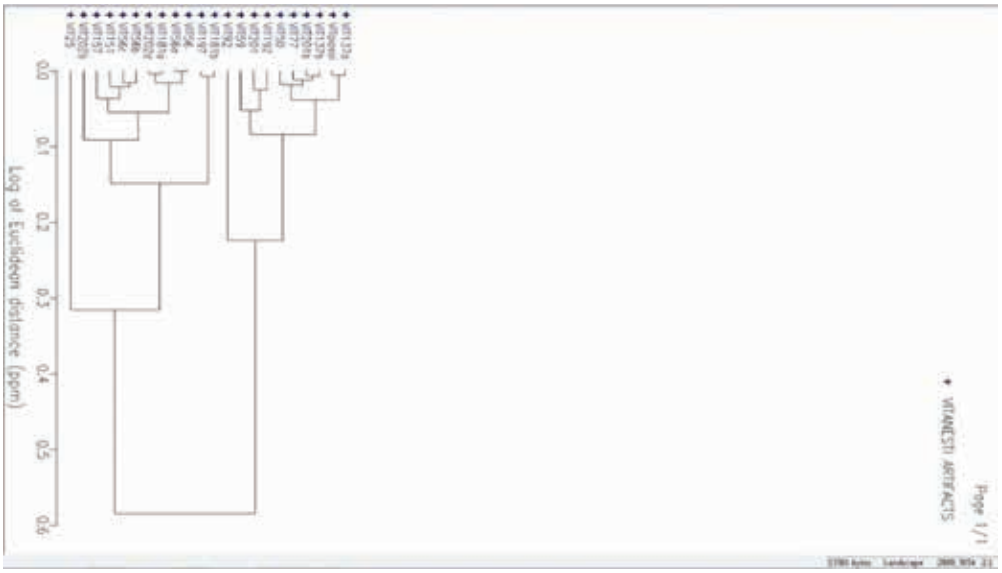

Figure 13. Cluster analysis applied to the Vitănești artifacts.

Correlation Between Outcrops and Artifacts

Two of the three groups identified from the Goljamo Delčevo artifacts (Fig. 12) are attributed to the Ludgorie region and Nikopol. The third group (represented by black pieces) could not be attributed to either group (Fig. 14). The Goljamo Delčevo artifacts have relatively high iron concentrations, and potentially come from the northern outcrops in the Ludgorie region (i.e., Ciukata, Ravno and Ceakmaka) found approximately100 km to the west from the site.

The artifacts from Vitănești are potentially derived from at least four sources (Fig. 13). Three of the groups are defined as Nikopol, Ciuperceni, and the Ludgorie region. The remaining artifacts group with an undetermined source. The artifacts attributed to the Ludgorie region group are observed to have relatively low Fe concentrations when compared to the other materials. Therefore, we suspect these artifacts are derived from the southern portion of the Ludgorie region, located approximately 230 km to the southeast of Vitănești. However, it is also possible that some artifacts are derived from alluvial deposits found in the Ciuperceni area located approximately 30 km to the southwest of the site. Specifically, artifact VIT 92 has visual characteristics similar to the Ciuperceni material (i.e., black colour), and is found to group with the values determined for this source. (Fig. 15).

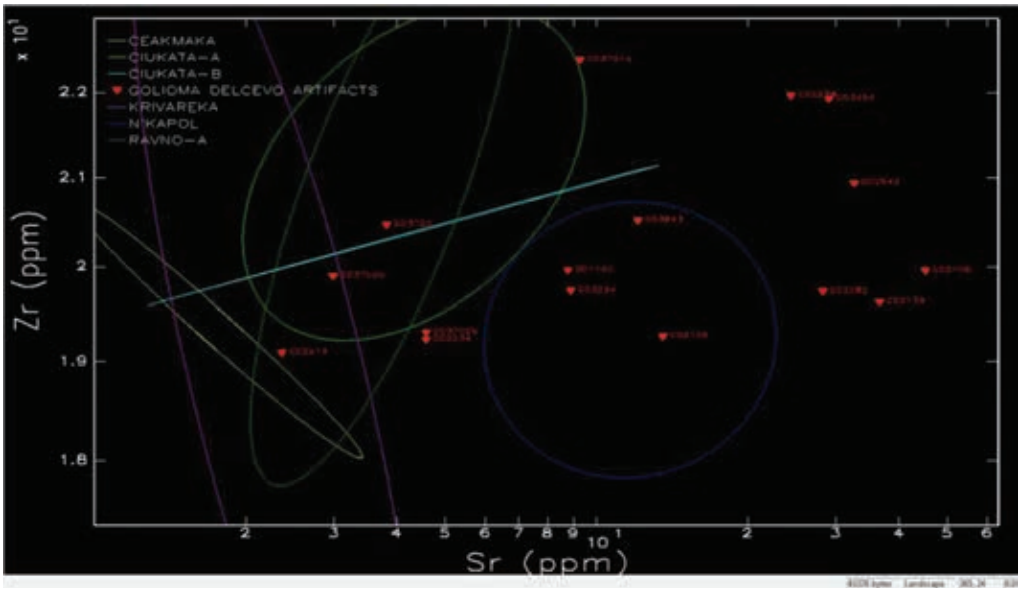

Figure 14. Comparison of the Goljamo Delcevo artifacts with the analyzed sources.

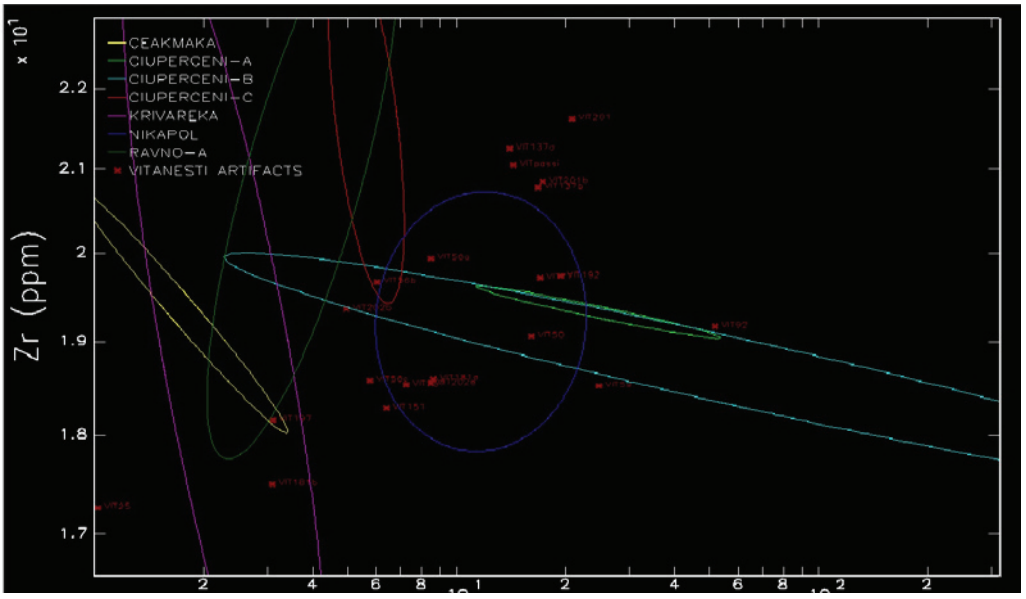

Figure 15. Comparison of the Vitănești artifacts with the analyzed sources.

The analyses of the artifacts collected from lithic processing sites at Ravno and Ciukata are presented in Figures 16 and 17. It is suspected that the artifacts collected from these sites are derived from the sources found in their immediate vicinity. However, as we could not distinguish the sources found in the Ludgoire region based

on the elements we examined, further analyses are needed to accurately determine if in fact these artifacts are derived entirely from these respective sources.

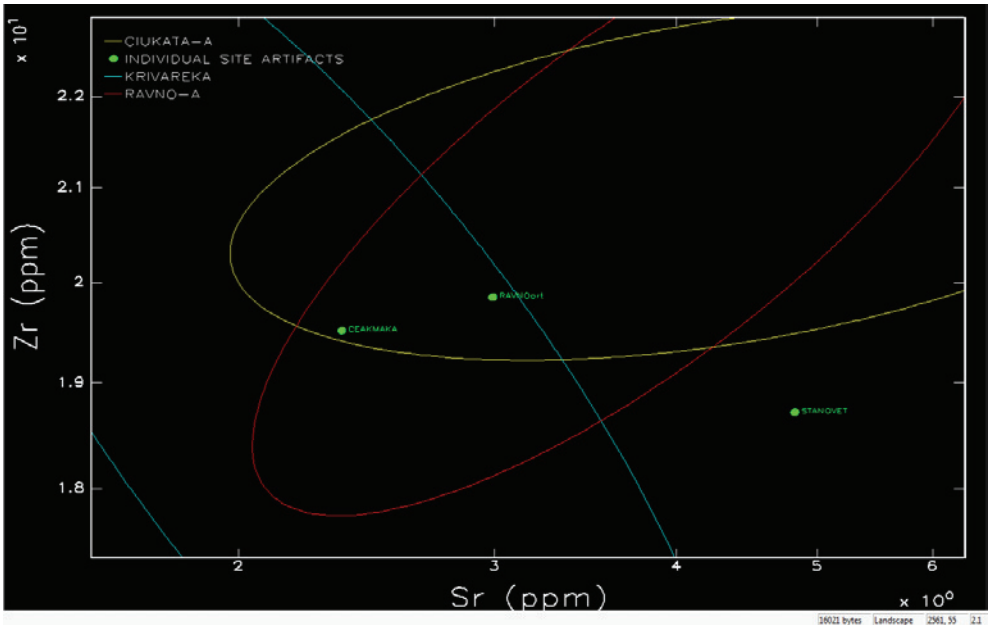

Figure 16. Comparison of the Ceakmaka, Ravno and Stanoveț artifacts with sources.

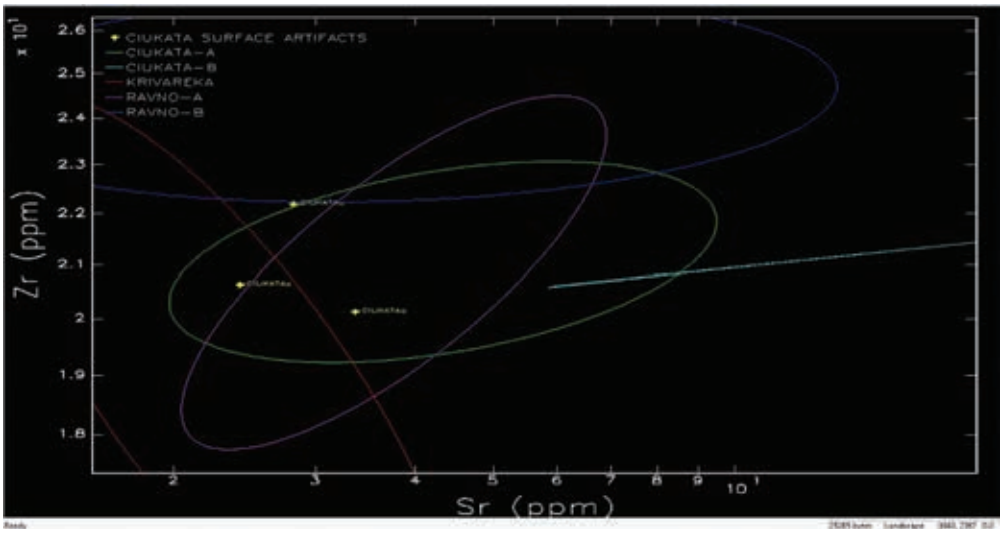

Figure 17. Comparison of the Ciukata artifacts with the sources.

Discussion

The Ciuperceni raw material is seen to have concentrations of Sr and Zr that are similar to those determined for Nikopol. However, the materials analyzed from Ciuperceni b have much higher concentrations of Sr when compared to Nikopol or the other Ciuperceni materials. Concentrations of Fe were slightly lower in the materials from Nikopol. Concentrations of Fe may provide a starting point to differentiate the materials from Ciuperceni and Nikopol. Future studies carried out on a larger group of samples may confirm this possibility. Additionally, the higher Sr levels in the analyzed samples from Nikopol and Ciuperceni may be tied to the proportions of calcium in each specimen. Therefore, special attention during the analyses was paid to avoid the inclusion of cortex within the analyzed regions of each specimen. Additionally, the potential effects of surface weathering on the analyzed specimens was considered during the analysis of all artifacts[12]. Future analyses of Balkan flints should evaluate the possible influence of deposition and weathering on the surface composition of individual specimens.

In the Ludgoire region, the materials from Tetovo, Kriva-Reka, Ravno, Ceakmaka and Ciukata are shown to overlap when the elements examined in this study are compared. As a result, we could not distinguish these sources. However, the variability observed between Mn and Fe may indicate a possible distinction between the northern outcrops of Tetovo, Ravno, Ceakmaka and Ciukata, from the Kriva-Reka deposit found in the south of the region. With a wider range of samples in this area it will be possible to determine whether such differentiation can be made. A previous study has shown that differentiating these deposits is possible by comparing elements Al, K, Na and Mg[13].

The analyses of artifacts from Goljamo Delčevo suggest that at least three sources of raw material were used by prehistoric people at these sites. Two of the groups correlate with the geological samples analyzed from the Ludgorie region and Nikopol. The results from Vitănești suggest at least four raw material groups are represented. Additionally, one artifact from this site was found to have the morphological characteristics similar to Ciuperceni alluvial deposit materials. Whereas, other groups of artifacts are attributed to the Ludgorie region located approximately 230 km to the southeast from the site, and the Nikopol region located approximately 40 km to the southwest, south of the Danube. The artifacts from the Stanoveț and the materials from the flint-knapping sites at the Ravno, Ceakmaka, and Ciukata sources, are attributed to the Ludgorie region.

Based on the analyzed assemblages from Goljamo Delčevo and Vitănești it appears that no preference was given to local or distant sources. This indicates the existence of exchange networks and procurement strategies whereby raw materials from local and distant sources were broadly distributed throughout the Balkans during prehistory. However, further research is needed to determine the source locations for the unidentified materials analyzed from Vitănești and Goljamo Delčevo.

[12] Gauthier, Burke 2011; Högberg *et alii* 2012; Gauthier *et alii* 2012.
[13] Andreeva *et alii* 2014.

Conclusion

Sedimentary lithic materials including flint can be difficult to source as the geological formation of these materials can result in extremely variable compositions even within well-defined localities[14]. Established methods of geochemical analysis such as INAA, EPMA, ICP-MS and higher powered XRF devices, have been demonstrated to produce accurate, reliable and reproducible characterizations of flint materials and artifacts. This study demonstrates the potential of pXRF to provide rapid characterization of flint artifacts from the Lower Danube Basin. Regardless of the technique, the ability to determine the provenance of individual artifacts is dependent on the thorough characterization of individual deposits through the analysis of many representative samples, the degree of variability within a deposit, as well as the elements quantified and detected by a given technique. Given the overlap in element concentrations between the deposits found in the Ludgorie region, only the distinction between the Nikopol and Ciuperceni deposits, and the sources found in the Ludgorie region could be made at this time through pXRF. The results of the Ciuperceni b type show higher Sr concentrations when compared to the results form Nikopol. However, the other types from Ciuperceni could not be completely distinguished from the Nikopol materials.

Statistical analyses were used to interpret the results obtained by pXRF. These analyses include 2D bivariate plots with defined confidence ellipses, and Euclidian distance analysis. The GAUSSRUN software developed at the University of Missouri is a straightforward program for completing these statistical analyses and producing visualizations of results. This is due to the variety of statistical analyses available in the software, its simplicity, and given the fact it is free of charge. Additionally, the 2D and 3D graphics produced by this software are easy to interpret.

We believe that differentiating raw materials from Nikopol and Ciuperceni, and those from the northeastern part of Bulgaria found in the Ludgorie region is possible through the comparison of trace elements Rb, Y, Sr and Zr. Elements such as Al, Na, K, B[15] and La, B and Ba have been demonstrated to be useful for the characterization and differentiation of Nikopol materials[16]. However, these elements were not examined or quantified in this study. The development of a material specific calibration for pXRF for Balkan flints will permit the examination of additional elements, and potentially aid in the further differentiation of individual deposits and the attribution of artifacts to discrete source locations. Overall this study demonstrated the potential of pXRF to advancing the study of Balkan flints while providing quantifiable results suitable for comparison with other methods of geochemical analysis.

Acknowledgements

We are very grateful to Prof. Dr. Andrzej Weber (University of Alberta) and to the Canada Foundation of Innovation for the funding and use of the pXRF equipment

[14] Luedtke 1992.
[15] Gurova *et alii* 2016.
[16] Bonsall *et alii* 2010.

for this project. We also thank Prof. Dr. Lucian Matei (Bucharest University) for geological guidance. For the field guidance research in northern Bulgaria, we thank Prof. Dr. Stefan Chohadzhiev and Associate Prof. Dr. Rossina Kostova (St. Cyril and St. Methodius University of Veliko Tarnovo) and Dr. Chavdar Nachev (Museum of Earth and Man, Sofia). Thanks to Boryana Mateeva (Isperich History Museum), Dr. Radian-Romulus Andreescu (National History Museum of Romania), Ion Torcică (Teleorman County Museum), Dr. Vladimir Slavchev (Varna Museum of Archeology) for the access to the lithic artifacts used in this study.

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Sample Name	Deposit Name	Deposit type
CIUKATA a	Ciukata	Secondary geological deposit (deluviale-proluviale)
CIUKATA b	Ciukata	Secondary geological deposit (deluviale-proluviale)
RAVNO a	Ravno	Secondary Geological deposit (deluviale-proluviale)
RAVNO b	Ravno	Secondary geological deposit (deluviale-proluviale)
CEAKMAKA	Ceakmaka	Secondary geological deposit (deluviale-proluviale)
TETOVO	Tetovo	Primary geological deposit (in Lower Cretaceous-Aptian- limestones)
NIKOPOL	Nikopol	Primary geological deposit (in Upper Cretaceous –Campanian- chalk)
CIUPERCENI a	Ciuperceni	Secondary Geological deposit
CIUPERCENI b	Ciuperceni	Secondary geological deposit
CIUPERCENI c	Ciuperceni	Secondary geological deposit

Table 1. Geological Samples

Artifact	Site	Period
GD3863	Goljamo Delčevo	Eneolithic (Karanovo VI)
GD3720	Goljamo Delčevo	Eneolithic (Karanovo VI)
GD3702b	Goljamo Delčevo	Eneolithic (Karanovo VI)
GD3702a	Goljamo Delčevo	Eneolithic (Karanovo VI)
GD3701a	Goljamo Delčevo	Eneolithic (Karanovo VI)
GD3454	Goljamo Delčevo	Eneolithic (Karanovo VI)
GD3294	Goljamo Delčevo	Eneolithic (Karanovo VI)
GD2549	Goljamo Delčevo	Eneolithic (Karanovo VI)
GD2238	Goljamo Delčevo	Eneolithic (Karanovo VI)
GD2234	Goljamo Delčevo	Eneolithic (Karanovo VI)
GD2213	Goljamo Delčevo	Eneolithic (Karanovo VI)
GD2139	Goljamo Delčevo	Eneolithic (Karanovo VI)
GD2106	Goljamo Delčevo	Eneolithic(Karanovo VI)
GD2105	Goljamo Delčevo	Eneolithic(Karanovo VI)
GD2082	Goljamo Delčevo	Eneolithic(Karanovo VI)
VIT92	Vitănești	Eneolithic (Gumelnița B1)
VIT59	Vitănești	Eneolithic (Gumelnița B1)
VIT56c	Vitănești	Eneolithic (Gumelnița B1)
VIT56b	Vitănești	Eneolithic (Gumelnița B1)
VIT56a	Vitănești	Eneolithic (Gumelnița B1)

VIT50	Vitănești	Eneolithic (Gumelnița B1)
VIT25	Vitănești	Eneolithic (Gumelnița B1)
VIT201	Vitănești	Eneolithic (Gumelnița B1)
VIT197	Vitănești	Eneolithic (Gumelnița B1)
VIT192	Vitănești	Eneolithic (Gumelnița B1)
VIT181b	Vitănești	Eneolithic (Gumelnița B1)
VIT181a	Vitănești	Eneolithic (Gumelnița B1)
VIT157	Vitănești	Eneolithic (Gumelnița B1)
VIT151	Vitănești	Eneolithic (Gumelnița B1)
VIT137a	Vitănești	Eneolithic (Gumelnița B1)
VIT137b	Vitănești	Eneolithic (Gumelnița B1)
VIT201b	Vitănești	Eneolithic (Gumelnița B1)
VIT202a	Vitănești	Eneolithic (Gumelnița B1)
VIT202b	Vitănești	Eneolithic (Gumelnița B1)
VIT56	Vitănești	Eneolithic (Gumelnița B1)
VIT77	Vitănești	Eneolithic (Gumelnița B1)
VITpassim	Vitănești	Eneolithic (Gumelnița B1)
STANOVETsit	Stanoveț	Eneolithic (Karanovo V)
CEAKMAKAsit	Ceakmaka	Eneolithic (Karanovo VI)
RAVNOart	Ravno	Eneolithic ?
CIUKATAart3	Ciukata	Eneolithic?
CIUKATAart2	Ciukata	Eneolithic?
CIUKATAart1	Ciukata	Eneolithic?

Table 2. Artifacts

NIST 278	Mn	Fe	Zn	Ga	Rb	Sr	Y	Zr	Nb
1	368	14039	59	15	128	61	41	284	16
2	300	14128	59	16	124	61	42	280	16
3	356	14010	59	15	125	61	40	273	17
4	391	13818	57	17	129	62	42	281	15
5	317	14024	53	18	127	60	40	282	17
6	316	14232	59	17	127	63	43	284	16
7	348	14057	61	15	132	63	41	282	17
8	259	14044	57	16	131	62	41	281	16
9	367	14312	63	17	128	63	39	282	16
10	370	13993	52	17	127	59	41	282	17
11	285	14210	61	17	132	60	41	283	16
12	296	14159	58	17	131	62	40	282	15
13	368	14055	51	16	126	60	44	284	15
14	339	13966	57	14	132	61	41	285	17

15	367	14260	62	17	129	58	43	284	16
Average	336	14087	58	16	129	61	41	282	16
Standard Deviation	38.6	129.8	3.4	1.0	2.6	1.4	1.3	2.7	0.6
Relative Standard Deviation	11.5	0.9	5.9	6.1	2.1	2.3	3.1	1.0	3.5
Relative Percent Difference	43%	37%	5%	NA	2%	4%	NA	3%	NA
Recommended value	520±20	20400±200	55±0	NA	127.5±0.3	63.5±0.1	NA	290±30	NA

Table 3. Results for NIST 278 (Obsidian) at a live count of 180 seconds. Results in parts per-millon (ppm).

NIST 2710a	Mn	Fe	Zn	Ga	Rb	Sr	Y	Zr	Nb
1	2264	48613	4412	N.D.	125	247	121	223	8
2	2298	48040	4350	n.r.	126	244	117	228	7
3	2341	47709	4371	n.r.	128	241	123	229	7
4	2282	47795	4363	n.r.	127	245	120	227	9
5	2253	47612	4345	n.r.	125	244	120	229	8
6	2241	48223	4394	n.r.	129	238	123	223	9
7	2314	47433	4255	n.r.	124	241	121	234	9
8	2234	47092	4330	n.r.	123	241	125	231	8
9	2411	47758	4407	n.r.	129	245	121	226	8
10	2280	48999	4489	n.r.	129	240	124	219	8
11	2320	47376	4252	n.r.	123	238	120	228	8
12	2274	48342	4426	n.r.	124	242	126	227	7
13	2266	48363	4463	n.r.	125	246	125	228	9
14	2229	47724	4363	n.r.	125	243	122	221	9
15	2228	48373	4383	n.r.	123	245	122	231	7
Average	2282	47963	4374	NA	126	243	122	227	8
Standard Deviation	49.5	516.8	65.2	NA	2.2	2.8	2.5	4.0	0.6
Relative Standard Deviation	2.2	1.1	1.5	NA	1.7	1.2	2.0	1.8	7.9
Relative Percent Difference	6%	10%	5%	NA	7%	5%	NA	13%	NA
Recommended value	2140±60	43200±800	4180±150	NA	117±3	255±7	NA	200±0	NA

Table 4. Results for NIST 2710a (Montana Soil) at a live count of 180 seconds. Results in parts per-millon (ppm)

SPECIMEN	Mn	Fe	Zn	Ga	Rb	Sr	Y	Zr	Nb
CIUKATA(1a)	25	2153	21	7	3	6	3	21	ND*
CIUKATA(2a)	29	1593	20	1	3	3	3	21	ND*
CIUKATA(3a)	32	1491	19	4	3	3	3	20	ND*
CIUKATA(1b)	23	2063	21	4	2	4	2	20	ND*
CIUKATA(2b)	13	1797	20	8	3	17	2	21	ND*
CIUKATA(3b)	58	1625	20	5	2	4	2	20	ND*
RAVNO(1a)	30	1618	19	6	3	4	2	20	ND*
RAVNO(2a)	33	1622	19	5	2	4	3	22	ND*
RAVNO(3a)	20	1643	19	5	2	2	2	19	ND*
RAVNO(1b)	75	1997	23	6	5	4	8	25	1
RAVNO(2b)	32	1796	22	5	5	5	5	23	ND*
RAVNO(3b)	36	2893	23	5	5	1	5	24	1
CEAKMAKA(1)	48	1613	25	6	3	1	2	19	ND*
CEAKMAKA(2)	55	1582	27	6	2	2	2	18	ND*
CEAKMAKA(3)	29	1487	30	6	2	1	2	19	ND*
TETOVO(1)	27	939	19	5	2	0	2	17	ND*
TETOVO(2)	46	950	19	5	2	1	2	17	ND*
TETOVO(3)	41	938	20	6	2	0	5	17	ND*
NIKOPOL (1)	50	986	23	4	2	13	2	19	ND*
NIKOPOL (2)	47	945	21	6	2	8	2	18	ND*
NIKOPOL (3)	0	954	18	5	2	15	2	19	ND*
NIKOPOL (4)	31	1005	17	3	2	10	2	19	1
CIUPERCENI(1a)	90	1125	20	4	2	29	2	19	ND*
CIUPERCENI (2a)	81	1048	19	7	2	29	2	19	ND*
CIUPERCENI (3a)	50	1092	18	5	2	17	2	19	ND*
CIUPERCENI(1b)	73	1048	21	4	4	173	2	18	ND*
CIUPERCENI (2b)	30	1188	20	6	3	145	2	18	ND*
CIUPECRCENI (3b)	60	1725	25	5	2	10	2	19	ND*
CIUPERCENI (4b)	35	1180	18	10	2	44	2	18	ND*
CIUPERCENI(1c)	23	1160	19	5	3	5	1	22	ND*
CIUPERCENI (2c)	45	1309	22	3	3	5	2	20	ND*
CIUPERCENI (3c)	24	1180	23	4	3	6	2	21	ND*

**not determined*

Table 5. Geological sample results in ppm

SPECIMEN	Mn	Fe	Zn	Ga	Rb	Sr	Y	Zr	Nb
VIT92	31	1012	20	5	2	51	2	19	ND*
VIT59	24	1844	22	8	2	24	1	18	ND*
VIT56c	39	1075	20	5	2	5	2	18	ND*
VIT56b	26	1215	19	5	2	6	2	19	ND*
VIT56a	ND	2926	24	6	3	8	2	19	1
VIT50	11	1168	20	6	2	16	2	19	ND*
VIT25	16	891	19	7	1	1	1	17	ND*
VIT201	11	1152	19	8	3	20	2	21	ND*
VIT197	29	1236	19	6	2	3	1	18	ND*
VIT192	20	1140	19	8	3	19	2	19	ND*
VIT181b	22	1241	22	7	1	3	1	17	ND*
VIT181a	17	1125	19	6	2	8	2	18	ND*
VIT157	27	1032	19	4	2	7	1	18	ND*
VIT151	11	3279	21	7	2	6	2	18	ND*
VIT137a	20	1208	23	6	3	14	2	21	ND*
VIT137b	22	1224	22	8	2	16	2	20	ND*
VIT201b	37	1168	22	7	3	17	2	20	ND*
VIT202a	31	1662	26	7	2	8	2	18	ND*
VIT202b	5	1492	20	9	2	4	2	19	ND*
VIT56	0	2926	24	6	3	8	2	19	1
VIT77	33	971	21	5	2	16	2	19	ND*
VITpassim	6	1462	28	11	3	14	2	21	ND*
GD3863	37	1632	22	4	2	12	2	20	ND*
GD3720	23	2542	25	5	3	3	2	20	ND*
GD3702b	18	1562	19	5	3	4	1	19	ND*
GD3702a	29	1615	22	4	2	2	2	19	ND*
GD3701a	7	2210	21	6	3	9	2	22	ND*
GD3454	41	1740	25	4	3	29	1	21	ND*
GD3294	32	1754	22	6	3	8	2	19	ND*
GD2549	22	1340	26	7	2	32	2	20	ND*
GD2238	46	1557	28	5	2	24	2	21	ND*
GD2234	11	1792	23	5	3	4	2	19	ND*
GD2213	36	1926	18	7	2	2	2	19	ND*
GD2139	37	1408	23	6	2	36	2	19	ND*
GD2106	24	1199	22	4	3	45	2	19	ND*
GD2105	55	1292	24	6	3	13	1	19	ND*
GD2082	48	1836	26	4	2	28	2	19	ND*
CIUKATAart3	33	2438	24	5	3	3	4	20	ND*
CIUKATAart2	51	1798	22	4	3	2	3	20	ND*
CIUKATAart1	35	1967	21	4	3	2	2	22	ND*
STANOVETsit	24	1135	22	5	2	4	2	18	ND*
CEAKMAKAsit	10	1550	22	7	3	2	8	19	1
RAVNOart	30	1660	23	3	3	2	3	19	ND*

**not determined*

Table 6. Artifact results in ppm

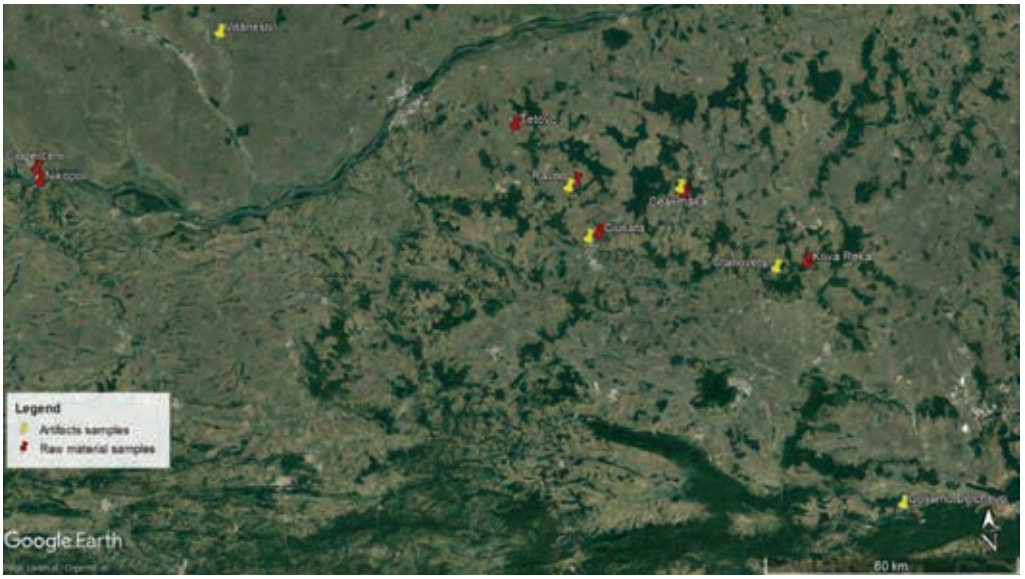


Figure 1. Approximate location of geological deposits and archaeological sites from where the samples were collected.

Figure 2. Siliceous inclusions in limestones, Tetovo.

a)

b)

Figure 3. At Nikopol, siliceous inclusions in chalks, Nikopol.

a)

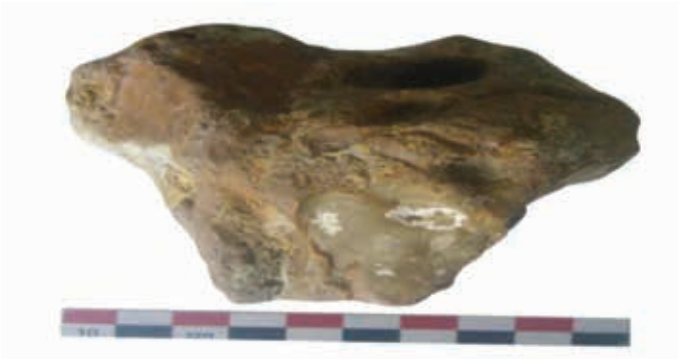
b)

c)

Figure 4. Flint from the Razgrad district deposits: a) Ceakmaka; b) Ciukata; c) Kriva Reka.

Figure 5. Flint from the Tetovo deposit.

Figure 6. Raw material, Nikopol.



a)

b)

c)

Figure 7. The siliceous rocks from Ciuperceni: a) type a; b) type b; c) type c.