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CHARACTERIZATION OF OBSIDIAN FOUND IN ROMANIA BY NEUTRON ACTIVATION METHOD*

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Abstract. Significant elements for provenance studies on obsidians were measured by INAA at IBR-2 pulse reactor from JINR, Dubna, Rusia. The aims of this study were to identify an obsidian source in Orasu Nou (Maramures County, Romania). Comparatively with geological studies, new results of correlation and dendrological diagrams of the analyzed samples are presented. So far, the geologists assumed that the obsidian from Oaş area (from Romania) is a new source, but this was not confirmed by our experimental results. We can therefore conclude that in Paleolithic these materials were extracted from Slovakia and were brought by the river Tisa and exchanged for any kind of products.

Key words: obsidian, INAA, nuclear reactor, correlation diagrams, provenance studies.

1. INTRODUCTION

Obsidian is a natural glass of volcanic origin. It is hard and brittle and breaks with conchoidal fracture. It can be readily flaked in any direction and thus fashioned into sharp edges. Where available it was the basic material for making Man's tools until the advent of metals. Obsidian was widely traded from the restricted areas where it was found and was shaped into tools, weapons and statuary [1]. Obsidian is certainly the lithic material providing archaeologists with the clearest evidence of contact between different cultures. In fact, obsidian is almost the ideal material for source characterization by elemental analysis. Moreover, it permits analysis, on a methodological level, of factors which could have influenced the choice of deposit by prehistoric people [2].

According to the data of the International Association for Obsidian Studies near to Romanian border exist several defined sources of obsidian in Slovakia (Banska Stiavnica, Bysta, Cejkov, Hlinik nad Hronom, Kremnitz, Mala Torona,

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Nora Bana, Sklene Teplice, Streda nad Bodrogom, Szolloske), Hungary (Csepego Forras, Erdobenye, Olaszliska, Tolcsva, Telkibanya, Tokaj) and Ukraine (Beregovo, Gertsovtse-Fedeleshovtse, Khust, Mukacevo). The most investigated are such named Carpathian I and Carpathian II sources located in eastern Slovakia and north-eastern Hungary, respectively [3-8]. According to the literature data, the Carpathian obsidian is responsible for a few artifacts found even in northern Italy and some in far east as Greek Macedonia [9, 10].

In the last 30 years a quite large number of Romanian and foreign specialists were interested in dating and provenance of obsidian samples found on Romanian territory [11–14]. Extensive research on obsidian has shown that no sources are found in Romania [15], despite claims of the existence of such sources in the country [6, 10, 16, 17].

On the other hand, obsidian appeared during recent volcanic erruptions. Some experimental data indicate obsidian changes to perlite in about 2000 years. In this sense, a single region exists with vitrous acide vulcanite of recent provenience in Romania: Oas mountains, North-Western Romania. With this very limited zone the hope of Romanian specialists to find a source of obsidian is connected. It should be mentioned that in the North-Western Romania the production of obsidian tools is significant, starting with the Aurignacian and evolving throughout the Gravettian [11]. The majority of samples investigated in our study are from this region. Samples of obsidian, rhyolite and perlite were investigated together with samples from Slovakia and Ukraine.

The chemical composition of obsidian is not altered in the hands of the artisan, therefore, multielemental analytical techniques are suitable for identification of the obsidian geological pattern. A variety of methods for multielemental characterization and dating of obsidians: PIXE, PIGE, LA-ICP-MS, XRF, PIXE-PIGE-RBS, FTD and SIMS were used in the last fifty years [2, 4, 8, 19, 20]. Nevertheless, instrumental neutron activation analysis (INAA) [13, 14] has been the technique of choice in provenance investigation for a long time [22–25], largely due to the high sensitivity to many trace elements along multiple dimensions of element concentration. It also ensures good precision and accuracy of data compared to other techniques.

The aim of the present research was to identify by means INAA of multielemental characterization and statistical methods the origin of geological and archeological fragments of obsidian which were collected from Romania.

2. MATERIALS AND METHODS

Conventional and epithermal neutron activation analysis at the IBR-2 pulsed fast reactor of FLNP JINR Dubna, Russia [26], were used to determine the content of 36 elements in 8 samples of obsidian, rhyolite and perlite (Table 1).

Table 1

Sample location

Nr.	Code	Location	Type
1.	I	Ungvar	arch
2.	II	Orasu Nou	geo
3.	III	Turt	geo
4.	IV	Carei	arch
5.	VI	Rocsa Vii	geo
6.	SK	Slovakia, Cejkov	geo
7.	VII	Orasu Nou	Rhyolite
8.	VIII	Orasu Nou	Perlite

Archeological samples I and IV were found in Ukraine and near Carei (from Romania), respectively. Geological sample II was found in a slag-heap of bentonite quarry Mujdeni without any references to the original level of exploitation or outcrop. Geological sample III was collected in 1975 in Valea Sunatoare (Turt) at approx. 18 km NNW from Orasu Nou (from Romania). The sample was surrounded by dacite, pumice stone, marl and clay. Sample VI is geological obsidian found in a peroclastic breach (98% pumice stone and 2% obsidian) of Pannonian age located in the North of Racsa Vii. Samples VII and VIII found in Orasu Nou are rhyolite and perlite, respectively.

Samples of 50 mg were irradiated for 60 seconds and after 2 and 7 minutes γ-ray spectra were obtained for 5 and 12 minutes, respectively. Independently, samples of 100 mg were irradiated by neutrons at Dubna nuclear reactor for 72 hours. These samples were allowed to decay for 4 and 20 days, and then γ-ray spectra were recorded for 45 and 120 minutes, respectively. All radioactivity values were corrected, taking into account the half-life and decay times. The relative method based on SL-1 (lake sediment) (IAEA) and SRM 2709 (soil) (NIST) reference materials was used.

3. RESULTS

Results of the NAA analysis of obsidians were done in Table 2.

Table 2

Results of the NAA analysis of obsidians (chemical levels of elements is indicated in ppm units and the uncertainties of determinations in %)

a) Results of the NAA analysis of obsidians (Na, Al, K, Sc, Ca)

Index	Name	Na	%	Al	%	K	%	Sc	%	Ca	%
1L	**Ungvar**	2.25E+04	8.3	7.37E+04	2.3	3.99E+04	9.8	3.24E+00	6.7	5.08E+03	28.5
2L	**Sample 2**	1.97E+04	8.3	9.84E+04	2.4	3.46E+04	9.9	2.78E+00	6.7	2.09E+04	21.4

Table 2 (continued)

3L	**Sample 3**	2.33E+04	8.3	6.82E+04	2.3	4.01E+04	10.6	3.65E+00	6.7	7.21E+03	18.3
4L	**Carei**	2.28E+04	8.3	9.89E+04	2.4	4.00E+04	10	3.38E+00	6.7	1.60E+04	22.8
5L	**Slovakia**	2.16E+04	8.3	7.29E+04	2.3	3.46E+04	10.2	3.23E+00	6.6	8.77E+03	15.7
6L	**Racşa**	1.58E+04	8.3	n.m.	-	3.71E+04	12	3.29E+00	9.2	n.m.	-
7L	**Rhyolite**	1.73E+04	8.3	1.18E+05	2.4	4.45E+04	9.1	3.77E+00	6.6	1.30E+04	18.7
8L	**Perlite**	1.51E+04	8.3	6.54E+04	2.2	3.30E+04	12.5	3.47E+00	6.6	1.24E+04	12.7

b) Results of the NAA analysis of obsidians (Ti, V, Cr, Mn, Fe)

Name	Ti	%	V	%	Cr	%	Mn	%	Fe	%
Ungvar	5.56E+02	52.5	9.61E+00	607.7	6.39E+00	392.3	3.79E+02	5	8.04E+03	3.8
Sample 2	1.06E+03	148.2	1.66E+01	206.2	5.62E+00	360.7	4.99E+02	6.1	7.04E+03	3.7
Sample 3	4.83E+02	88.1	6.57E+00	124.4	7.81E+00	300	3.01E+02	4.6	9.85E+03	3.8
Carei	1.04E+03	85.6	1.13E+01	204.3	7.31E+00	320	5.11E+02	5.9	8.37E+03	3.7
Slovakia	4.56E+02	84.5	5.69E+00	103.9	6.36E+00	333.3	3.76E+02	4.5	8.10E+03	3.6
Racşa	n.m.	-	n.m.	-	2.88E+01	13.4	n.m.	-	9.23E+03	9.9
Rhyolite	1.03E+03	32.8	1.19E+01	66.8	6.55E+00	359.3	5.56E+01	13.1	3.58E+03	5
Perlite	7.62E+02	24.8	8.00E+00	42.4	7.65E+00	521.7	3.49E+02	4.4	1.01E+04	3.4

c) Results of the NAA analysis of obsidians (Zn, Br, Sr, Rb, Zr)

Name	Zn	%	Br	%	Sr	%	Rb	%	Zr	%
Ungvar	3.87E+01	5.4	2.03E+00	26	6.71E+01	6.2	2.17E+02	9.8	1.18E+02	6.9
Sample 2	3.35E+01	5.4	1.85E+00	26	4.66E+01	7.5	1.95E+02	9.8	9.71E+01	7.2
Sample 3	5.20E+01	5.3	3.93E+00	25.6	7.19E+01	7	1.87E+02	9.8	1.99E+02	5.9
Carei	3.71E+01	5.4	2.10E+00	26	7.41E+01	6.2	2.18E+02	9.8	1.18E+02	7.1
Slovakia	3.68E+01	5.3	1.94E+00	25.9	5.97E+01	6.4	2.09E+02	9.8	1.18E+02	6.6
Racşa	6.83E+01	9.3	1.44E+00	27.9	1.03E+02	17.9	1.72E+02	10	8.52E+01	32.1
Rhyolite	2.41E+01	6	4.15E-01	35.5	9.01E+01	4.9	1.99E+02	9.8	2.31E+02	5.1
Perlite	4.08E+01	5.3	2.46E+00	25.8	1.11E+02	4.5	1.59E+02	9.8	1.87E+02	5.3

d) Results of the NAA analysis of obsidians (Mo, Sn, Sb, Ba, Cs)

Name	Mo	%	Sn	%	Sb	%	Ba	%	Cs	%
Ungvar	1.10E+00	21.4	2.27E+01	23.1	5.73E-01	10.9	5.02E+02	4.3	1.30E+01	12.7
Sample 2	8.45E-01	21.4	2.43E+01	20.6	5.24E-01	10.9	4.06E+02	4.4	1.16E+01	12.7
Sample 3	1.06E+00	22.7	2.04E+01	26.5	4.67E-01	11.7	6.23E+02	4.4	9.21E+00	12.7
Carei	1.32E+00	20.5	2.23E+01	23.7	5.55E-01	11	5.26E+02	4.4	1.28E+01	12.7
Slovakia	8.65E-01	21.8	2.17E+01	22.2	5.72E-01	10.8	4.81E+02	4.4	1.21E+01	12.7
Racşa	2.55E+00	14.9	3.25E+01	48.3	1.68E+00	14.3	6.69E+02	6.3	9.36E+00	13
Rhyolite	6.11E-01	20.3	3.17E+01	19.3	7.39E-01	10.7	6.64E+02	4.3	1.07E+01	12.7
Perlite	1.23E+00	17.3	1.28E+01	32.5	2.42E-01	12.5	5.98E+02	4.3	2.64E+01	12.7

e) Results of the NAA analysis of obsidians (La, Ce, Nd, Eu, Sm)

Name	La	%	Ce	%	Nd	%	Eu	%	Sm	%
Ungvar	3.34E+01	6.5	7.27E+01	14.5	1.96E+01	19.7	6.08E-01	12.7	7.17E+00	5.5
Sample 2	2.43E+01	6.7	5.24E+01	14.6	1.62E+01	20.8	6.08E-01	11.8	5.75E+00	5.5
Sample 3	4.34E+01	6.5	7.87E+01	14.6	3.16E+01	18.4	6.52E-01	13.8	7.00E+00	5.5
Carei	2.95E+01	6.6	6.57E+01	14.5	2.41E+01	19.3	6.34E-01	12.3	6.79E+00	5.5
Slovakia	2.99E+01	6.5	6.67E+01	14.5	2.27E+01	18.1	3.93E-01	15.3	6.52E+00	5.5
Racşa	2.57E+01	7.3	5.94E+01	16.5	2.90E+01	43.1	2.97E+00	21.2	5.87E+00	5.5
Rhyolite	3.95E+01	6.3	8.08E+01	14.5	3.13E+01	17	1.04E+00	10.6	8.81E+00	5.5
Perlite	2.64E+01	6.7	5.74E+01	14.5	2.14E+01	23.3	1.01E+00	9.7	4.60E+00	5.5

f) Results of the NAA analysis of obsidians (Gd, Tb, Yb, Tm, Hf)

Name	Gd	%	Tb	%	Yb	%	Tm	%	Hf	%
Ungvar	6.74E+00	50.2	1.01E+00	2.2	3.30E+00	18.9	7.49E-01	3.7	2.81E+00	14.1
Sample 2	5.32E+00	50.2	8.68E-01	2.2	2.92E+00	18.9	6.74E-01	3.7	2.25E+00	14.1
Sample 3	6.33E+00	50.2	9.82E-01	2.4	2.95E+00	19	5.77E-01	5.1	4.06E+00	14.1
Carei	5.15E+00	50.2	1.01E+00	2.2	3.25E+00	18.9	7.60E-01	4	2.86E+00	14.1
Slovakia	5.04E+00	50.2	9.48E-01	2.1	3.18E+00	18.9	7.23E-01	3.7	2.68E+00	14.1
Racşa	1.14E+00	113.3	8.61E-01	7.1	2.58E+00	21.5	5.27E-01	13.3	2.98E+00	15.5
Rhyolite	3.21E+00	51	1.53E+00	1.9	4.78E+00	18.9	8.23E-01	3.6	3.94E+00	14
Perlite	2.70E+00	51.1	7.55E-01	2.2	2.36E+00	19	4.56E-01	4.4	3.67E+00	14.1

g) Results of the NAA analysis of obsidians (Ta, W, Au, Th, U, Co)

Name	Ta	%	W	%	Au	%	Th	%	U	%	Co	%
Ungvar	2.51E+00	2.3	9.49E+00	12.5	8.64E-02	503.6	1.95E+01	5.1	1.07E+01	8.3	4.67E-01	17.4
Sample 2	2.18E+00	2.3	6.81E+00	13.4	7.57E-02	332.6	1.45E+01	5.2	9.42E+00	8.4	2.60E-01	24.3
Sample 3	1.62E+00	2.8	5.84E+00	17.7	1.07E-01	309.1	2.18E+01	5.1	5.68E+00	8.5	6.34E-01	16.3
Carei	2.45E+00	2.3	8.48E+00	13	8.33E-02	319	1.78E+01	5.1	1.03E+01	8.3	3.79E-01	20.1
Slovakia	2.31E+00	2.3	7.28E+00	13.5	7.63E-02	295.1	1.80E+01	5.2	9.64E+00	8.3	3.69E-01	18.2
Racşa	1.22E+00	9.2	5.45E+00	20.2	1.26E-01	293.3	1.09E+01	5.4	3.57E+00	8.9	1.89E+00	31.6
Rhyolite	1.29E+00	2.8	6.04E+00	13	6.33E-02	293.2	1.24E+01	5.2	4.95E+00	8.4	4.48E-01	17.4
Perlite	1.23E+00	2.7	4.93E+00	18.4	7.27E-02	781.8	1.14E+01	5.2	3.84E+00	8.5	7.01E-01	12.7

Literature data were also used in order to determine the provenance of obsidian samples (Table 3).

Table 3

Description of obsidian samples from literature used in discussion

Nr.	Cod	Location	Type	References
1.	SK1	Slovakia (Streda nad Bodrogom)	geo	[3]Oddone et al., 1999
2.	SK2	Slovakia (Vinicky)	geo	[3]Oddone et al., 1999
3.	SK3	Slovacia (Mala Bara)	geo	[3]Oddone et al., 1999
4.	SK4	Slovakia (Cejkov)	geo	[3]Oddone et al., 1999
5.	SK5	Slovakia (Cejkov)	geo	[3]Oddone et al., 1999
6.	H	Hungary (Tolcsva)	geo	[21]Bugoi et al.,2004
7.	SK6	Slovakia (Vinicky)	geo	[21]Bugoi et al.,2004
8.	R	Romania (Oradea)	arch	[21]Bugoi et al.,2004
9.	P	Romania (Parta)	arch	[13]Salagean et al., 1988

The first attempt to identify possible similarities between new investigated samples (Fig. 1) was to apply a discriminant factor known from literature [13]. The rhyolite and perlite clearly separate from other samples. The geological samples samples III and VI originated from Turt and Racsa Vii, respectively, indicate also another structure. Using this results and the discrimination factor calculated from elements concentrations:

$$\Delta = (1/Sc)[Cs+Ta+(Rb/100)+(Th+La+Ce)/10], \quad (1)$$

we have constructed a correlation diagram from which we can say that the samples are from Slovakia where are natural sources of obsidian. Until now the geologists assumed that the obsidian from Oaş area is a new source.

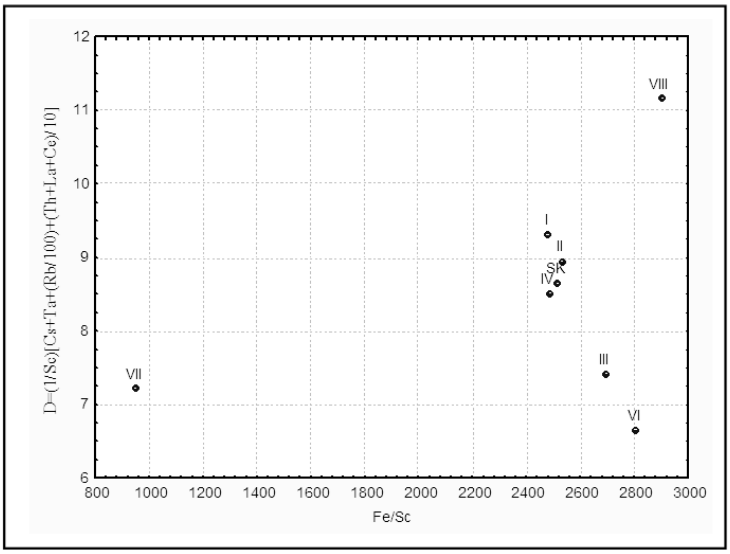

Fig. 1 – Discrimination factor *versus* Fe/Sc.

Further, the cluster analysis was applied to a group of samples formed from ours and data from literature regarding Slovak samples [3]. We remark a very compact Slovak group. The sample II, found in a slag-heap in Orasu Nou joins this group, but sample III geological from Turt joins archeological samples I and IV.

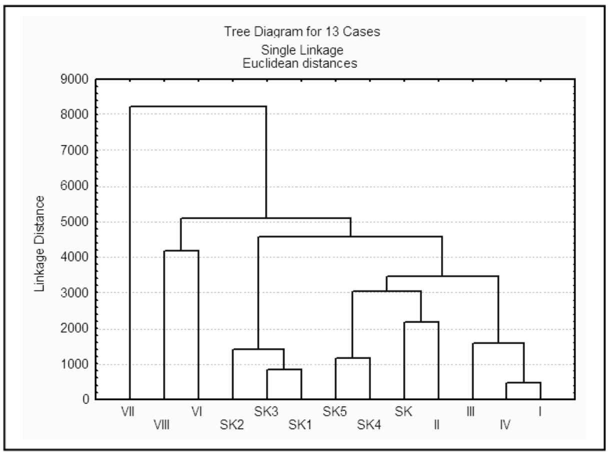

Fig. 2 – Dendrogram of obsidian, perlite and rhyolite samples, including literature data on Slovak geological obsidian ([3] Oddone et al., 1999), based on Na, K, Sc, Cr, Fe, Co, Zn, As, Sr, Rb, Zr, Sb, Ba, Cs, La, Ce, Nd, Sm, Eu, Gd, Tb, Yb, Tm, Hf, Ta, Th and U.

When a sample from Parta (Timis region) [13] was included in analysis, we found that this sample of Vinča culture, which previously was compared with samples from Melos and Sardinia, associates very well with Slovak samples.

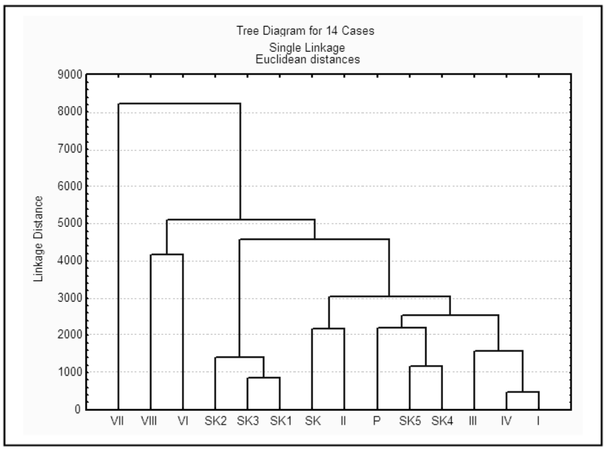

Fig. 3 – Dendrogram of obsidian, perlite and rhyolite samples, including literature data on Slovak geological obsidian ([3] Oddone *et al.,* 1999) and Romanian archeological obsidian ([13] Salagean *et al.,* 1988), based on Na, K, Sc, Cr, Fe, Co, Zn, As, Sr, Rb, Ba, Cs, La, Ce, Nd, Sm, Eu, Tb, Yb, Hf, Ta, Th and U.

When the whole set of samples was supplied to cluster analysis, unfortunately for a narrow spectra of elements, we saw that the sample R from Oradea region with an early attributed Slovak origin make a distinguish note.

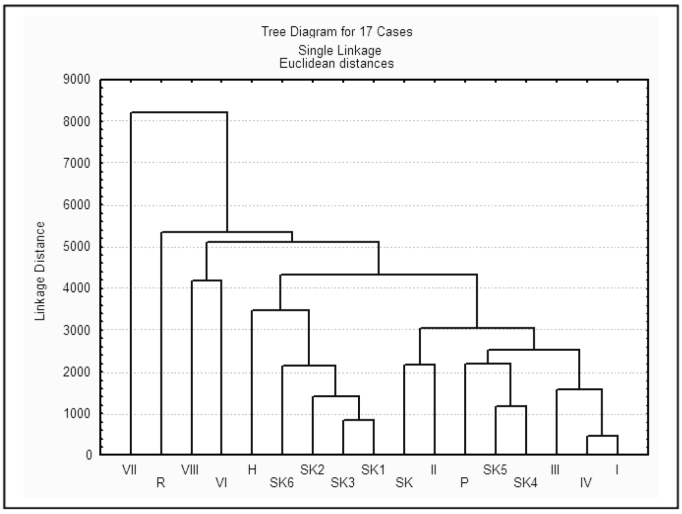

Fig. 4 – Dendrogram of obsidian, perlite and rhyolite samples, including all set of experimental and literature data, based on Na, K, Fe, Zn, As, Sr, Rb, Ba.

4. CONCLUSIONS

The hypothesis regarding a possible source of obsidian in Turt founds a weak allusion in our study. This has to be confirmed or not in further studies, including beside Slovak samples, a larger number of Hungarian samples and samples from Zakarpatya, Ukraine;

The earlier supposition regarding a possible Slovak origin of sample from Parta was confirmed;

The origin of the sample from Oradea has to be investigated in a larger context of samples.

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