Journal of Radioanalytical and Nuclear Chemistry, Vol. 240, No. 1 (1999) 147–153

Chemical characterisations of Carpathian obsidian sources by instrumental and epithermal neutron activation analysis

M. Oddone,[1] P. Márton,[2] G. Bigazzi,[3] K. T. Biró[4]

[1] *Centro CNR di Radiochimica ed Analisi per Attivazione, Dipartimento di Chimica Generale, Università, Pavia, Italy*
[2] *Eötvös Loránd Tudományegyetem, Geofizikai Tanszék, Ludovika sq., Budapest, Hungary*
[3] *Istituto di Geocronologia e Geochimica Isotopica, CNR, Pisa, Italy*
[4] *Hungarian National Museum, Department of Information, P.O.B. 124 VIII, H-1450 Budapest, Hungary*

(Received April 23, 1998)

Obsidian samples from the Tokaj Mountains (Hungary) and from the neighbouring Zemplin Hills (Slovakia) were analysed by instrumental and epithermal neutron activation analysis for obtaining a "fingerprint" for discrimination of potential natural sources of raw material that would permit tracing the origin of archaeological obsidian artefacts. These techniques fully discriminate the Zemplin Hills sources (Carpathian I, eastern Slovakia) and the Tokaj Mountain sources (Carpathian II, north-eastern Hungary) as well as these Central European sources from those already studied of the Mediterranean basin and adjacent regions.

Introduction

In the earlier phases of prehistory trade items that archaeologists can use for documenting indubitable contacts between distant human communities were very rare. Obsidian is among the few materials that may prove cultural interaction between distinct geographical areas, as this glass was widely used for tool-making especially during Neolithic times.[1] Obsidian artefacts are found in archaeological sites located also at great distances from potential natural sources. In addition, obsidian is an ideal material for source identification, as it is distributed in a limited number of volcanic districts. Moreover, physical and/or chemical properties of this volcanic glass are potentially efficient tools for discrimination. For these reasons, source determination of obsidian is a very popular concern of archaeometric studies.

The important changes produced by natural events (for example, burial of obsidian occurrences under alluvium or under recent volcanic products) and by human activities (sources exhausted by strong prehistoric exploitation, transformation of territory due to agriculture or other activities) during the last thousands of years may have made impossible to collect today samples from some sources exploited during prehistory. In that case, provenance identification of artefacts could be an arduous task.

Europe is an excellent region for obsidian studies, as obsidian-bearing volcanics are present only in restricted areas: volcanic glasses suitable for tool-making were recognised only in some Italian and Aegean islands and in north-eastern Hungary (Tokaj Mountains) and eastern Slovakia (Zemplin Hills).

Among the several approaches used for characterisation and discrimination of obsidians, the chemical composition by major element and/or trace element analysis appears the most popular technique. Application of instrumental (INAA) and epithermal neutron activation analysis (ENAA) for correlation of artefacts with natural sources yielded reliable results in various region of the earth. These methods are being routinely used by the Pavia radiochemistry group.[2,3]

The aim of this work is to study the chemical compositions of the Carpathian obsidian sources, which so far have been subject of very few chemical investigations, and to optimise the experimental conditions to improve the sensitivity of chemical element determinations in obsidian samples.

Carpathian obsidian sources

The Carpathian obsidian sources are (or, more properly, were) located in major and minor rhyolite bodies distributed in a relatively wide area cut by the modern Hungary – Slovakia border (Fig. 1). Although the total amount of glass produced by multiple eruptions was relatively small, these obsidians are very important because they are the unique natural sources of raw material recognised in Central Europe.

A first comprehensive study of the geology of Carpathian obsidians was published at the end of last century by Szádeczky,[4] who described horizons made up by dense glass pieces in pearlite matrix layered with banded tuff. Szádeczky's work is a precious testimony, as radical changes were produced by intense cultivation of land during the last century.

[1] E-mail: oddone@ipv32.unipv.it
[3] E-mail: iggi@iggi.pi.cnr.it
[4] E-mail: h5852tbi@ella.hu

0236–5731/99/USD 17.00

Elsevier Science B. V., Amsterdam
Akadémiai Kiadó, Budapest

Fig. 1. Schematic map showing the location of the Carpathian obsidians analysed in this study. A map on the rhyolite bodies of the region was published by BIGAZZI et al.[3]

The obsidian-bearing occurrences suitable for prehistoric exploitation described by SZÁDECZKY in 1886 no longer exist nowadays. However, also at that time some sources had already disappeared, as this author noted that the excellent quality glass of numerous artefacts scattered through the country by prehistoric men was not present in the occurrences still existing. SZÁDECZKY had concluded that very probably some sources had been fully exhausted by our ancestors.

Nowadays, only millimetric hard grains of glass in pearlite (marekanites) can be collected in situ (for example in a quarry near Streda nad Bodrogom or near the Bodrogkeresztúr village, along the Bodrogkeresztúr-Tokaj road). Only 'remains' of the original sources suitable for tool-making exist; they consist of bands of agricultural ground containing a high concentration of obsidian pebbles of various sizes (commonly between 2 and 10 cm). Most of these remains were recognised in vineyards in the large rhyolite areas located west of Tolcsva in the Tokaj Mountains and near Viničky in the Zemplin Hills: Obsidian can be collected also from minor rhyolite bodies at Kakas-hegy, near Mád, and at Mala Bara, north-west of Viničky.

The obsidian subject of this study were collected during a sampling campaign planned in late 80's for their geochemical–geochronological characterisation.[5] These authors synthetically discussed the geology of the study area and presented the results of the application of the fission-track dating method. All samples yielded Miocene ages, mostly distributed into two distinct groups (around 15 Ma, Zemplin Hills, and around 9 Ma, Tokaj Mountains) which correspond to the main groups Carpathian I and Carpathian II introduced by BIRÓ et al.[6] The fission-track dating method turned to be an excellent discriminating technique for these sources, as none of the known obsidians located in Europe or in neighbouring Anatolia has a similar age. However, this method for its laboriousness is not very suitable for large sets of samples. Chemical composition analysis appears more cut out for a routinary application.

Experimental

From the obsidian pebbles collected from each remain of source overlooked in late 80's[5] were selected two samples for INAA and ENAA. Only one sample consisting of a population of grains of marekanite was considered for the occurrence located near Bodrogkeresztúr (sample 11M, Fig. 1). In addition, also four samples from a homogeneous group of artefacts excavated from loess at an archaeological site (Cejkov, samples 5.1M and 5.2M) and from obsidian pieces collected on a hill near Cejkov from a 'secondary geological locality or workshop'[7] (samples 18M1 and 18M2) were analysed. The previous fission-track study had revealed that these glasses showed affinities with the Slovakian sources and had to be considered originated from the Zemplin Hills. Nevertheless, their exact provenance remained unidentified. Therefore, for the Carpathian region disappeared ancient sources of raw materials may be represented by groups of artefacts. Otherwise, glasses originated from that region found at long distance might remain unidentified due to an incomplete reference data-set regarding potential sources.

Chemical analyses were performed at the radiochemistry laboratory of the University of Pavia, using the techniques recently described by BIGAZZI et al.[3] From each sample four aliquots were selected to be processed in different ways according to the peculiar elements to be determined.

The standard Obsidian Rock NIST-SRM 278,[8,9] a nitric solution of the analysed elements, high purity Al and Si (semiconductor grade) were used as reference materials. Irradiations were performed at the Triga-Mark II reactor of Pavia. Induced radioactivity was measured by gamma-ray spectrometry using a Ge hyperpure detector connected to a multichannel pulse height analyser and a personal computer. Data reduction was carried out using a software for spectral analysis. The following elements have been determined: Na, Mg, Si, Al, K, Ca, Sc, Ti, Cr, Mn, Fe, Co, Ni, Zn, As, Se, Rb, Sr, Zr, Nb, Sb, Cs, Ba, La, Ce, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Tm, Yb, Lu, Hf, Ta, Th and U.

For experimentail details and evaluation of accuracy of the methodologies employed in this work we refer to the recent paper quoted above.[3]

Results and discussion

Major, minor and trace element contents determined on the Carpathian obsidian samples subject of this work are reported in Tables 1–4 as the average of three or more independent determinations. Precision for most elements is about 4%.

The present data-set satisfy two criteria: (1) the elemental concentrations within a given source of obsidian are homogeneous and (2) the source-to-source variations in the concentrations of the elements detected are sufficient to discriminate the different sources. In addition, these elemental concentrations well differentiate the Carpathian obsidians from those located in the Mediterranean basin and in Anatolia.[2,3] Therefore, the results of the present study appear very promising for unambiguous correlation of artefacts with natural sources in Europe and adjacent regions.

The Th/U ratio appears an excellent marker of the Zemplin Hills sources. Th/U resulted >2.5 for all obsidians analysed at the Pavia radiochemistry laboratory (>3.5 for the Tokaj Mountains samples), whereas is <2 for the Zemplin Hill obsidians.

In conclusion, the technique employed in this research consist of a fast and efficient tool for characterising obsidian. The present study confirms the classification introduced by BIRÓ et al.[6] of Carpathian sources in two main groups (Carpathian I and Carpathian II) named more recently Zemplin Hills sources and Tokaj Mountains sources.[5] Besides geographical, the above classification corresponds to a substantial difference in age and chemical properties.

Table 1. Major (in %), minor and trace (in μg/g) element contents in Carpathian obsidians

Element	2M1	2M2	3M1	3M2	4M1	4M2
Na%	2.83 ± 0.06	2.84 ± 0.03	2.88 ± 0.08	2.86 ± 0.02	2.82 ± 0.07	2.84 ± 0.05
Mg	60.7 ± 0.2	60.9 ± 0.5	61 ± 0.2	61.2 ± 0.5	60.9 ± 0.6	61.1 ± 0.2
Si%	35.75 ± 0.03	37.83 ± 0.01	35.83 ± 0.03	35.91 ± 0.07	35.81 ± 0.07	35.8 ± 0.06
Al%	6.58 ± 0.06	6.58 ± 0.05	6.51 ± 0.07	6.53 ± 0.04	6.6 ± 0.08	6.62 ± 0.06
K%	3.67 ± 0.07	3.691 ± 0.003	3.69 ± 0.07	3.63 ± 0.05	3.69 ± 0.06	3.72 ± 0.03
Ca%	0.543 ± 0.003	0.551 ± 0.004	0.553 ± 0.003	0.543 ± 0.007	0.555 ± 0.005	0.553 ± 0.007
Sc	3.710 ± 0.008	3.326 ± 0.004	2.960 ± 0.003	2.870 ± 0.003	3.550 ± 0.009	3.220 ± 0.007
Ti	479.4 ± 0.8	480.7 ± 0.3	491.0 ± 0.6	492.3 ± 0.9	496.0 ± 0.7	498.0 ± 0.7
Cr	2.91 ± 0.03	3.01 ± 0.06	3.09 ± 0.07	3.12 ± 0.05	3.45 ± 0.04	3.52 ± 0.03
Mn	383.1 ± 0.5	384.6 ± 0.5	389.3 ± 0.3	392.1 ± 0.7	385.3 ± 0.9	386.2 ± 0.9
Fe%	0.950 ± 0.002	0.820 ± 0.005	0.820 ± 0.004	0.910 ± 0.007	0.760 ± 0.008	0.750 ± 0.002
Co	2.98 ± 0.04	3.07 ± 0.01	3.11 ± 0.06	3.45 ± 0.06	3.04 ± 0.05	3.45 ± 0.04
Ni	3.11 ± 0.03	3.45 ± 0.02	3.67 ± 0.05	3.72 ± 0.02	3.74 ± 0.03	3.75 ± 0.01
Zn	89.34 ± 0.07	91.23 ± 0.05	92.45 ± 0.03	93.04 ± 0.04	95.67 ± 0.05	94.789 ± 0.03
As	457 ± 6	458 ± 7	461 ± 5	469 ± 4	479 ± 7	479 ± 5
Se	0.98 ± 0.06	1.09 ± 0.03	1.12 ± 0.04	1.23 ± 0.04	1.93 ± 0.03	1.91 ± 0.04
Rb	180.0 ± 0.6	207.0 ± 0.5	227.0 ± 0.7	200.0 ± 0.9	217.0 ± 0.8	196.0 ± 0.6
Sr	80.2 ± 0.4	79.9 ± 0.2	78.3 ± 0.3	78.4 ± 0.7	81.3 ± 0.9	80.9 ± 0.3
Zr	81.6 ± 0.5	80.7 ± 0.4	80.2 ± 0.2	80.2 ± 0.8	81.3 ± 0.6	80.9 ± 0.2
Nb	1.98 ± 0.03	1.97 ± 0.04	1.97 ± 0.02	1.97 ± 0.06	1.91 ± 0.03	1.90 ± 0.05
Sb	45.67 ± 0.02	46.78 ± 0.01	46.11 ± 0.03	45.99 ± 0.04	46.67 ± 0.02	46.71 ± 0.03
Cs	10.36 ± 0.01	11.40 ± 0.05	9.58 ± 0.04	9.33 ± 0.02	13.71 ± 0.01	10.95 ± 0.04
Ba	978.7 ± 0.3	981.2 ± 0.5	991.2 ± 0.5	994.6 ± 0.8	994.7 ± 0.5	993.9 ± 0.6
La	40.30 ± 0.07	39.90 ± 0.03	23.00 ± 0.07	25.00 ± 0.05	29.70 ± 0.03	34.20 ± 0.03
Ce	63.20 ± 0.03	58.90 ± 0.02	38.40 ± 0.06	37.80 ± 0.04	46.50 ± 0.02	50.20 ± 0.07
Nd	48.10 ± 0.07	44.40 ± 0.01	30.60 ± 0.01	31.80 ± 0.03	45.20 ± 0.01	47.20 ± 0.02
Sm	5.12 ± 0.05	4.88 ± 0.03	4.41 ± 0.02	4.12 ± 0.02	7.20 ± 0.02	4.31 ± 0.01
Eu	0.46 ± 0.03	0.41 ± 0.04	0.73 ± 0.03	0.34 ± 0.01	0.87 ± 0.02	0.39 ± 0.02
Gd	7.81 ± 0.07	7.36 ± 0.04	7.21 ± 0.03	7.39 ± 0.05	8.91 ± 0.04	6.73 ± 0.06
Tb	1.18 ± 0.05	1.27 ± 0.02	1.32 ± 0.01	1.36 ± 0.03	1.47 ± 0.01	1.27 ± 0.04
Dy	8.20 ± 0.03	7.80 ± 0.02	8.80 ± 0.02	9.20 ± 0.04	9.50 ± 0.02	8.20 ± 0.02
Ho	1.61 ± 0.06	1.40 ± 0.03	1.54 ± 0.01	1.54 ± 0.02	1.75 ± 0.05	1.61 ± 0.01
Tm	0.60 ± 0.03	0.51 ± 0.04	0.54 ± 0.03	0.57 ± 0.01	0.57 ± 0.01	0.57 ± 0.07
Yb	2.72 ± 0.05	2.73 ± 0.04	2.78 ± 0.05	2.74 ± 0.07	3.52 ± 0.04	3.46 ± 0.08
Lu	0.34 ± 0.04	0.35 ± 0.05	0.37 ± 0.01	0.36 ± 0.02	0.46 ± 0.03	0.45 ± 0.04
Hf	1.34 ± 0.02	1.31 ± 0.02	1.35 ± 0.01	1.35 ± 0.03	1.41 ± 0.02	1.41 ± 0.01
Ta	1.22 ± 0.05	1.27 ± 0.06	0.91 ± 0.02	0.95 ± 0.01	0.87 ± 0.04	1.33 ± 0.05
Th	20.00 ± 0.07	18.30 ± 0.02	11.81 ± 0.03	11.30 ± 0.04	16.60 ± 0.06	17.50 ± 0.08
U	11.90 ± 0.06	12.10 ± 0.01	6.90 ± 0.01	5.50 ± 0.02	12.50 ± 0.03	12.70 ± 0.04

Table 2. Major (in %), minor and trace (in μg/g) element contents in Carpathian obsidians

Element	5.1M	5.2M	10M1	10M2	11M
Na%	2.37 ± 0.07	2.38 ± 0.03	2.96 ± 0.06	2.97 ± 0.07	2.98 ± 0.05
Mg	301.6 ± 0.2	302.7 ± 0.7	241.7 ± 0.5	242.3 ± 0.4	251.3 ± 0.6
Si%	36.1 ± 0.01	36.12 ± 0.06	34.57 ± 0.04	34.67 ± 0.07	34.54 ± 0.08
Al%	6.74 ± 0.09	6.76 ± 0.09	6.95 ± 0.08	6.96 ± 0.06	6.91 ± 0.03
K%	3.67 ± 0.04	3.68 ± 0.09	4.06 ± 0.01	4.07 ± 0.08	4.11 ± 0.05
Ca%	0.581 ± 0.003	0.584 ± 0.003	0.678 ± 0.03	0.673 ± 0.03	0.687 ± 0.06
Sc	3.670 ± 0.007	3.870 ± 0.002	4.890 ± 0.008	4.700 ± 0.003	4.430 ± 0.004
Ti	359.7 ± 0.3	360.3 ± 0.4	1020.3 ± 0.2	1019.7 ± 0.5	1021.6 ± 0.9
Cr	2.87 ± 0.04	2.84 ± 0.03	4.56 ± 0.03	4.57 ± 0.03	4.53 ± 0.05
Mn	464.1 ± 0.5	465.2 ± 0.3	309.8 ± 0.2	310.2 ± 0.2	311.4 ± 0.7
Fe%	0.840 ± 0.009	0.890 ± 0.002	1.400 ± 0.003	1.380 ± 0.005	0.930 ± 0.007
Co	3.67 ± 0.02	3.68 ± 0.04	3.87 ± 0.02	3.86 ± 0.04	3.67 ± 0.06
Ni	3.89 ± 0.05	3.91 ± 0.01	4.10 ± 0.04	4.09 ± 0.02	3.99 ± 0.02
Zn	96.78 ± 0.03	97.004 ± 0.06	100.23 ± 0.03	100.46 ± 0.04	101.23 ± 0.04
As	480 ± 7	480 ± 9	568 ± 5	569 ± 6	577 ± 6
Se	1.89 ± 0.03	1.89 ± 0.05	2.00 ± 0.04	2.00 ± 0.03	2.03 ± 0.04
Rb	232.0 ± 0.3	230.0 ± 0.4	222.0 ± 0.3	204.0 ± 0.7	259.0 ± 0.7
Sr	81.7 ± 0.2	82.3 ± 0.5	81.7 ± 0.5	81.8 ± 0.5	183.4 ± 0.6
Zr	81.7 ± 0.1	82.3 ± 0.3	183.2 ± 0.5	184.4 ± 0.3	189.4 ± 0.8
Nb	1.97 ± 0.09	1.97 ± 0.04	1.13 ± 0.08	1.14 ± 0.02	1.21 ± 0.06
Sb	47.01 ± 0.06	47.23 ± 0.02	45.68 ± 0.03	46.01 ± 0.03	47.89 ± 0.04
Cs	12.29 ± 0.02	15.79 ± 0.01	14.79 ± 0.05	15.04 ± 0.01	13.60 ± 0.02
Ba	995.7 ± 0.3	996.0 ± 0.4	100.2 ± 0.3	100.5 ± 0.6	101.2 ± 0.4
La	38.90 ± 0.03	35.00 ± 0.03	61.20 ± 0.07	55.10 ± 0.03	53.60 ± 0.05
Ce	59.10 ± 0.04	55.00 ± 0.02	78.80 ± 0.05	78.60 ± 0.03	70.10 ± 0.04
Nd	46.80 ± 0.02	45.60 ± 0.05	55.80 ± 0.05	58.20 ± 0.07	48.60 ± 0.03
Sm	4.94 ± 0.01	8.56 ± 0.06	6.16 ± 0.07	5.98 ± 0.01	6.70 ± 0.02
Eu	0.33 ± 0.05	0.32 ± 0.03	0.51 ± 0.03	0.51 ± 0.03	0.47 ± 0.01
Gd	7.61 ± 0.06	6.80 ± 0.04	8.71 ± 0.06	8.10 ± 0.07	6.31 ± 0.02
Tb	1.32 ± 0.07	1.17 ± 0.02	1.27 ± 0.04	1.22 ± 0.01	1.08 ± 0.03
Dy	8.80 ± 0.03	7.80 ± 0.03	8.20 ± 0.03	7.80 ± 0.03	7.10 ± 0.04
Ho	1.47 ± 0.01	1.40 ± 0.01	1.40 ± 0.05	1.47 ± 0.05	1.40 ± 0.02
Tm	0.55 ± 0.06	0.58 ± 0.07	0.60 ± 0.05	0.58 ± 0.02	0.59 ± 0.01
Yb	3.62 ± 0.04	3.74 ± 0.02	3.55 ± 0.07	3.53 ± 0.05	3.98 ± 0.09
Lu	0.46 ± 0.02	0.47 ± 0.01	0.47 ± 0.02	0.47 ± 0.02	0.50 ± 0.02
Hf	1.51 ± 0.05	1.51 ± 0.04	1.79 ± 0.04	1.80 ± 0.03	1.90 ± 0.03
Ta	1.93 ± 0.03	1.89 ± 0.04	0.89 ± 0.05	0.93 ± 0.01	0.81 ± 0.01
Th	19.33 ± 0.07	18.30 ± 0.05	24.80 ± 0.02	25.10 ± 0.06	31.80 ± 0.04
U	13.30 ± 0.01	16.90 ± 0.07	6.30 ± 0.01	6.90 ± 0.08	7.70 ± 0.02

Table 3. Major (in %), minor and trace (in µg/g) element contents in Carpathian obsidians

Element	12M1	12M2	14M1	14M2	15M1	15M2
Na%	3.04 ± 0.05	3.06 ± 0.09	3.07 ± 0.01	3.06 ± 0.05	3.05 ± 0.03	3.06 ± 0.09
Mg	60.2 ± 0.4	60.3 ± 0.4	61.31 ± 0.3	61.41 ± 0.6	60.9 ± 0.4	60.3 ± 0.6
Si%	35.05 ± 0.05	35.05 ± 0.03	35.11 ± 0.07	35.09 ± 0.05	35.12 ± 0.05	35.14 ± 0.05
Al%	6.76 ± 0.05	6.77 ± 0.05	6.79 ± 0.04	6.81 ± 0.09	6.77 ± 0.05	6.73 ± 0.05
K%	3.86 ± 0.05	3.89 ± 0.07	3.83 ± 0.08	3.84 ± 0.05	3.87 ± 0.05	3.86 ± 0.03
Ca%	0.565 ± 0.06	0.57 ± 0.06	0.571 ± 0.03	0.573 ± 0.06	0.572 ± 0.006	0.574 ± 0.007
Sc	4.410 ± 0.006	3.450 ± 0.006	3.100 ± 0.002	3.260 ± 0.009	3.030 ± 0.006	2.980 ± 0.002
Ti	599.5 ± 0.9	600.1 ± 0.9	601.1 ± 0.7	602.3 ± 0.9	603.4 ± 0.9	604.1 ± 0.3
Cr	4.54 ± 0.05	3.11 ± 0.05	3.09 ± 0.03	3.12 ± 0.05	3.13 ± 0.05	3.14 ± 0.07
Mn	387.3 ± 0.7	388.1 ± 0.7	389.3 ± 0.5	390.2 ± 0.7	392.4 ± 0.7	391.7 ± 0.9
Fe%	1.150 ± 0.007	1.145 ± 0.007	0.800 ± 0.009	0.850 ± 0.007	0.850 ± 0.007	0.830 ± 0.003
Co	3.98 ± 0.06	3.99 ± 0.06	3.57 ± 0.08	3.58 ± 0.06	3.68 ± 0.06	3.69 ± 0.06
Ni	3.82 ± 0.02	3.82 ± 0.03	2.99 ± 0.06	2.96 ± 0.02	2.90 ± 0.02	2.99 ± 0.02
Zn	102.34 ± 0.04	102.45 ± 0.04	97.05 ± 0.01	97.12 ± 0.04	96.79 ± 0.04	96.35 ± 0.04
As	577 ± 7	581 ± 6	582 ± 7	582 ± 8	578 ± 4	579 ± 9
Se	2.05 ± 0.04	2.11 ± 0.04	2.16 ± 0.06	2.57 ± 0.04	2.55 ± 0.04	2.57 ± 0.04
Rb	203.0 ± 0.9	203.0 ± 0.9	127.0 ± 0.8	139.0 ± 0.9	140.0 ± 0.9	150.0 ± 0.9
Sr	184.7 ± 0.7	147.4 ± 0.7	148.3 ± 0.5	149.5 ± 0.5	150.2 ± 0.4	152.4 ± 0.7
Zr	140.6 ± 0.8	148.6 ± 0.3	149.1 ± 0.3	151.3 ± 0.7	152.7 ± 0.2	153.5 ± 0.8
Nb	2.95 ± 0.04	2.99 ± 0.06	2.88 ± 0.03	2.89 ± 0.03	2.87 ± 0.02	2.88 ± 0.06
Sb	45.10 ± 0.04	45.11 ± 0.04	45.34 ± 0.02	46.10 ± 0.08	46.11 ± 0.04	46.10 ± 0.04
Cs	15.15 ± 0.02	16.12 ± 0.02	9.36 ± 0.03	10.01 ± 0.03	8.26 ± 0.02	8.25 ± 0.02
Ba	104.6 ± 0.8	106.8 ± 0.8	98.8 ± 0.4	99.0 ± 0.4	95.7 ± 0.3	95.3 ± 0.8
La	52.20 ± 0.05	50.60 ± 0.05	37.40 ± 0.08	37.50 ± 0.03	33.60 ± 0.01	32.80 ± 0.05
Ce	72.80 ± 0.04	73.80 ± 0.06	60.50 ± 0.03	60.90 ± 0.02	52.60 ± 0.06	47.80 ± 0.04
Nd	47.40 ± 0.03	43.80 ± 0.03	45.90 ± 0.03	46.30 ± 0.03	44.40 ± 0.03	32.50 ± 0.03
Sm	5.82 ± 0.02	4.18 ± 0.02	4.10 ± 0.01	4.12 ± 0.07	3.80 ± 0.02	3.50 ± 0.02
Eu	0.53 ± 0.01	0.41 ± 0.01	0.43 ± 0.06	0.41 ± 0.07	0.41 ± 0.01	0.42 ± 0.01
Gd	8.46 ± 0.05	6.18 ± 0.05	7.31 ± 0.07	6.93 ± 0.08	6.90 ± 0.05	6.85 ± 0.05
Tb	1.27 ± 0.03	1.08 ± 0.03	1.22 ± 0.04	1.21 ± 0.04	1.21 ± 0.03	1.19 ± 0.03
Dy	8.50 ± 0.04	6.80 ± 0.04	7.55 ± 0.03	7.80 ± 0.02	7.80 ± 0.04	7.80 ± 0.04
Ho	1.54 ± 0.02	1.61 ± 0.02	1.40 ± 0.02	1.47 ± 0.01	1.47 ± 0.02	1.47 ± 0.02
Tm	0.59 ± 0.01	0.58 ± 0.01	0.52 ± 0.06	0.52 ± 0.02	0.39 ± 0.02	0.49 ± 0.01
Yb	2.73 ± 0.03	3.47 ± 0.07	3.08 ± 0.05	3.01 ± 0.06	2.59 ± 0.09	1.93 ± 0.07
Lu	0.37 ± 0.02	0.47 ± 0.02	0.48 ± 0.03	0.47 ± 0.04	0.36 ± 0.02	0.33 ± 0.02
Hf	1.78 ± 0.03	1.78 ± 0.03	1.71 ± 0.07	1.71 ± 0.06	1.68 ± 0.03	1.68 ± 0.03
Ta	0.94 ± 0.04	0.93 ± 0.01	0.94 ± 0.02	0.91 ± 0.05	0.81 ± 0.01	0.86 ± 0.01
Th	25.30 ± 0.04	28.10 ± 0.06	17.90 ± 0.03	17.91 ± 0.06	15.30 ± 0.04	16.30 ± 0.04
U	6.60 ± 0.05	6.20 ± 0.02	4.40 ± 0.02	3.41 ± 0.05	3.40 ± 0.02	3.50 ± 0.02

Table 4. Major (in %), minor and trace (in µg/g) element contents in Carpathian obsidians

Element	16M1	16M2	18M1	18M2	19M1	19M2
Na%	3.07 ± 0.05	3.08 ± 0.05	2.36 ± 0.01	2.35 ± 0.03	2.98 ± 0.04	2.99 ± 0.05
Mg	61.4 ± 0.4	61.7 ± 0.4	309.3 ± 0.4	310.6 ± 0.4	241.3 ± 0.4	242.6 ± 0.4
Si%	35.17 ± 0.05	35.19 ± 0.05	36.13 ± 0.05	36.17 ± 0.05	34.64 ± 0.05	34.73 ± 0.05
Al%	6.75 ± 0.05	6.74 ± 0.05	6.75 ± 0.05	6.77 ± 0.05	6.96 ± 0.05	6.95 ± 0.05
K%	3.89 ± 0.05	3.87 ± 0.05	3.65 ± 0.05	3.64 ± 0.05	4.1 ± 0.05	4.11 ± 0.05
Ca%	0.576 ± 0.006	0.579 ± 0.006	0.578 ± 0.003	0.581 ± 0.006	0.683 ± 0.004	0.685 ± 0.006
Sc	3.150 ± 0.006	4.340 ± 0.006	3.800 ± 0.006	3.530 ± 0.006	5.030 ± 0.006	5.140 ± 0.006
Ti	604.2 ± 0.9	603.7 ± 0.9	359.7 ± 0.9	359.4 ± 0.9	1031.1 ± 0.9	1041.2 ± 0.9
Cr	3.23 ± 0.05	3.22 ± 0.05	2.34 ± 0.03	2.45 ± 0.08	22.39 ± 0.05	3.98 ± 0.05
Mn	391.5 ± 0.7	392.7 ± 0.7	465.3 ± 0.3	463.3 ± 0.3	389.2 ± 0.7	389.6 ± 0.7
Fe%	0.770 ± 0.007	1.090 ± 0.007	0.910 ± 0.007	0.918 ± 0.002	1.434 ± 0.007	1.431 ± 0.007
Co	3.78 ± 0.06	3.796 ± 0.06	3.68 ± 0.06	3.71 ± 0.06	3.97 ± 0.06	3.985 ± 0.06
Ni	2.83 ± 0.02	2.84 ± 0.02	2.99 ± 0.02	2.97 ± 0.02	3.02 ± 0.02	3.03 ± 0.02
Zn	93.45 ± 0.04	94.03 ± 0.04	95.67 ± 0.04	95.34 ± 0.04	100.23 ± 0.04	100.56 ± 0.04
As	567 ± 4	570 ± 4	571 ± 3	572 ± 6	599 ± 5	599 ± 4
Se	2.47 ± 0.04	2.46 ± 0.04	2.40 ± 0.04	2.35 ± 0.04	2.57 ± 0.04	2.52 ± 0.04
Rb	127.0 ± 0.9	127.5 ± 0.9	248.0 ± 0.9	250.9 ± 0.9	231.0 ± 0.9	232.0 ± 0.9
Sr	153.6 ± 0.7	151.2 ± 0.7	152.3 ± 0.7	150.6 ± 0.7	79.9 ± 0.7	81.1 ± 0.7
Zr	153.3 ± 0.8	154.3 ± 0.8	81.7 ± 0.8	81.9 ± 0.8	171.6 ± 0.8	172.3 ± 0.8
Nb	2.91 ± 0.06	2.94 ± 0.06	1.96 ± 0.06	1.97 ± 0.06	3.00 ± 0.06	3.01 ± 0.06
Sb	47.11 ± 0.04	47.35 ± 0.04	47.23 ± 0.04	48.05 ± 0.04	48.55 ± 0.04	48.67 ± 0.04
Cs	10.86 ± 0.02	10.52 ± 0.02	13.33 ± 0.02	13.19 ± 0.02	10.95 ± 0.02	10.56 ± 0.02
Ba	97.2 ± 0.8	97.5 ± 0.8	101.2 ± 0.8	101.7 ± 0.4	99.5 ± 0.4	99.3 ± 0.8
La	35.20 ± 0.05	52.80 ± 0.05	34.90 ± 0.05	35.10 ± 0.03	52.80 ± 0.03	50.10 ± 0.05
Ce	53.60 ± 0.04	74.00 ± 0.04	54.40 ± 0.04	56.80 ± 0.02	83.30 ± 0.02	84.90 ± 0.04
Nd	36.60 ± 0.03	50.40 ± 0.03	37.20 ± 0.03	38.40 ± 0.05	57.00 ± 0.05	57.60 ± 0.03
Sm	3.60 ± 0.02	5.90 ± 0.02	5.20 ± 0.02	5.10 ± 0.06	6.00 ± 0.06	6.20 ± 0.02
Eu	0.33 ± 0.01	0.53 ± 0.01	0.40 ± 0.04	0.41 ± 0.03	0.59 ± 0.03	0.56 ± 0.01
Gd	6.93 ± 0.05	9.15 ± 0.05	7.36 ± 0.04	7.14 ± 0.04	8.12 ± 0.04	8.15 ± 0.05
Tb	1.20 ± 0.03	1.31 ± 0.03	1.25 ± 0.02	1.20 ± 0.03	1.28 ± 0.01	1.29 ± 0.03
Dy	8.16 ± 0.04	8.84 ± 0.04	7.81 ± 0.02	7.83 ± 0.04	7.14 ± 0.03	8.16 ± 0.04
Ho	1.54 ± 0.02	1.54 ± 0.02	1.55 ± 0.03	1.54 ± 0.02	1.33 ± 0.05	1.33 ± 0.02
Tm	0.52 ± 0.01	0.52 ± 0.01	0.65 ± 0.04	0.65 ± 0.01	0.52 ± 0.02	0.52 ± 0.01
Yb	2.40 ± 0.07	3.18 ± 0.07	4.00 ± 0.04	3.98 ± 0.07	3.02 ± 0.05	3.00 ± 0.07
Lu	0.40 ± 0.02	0.44 ± 0.02	0.43 ± 0.05	0.47 ± 0.02	0.43 ± 0.02	0.45 ± 0.02
Hf	1.55 ± 0.03	1.54 ± 0.03	1.53 ± 0.02	1.53 ± 0.03	1.46 ± 0.03	1.45 ± 0.03
Ta	0.73 ± 0.01	0.87 ± 0.01	1.53 ± 0.06	1.66 ± 0.01	0.97 ± 0.01	0.94 ± 0.01
Th	26.80 ± 0.04	25.70 ± 0.04	20.20 ± 0.02	19.40 ± 0.04	24.80 ± 0.06	25.10 ± 0.04
U	6.90 ± 0.02	7.30 ± 0.02	14.40 ± 0.01	14.20 ± 0.02	6.60 ± 0.02	7.30 ± 0.02

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