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Original research paper

MINERALOGY OF A STONE TOOL FROM THE PALAEOLITHIC STATION UZUN MERA VILLAGE MUSTAFINO BY THE SEM-EDS TECHNIQUE

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Abstract

The paper presents the results obtained during the examinations of a stone tool from from the Uzun Mera site using the SEM-EDS methods. The data obtained indicate that the stone tool is made of quartzite originating from the locality Strmos (Probistip) and that, as a consequence of the interaction with the soils in which the stone tool is, fluorite is formed in the pores of the tool and Fe- oxides and Fe-hydroxides are also formed on the surface of the tool.

Key words: *quartz, fluorite, Fe - oxides, Fe- hydroxides.*

INTRODUCTION

Stone tools are made in the course of processing stone (part of a rock) and have different applications. There are papers in which they are classified as tools for hunting and fishing, tools for food production, tools for harvesting, tools for home use, tools for decoration and other needs [1]. A large number of works that deal with stone tools from the Paleolithic, the Neolithic up to the Bronze Age have been published [2, 3, 4]. In certain research articles, special attention is directed towards the study of tools in the Neolithic, because from the appearance of the tools a lot can be deduced about the life of people at that time as well as about the level of technological development and stone processing techniques [5]. Most of the examinations of stone tools present results about their composition which is basically: quartzite, obsidian, quartz [6, 7, 8]. The researchers of stone tools from the Paleolithic and Neolithic also publish results that refer to the origin of the stone from which the stone tools were made, and, based on that data, conclusions are drawn about the connections that existed between people at that time [9, 10, 11, 12].

MATERIAL AND METHODS

Information about the palaeolitic station Uzun Mera

The Uzun Mera site is located between the villages Erdzelija and Mustafino on both sides of the road connecting these two villages. Artefacts form Middle Palaeolithic are spread over an area of about 1 km^2 on the elevated terrace on the left bank of the river Nemashnica (Figure 1). Using probes and systematic archaeological investigations at the site have revealed that, in addition to those found on the surface, Palaeolithic artefacts from carved stone are also found in geological layers up to a depth of 0.6 m. The stratigraphy of the terrain was determined, and, despite slight differences between the probes, we conclude that there is a correlation between the layers and the Palaeolithic artefacts throughout the territory of the site probably belonging to a common geological and / or anthropogenic process.

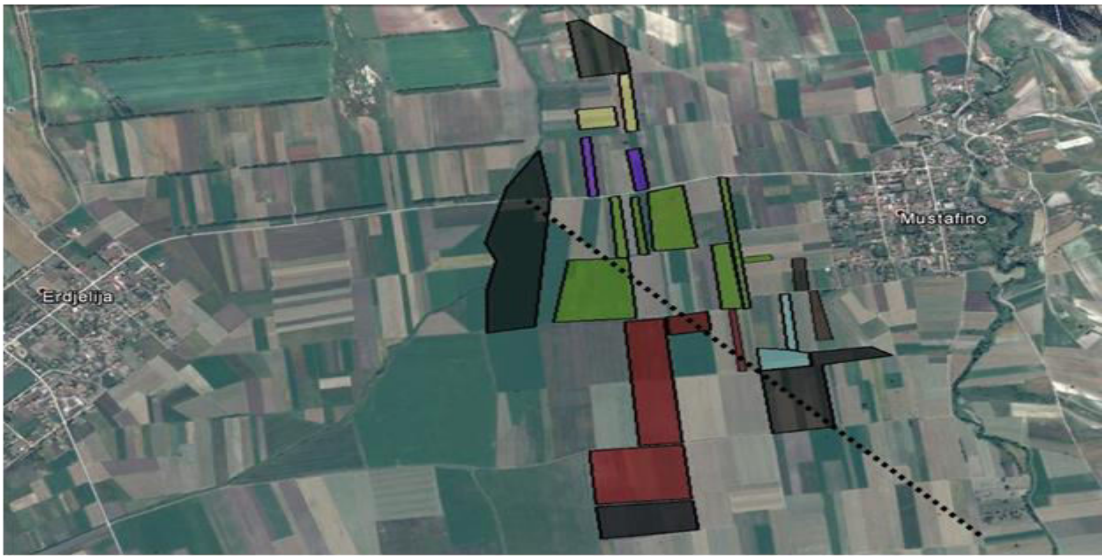

Figure 1. Uzun Mera archaeological Site, where carved stone tools are found; the five recognition zones are marked in different colors (green - zone 1, red - zone 2, blue zone 3, yellow - zone 4, light blue - zone 5); black represents the zones where no stone artefacts or site boundaries were detected; the dotted line represents the northeast boundary of the territory intended for construction of the airport

The purpose of this year's research was to provide detailed documentation on the density and distribution of artefacts in a smaller area. The research focused on a 6 m^2 (2x3m) probe, which was named probe 4 due to continuity last year. This probe is located half a meter south of probe 3. For more detailed documentation, the probe was divided into 6 squares, each of which is an individual research unit. 5 cm excavations were made, and the findings were documented based on each excavation and for each square separately.

Stratigraphy (Figure. 2) of the site based on research conducted so far:

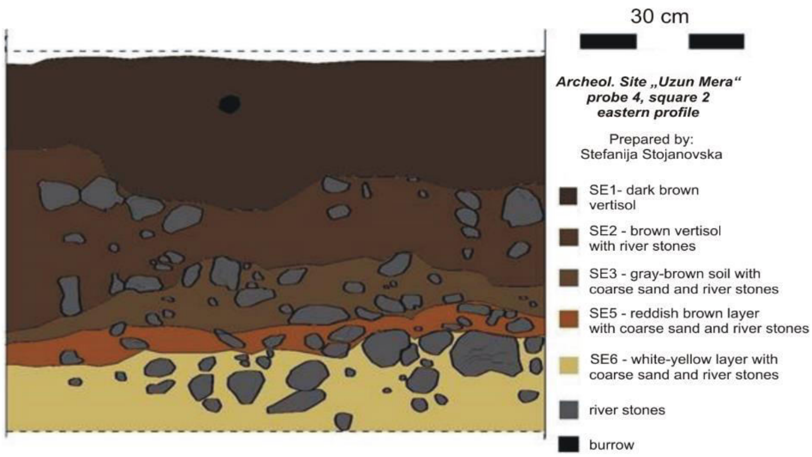

Figure 2. Stratigraphic section of location

The top layer 1 (SE 1), up to a depth of about 30 cm, is a dark brown vertisol in which, due to intensive agricultural processing, no rocks are found, except for artefacts of carved stone and finer fragments of the raw material that were broken by agricultural machinery during the processing of the surface.

Layer 2 (SE 2) represents the same matrix of dark brown vertisol, but in it a high concentration of river rocks of different dimensions and different geological origin can be noticed. Among the unprocessed stones, as in layer 1, traces are found, tools and cores - products of the Neanderthal of the Middle Palaeolithic. It should be noted that some of the river rocks were found completely cracked, most probably as a result of exposure to extreme temperature changes. This layer of river rocks continues to a depth of 0.8 m, when excavation was interrupted because archaeological artefacts were no longer observed, i.e., an archaeological sterile layer was reached.

Layer 3 (SE 3) - starting at a depth of 40 cm, and especially at 45 cm, on most of the probe surface, a layer of coarse sand (sediment) is observed. It also features archaeological artefacts and river rocks

Layer 4 (SE 4) - at a depth of 0.5m this mixture of earth and sand gets a bit of lighter tones (light brown). This layer is characterized by a reduced concentration of findings.

Layer 5 (SE 5) – it was found that very quickly, from a relative depth of 0.6 m, the light brown layer shifts to a very light (yellow to white) layer of sand, also with a high concentration of river rocks. The light tones come from the high amount of $CaCO_3$, which is also evident from the deposits on the rock surface. At a depth of 0.7 m, due to the absence of archaeological artefacts, the research was discontinued.

Layer 6 (SE 6) - white yellow layer of coarse sand and river rocks.

As a preliminary conclusion from the research so far, we can conclude that stratigraphic units 1-5 originate from one and the same geological process - sediment that occurred during any of the interstadial or interglacial phases of the Quarter [5]. This process, the most probable agent of which is atmospheric water, brought with itself a great variety of volcanic rocks suitable for the manufacture of tools by Paleolithic groups of people. For now, the question remains whether artefacts, together with the raw material, were brought here from some of the rocky massifs north-northeast of the site, or if the weapons were manufactured on the site, where Neanderthals found a rich raw material deposit. Further analysis of the artefacts will determine whether there are types and forms of a number of Paleolithic phases in this small area, as well as their concentration in the squares relative to the concentration of river rocks used as raw material (Figure. 3).

As for the next steps in the Palaeolithic exploration of the Uzun Mera site, it is of utmost importance to perform geo-morphological investigations on the terrain and the genesis of the geological layers, absolute dating of several levels of sandy sediment, as well as further detailed excavation and documentation of artefacts.

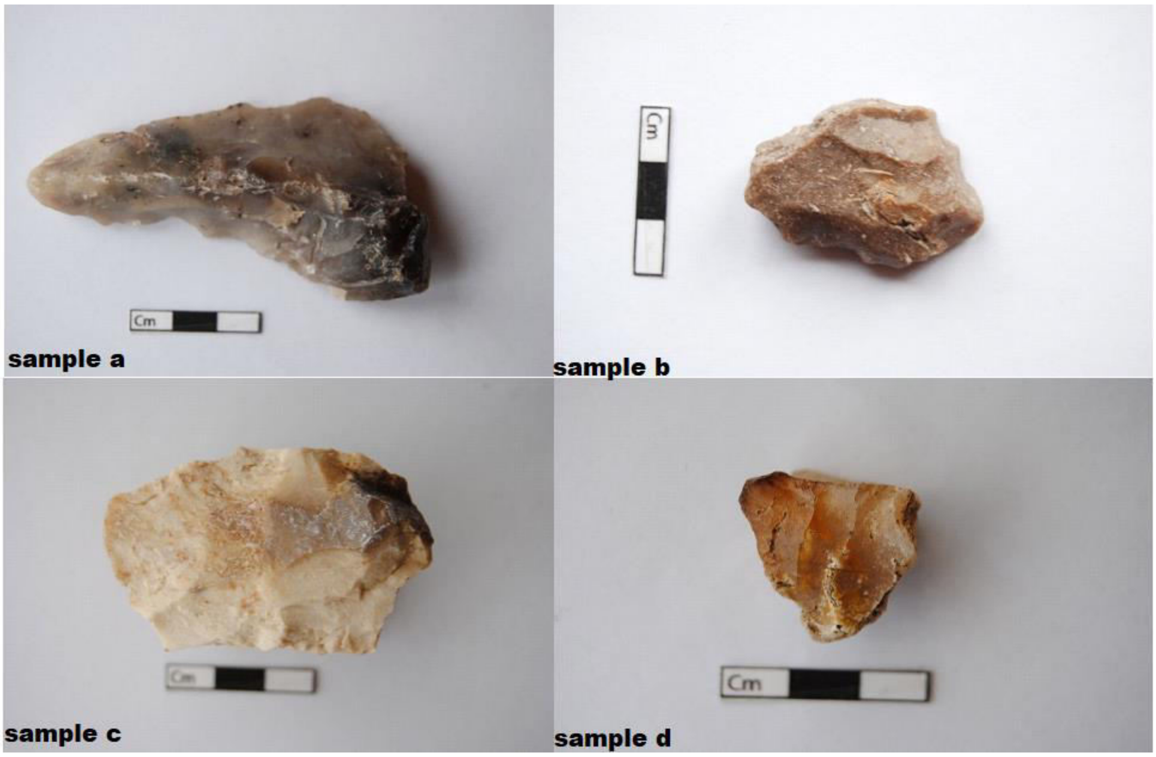

Figure 3. Artefacts from the site Uzun Mera village Mustafino

METHODOLOGY

Energy Dispersive Spectroscopy Analysis

The energy dispersive spectroscopy (EDS) technique is mostly used for qualitative analysis of materials but is capable of providing semi-quantitative results as well. Typically, SEM instrumentation is equipped with an EDS system to allow for the chemical analysis of features being observed in SEM monitor. Simultaneous SEM and EDS analysis is advantageous in failure analysis cases where spot analysis becomes extremely crucial in arriving at a valid conclusion. Signals produced in an SEM/EDS system includes secondary and backscattered electrons that are used in image forming for morphological analysis as well as X-rays that are used for identification and quantification of chemicals present at detectable concentrations. The detection limit in EDS depends on sample surface conditions, smoother the surface the lower the detection limit. EDS can detect major and minor elements with concentrations higher than 10 wt% (major) and minor concentrations (concentrations between 1 and 10 wt%). The detection limit for bulk materials is 0.1 wt% therefore EDS cannot detect trace elements (concentrations below 0.01 wt%).

Scanning electron microscopy

Scanning electron microscopy analyses and electron micro-photographs were conducted using a VEGA3LMU scanning electron microscopy (SEM) increasing 2×1000 000, Wwire, voltage up 200 V to 20 kV, infrared camera, maximum sample size 81 mm height, 30 mm width. The study utilized semi-quantitative analysis using appropriate standards. The standards used are as follows: O: SiO_2; Na: albite; Mg: MgO; Al: Al_2O_3; Si: SiO_2; P: GaP; Ca: wollastonite; Ti: Ti; Fe: Fe; Br: KBr.

RESULTS AND DISCUSSION

The electron microscopy (SEM-EDS) method was used to process a stone tool from the Uzun Mera Palaeolithic Station (Figure. 4) which is made of quartzite and the following results were obtained:

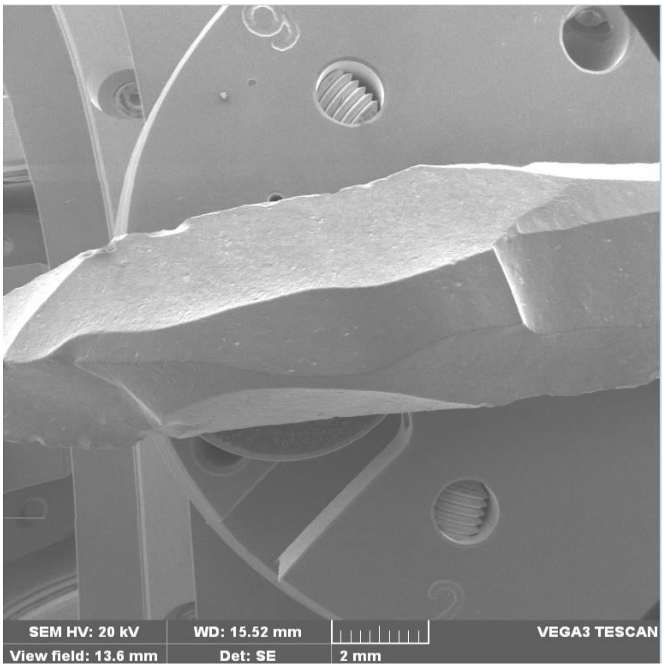

Figure 4. Electron microscope image of the stone tool from Uzun Mera (Figure 3, sample a)

The results obtained from the SEM-EDS analysis presented in Table 1 show that it is quartzite in which the presence of SiO_2 is predominant, while the presence of the other elements can be explained by the interaction of the stone tool with the surrounding soils. (Table 1, 2, 3 Figure.5, Figure.6)

Table 1. Chemical composition of the stone tool from Uzun Mera by SEM-EDS technique

Element	Weight%	Atomic%
O	25.14	38.07
Na	2.65	2.79
Si	56.42	48.67
S	2.64	2.00
Cl	6.16	4.21
K	2.13	1.32
Ca	4.86	2.94
Totals	100.00	100.00

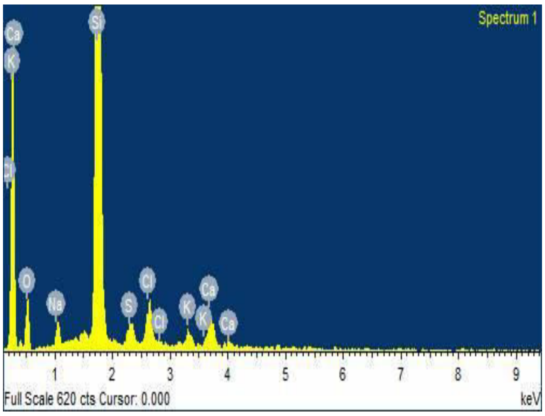

Figure 5. EDX spectrum 1 of the stone tool from the Uzun Mera site

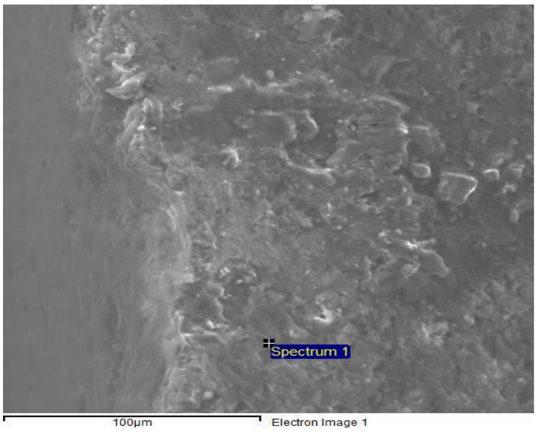

Figure. 6. SEM photography of the stone tool from the Uzun Mera site spectrum 1

Table 2. Chemical composition of the stone tool from Uzun Mera by SEM-EDS technique Spectrum 2

Element	Weight%	Atomic%
O	42.98	58.67
Na	0.80	0.76
Si	42.82	33.29
S	0.78	0.53
Ca	11.20	6.10
Ti	1.42	0.65
Totals	100.00	100.00

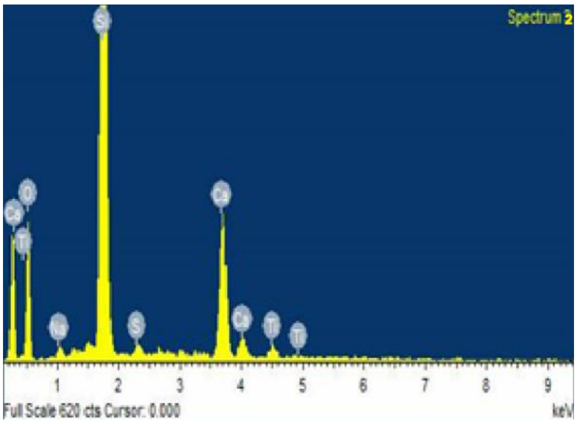

Figure 7. EDX spectrum 2 of the stone tool from the Uzun Mera site

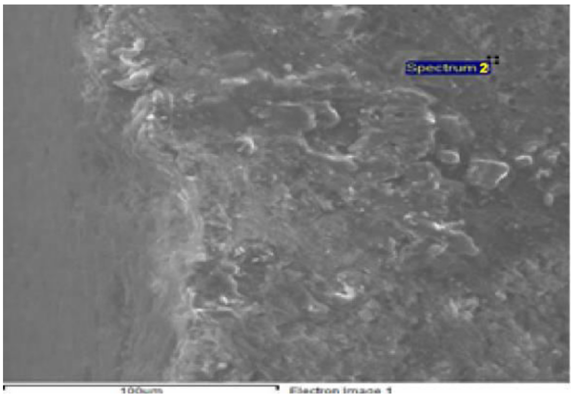

Figure 8. SEM photography of the stone tool from the Uzun Mera site spectrum 2

Table 3. Chemical composition of the stone tool from Uzun Mera by SEM-EDS technique spectrum 3

Element	Weight%	Atomic%
O	41.44	56.10
Na	0.62	0.58
Si	51.79	39.94
Cl	0.69	0.42
Ca	5.47	2.96
Totals	100.00	100.00

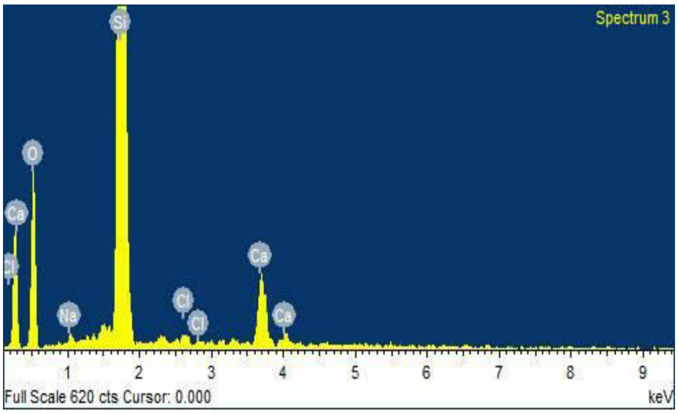

Figure 9. EDX spectrum3 of the stone tool from the Uzun Mera site

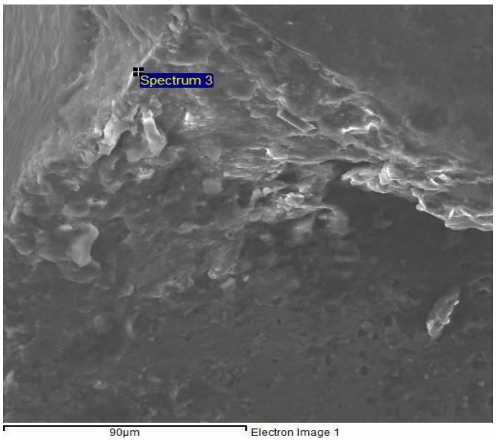

Figure 10. SEM photography of the stone tool from the Uzun Mera site spectrum 3

The data from the performed chemical analysis (Table 4) on one spot on the stone tool shown in Figure.12, clearly indicate that in surface conditions new minerals are formed; in this case fluorite is formed as an interaction of fluoride that is present in quartzite and calcium that originates from the surrounding soils in which the sample is found.

Table 4. Chemical composition of the fluorite formed in the pores of the stone tool from the site Uzun Mera by SEM-EDS technique

Element	Weight%	Atomic%
F	76.34	87.19
Ca	23.66	12.81
Totals	100.00	100.00

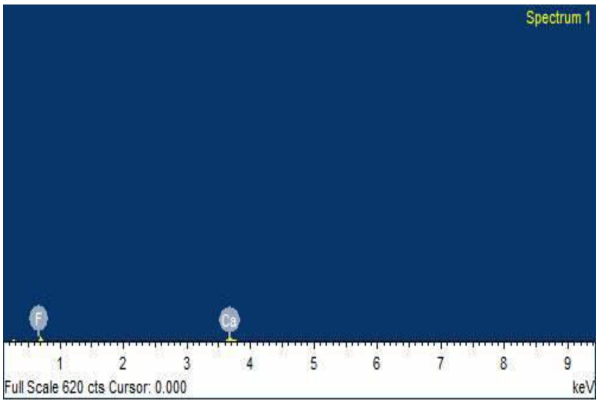

Figure 11. EDX spectrum of the fluorite formed in the pores of the stone tool from the Uzun Mera site

Figure 12. SEM photography of the fluorite formed in the pores of the stone tool from the Uzun Mera site

It should be mentioned that, as a result of the interaction of the soils in which the stone tools are located, secondary minerals are formed along the surfaces of the stone tools (Table 5, Figure. 13 and Figure. 14). In this case, it is the formation of aggregates of Fe-oxides and Fe-hydroxides.

Table 5. Chemical composition of Fe-oxides and Fe-hydroxides that form on the surface of the stone tool from the Uzun Mera site by SEM-EDS technique

Element	Weight%	Atomic%
O	36.40	64.91
Al	1.40	1.48
Si	2.91	2.96
K	0.49	0.35
Ca	1.29	0.92
Fe	57.52	29.38
Totals	100.00	100.00

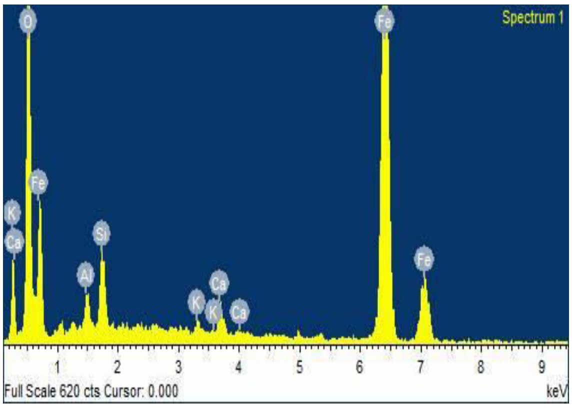

Figure 13. EDX spectrum of Fe-oxides and Fe-hydroxides that form on the surface of the stone tool from the Uzun Mera site

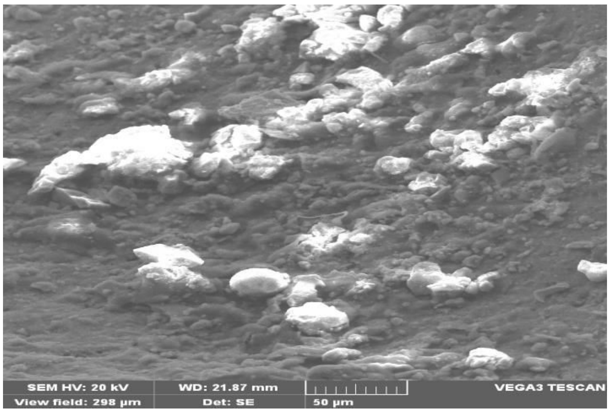

Figure 14. SEM photograph of Fe-oxides and Fe-hydroxides that form on the surface of the stone tool from the Uzun Mera site

CONCLUSION

From the examinations performed on the stone tool that originates from the locality Uzun Mera using the SEM-EDS method, it can be concluded that the stone tool from the Paleolithic station Uzun Mera is made of quartzite that probably originates in the vicinity of the village Strmos (Probistip). The morphology of the stone tool, the way in which its processing was performed, indicates a relatively developed settlement that existed at the time of the Paleolithic at the Uzun Mera site. The examinations of the stone tool also show that as a result of the interaction of the stone tool and the surrounding soils in which the tools were found, new minerals are formed on the surfaces of the stone tool (Fe-oxides and Fe-hydroxides), while in the pores of the stone tool new minerals (in this case fluorite) are formed.

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МИНЕРАЛОГИЈА НА КАМЕНА АЛАТКА ОД ПАЛЕОЛИТСКАТА СТАНИЦА УЗУН МЕРА СЕЛО МУСТАФИНО СО ПРИМЕНА НА СЕМ-ЕДС ТЕХНИКА

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Резиме

Во трудот се прикажани резултатите кои се добиени при испитувањата на камената алатка од локалитетот Узун Мера со примена на SEM-EDS методите. Добиените податоци укажуваат на тоа дека камената алатка е изработена од кварцит кој потекнува од локалитетот Стрмош (Пробиштип) и како последица на интеракцијата со почвите во кои се наоѓа камената алатка доаѓа до формирање на флуорит во порите на алатката, и на Fe-оксиди и Fe-хидроксиди по површината на алатката.

Клучни зборови: *кварц, флуорит, Fe-оксиди, Fe-хидроксиди.*