

## AN OVERVIEW OF THE ANALYTICAL TECHNIQUES APPLIED TO STUDY THE CARPATHIAN OBSIDIANS\*

### A KÁRPÁTI OBSZIDIÁNOK VIZSGÁLATÁRA ALKALMAZOTT ANALITIKAI MÓDSZEREK ÁTTEKINTÉSE

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#### Abstract

*In this paper, we give a brief overview of the analytical techniques applied on Carpathian obsidians, from the mid-sixties until present. Besides modern analytical techniques that are focussed especially on the determination of obsidian artefact provenance, microscopic methods are also applied: investigation in thin section under polarising microscope (flow fabric, inclusions, phenocrysts), characterization of individual microlites and trichites embedded in a glassy groundmass using microprobe, measurement of glass refractive index. Already in 1886, Gyula Szádeczky used the determination of specific gravity on Hungarian obsidians to describe black, translucent, green and red varieties. Magnetic susceptibility was used to distinguish obsidian tools from pieces of artificial glassy slag resembling to artefacts and found during field prospection.*

*The presented methods are discussed according to their physical features, i.e. how the information obtained, elemental-, isotopic- or structural analysis, bulk or surface methods, what elements can be measured, are they sensitive enough for trace element analysis, what are the advantages and limitations. Question of the non-destructivity, as well as economic aspects, i.e. the speed and costs of the analysis are also discussed. Some examples of the provenance research of Carpathian obsidians are shown.*

#### Kivonat

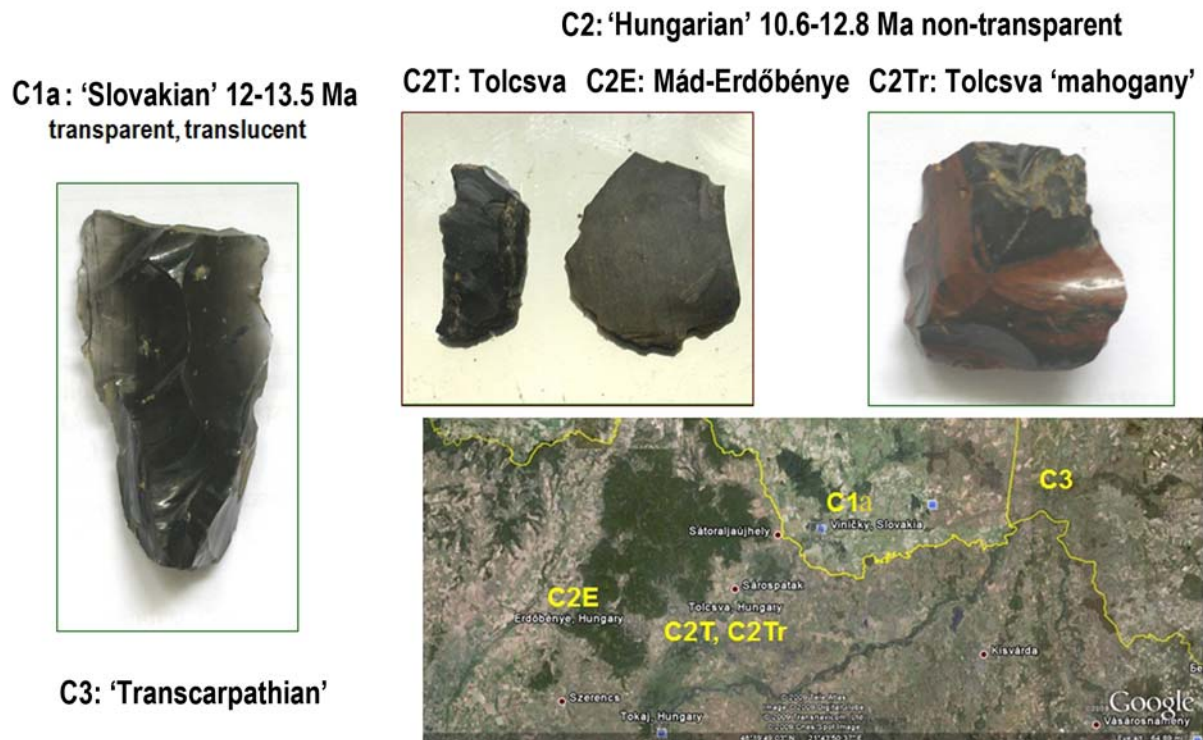
*Ebben a cikkben áttekintést kívánunk adni a kárpáti obszidiánok vizsgálatára alkalmazott analitikai módszerekről, az 1960-as évek közepétől napjainkig. Az obszidián nyersanyag leelőhelyek azonosítását célzó modern vizsgálati módszerek mellett hagyományos petrográfiai módszerek is alkalmazhatók az obszidiánok kutatására. Ilyen például a vékonycsiszolatok vizsgálata polarizációs mikroszkóppal, amely alkalmas a szöveti kép és irányítottság, zárványok, fenokristályok elemzésére. Mikroszondával vizsgálhatjuk az üveges mátrixba beágyazódó különálló mikrolitokat, trichiteket, és a hagyományos kőzettani vizsgálatok körébe tartozik az üveg törésmutatójának mérése is. Szádeczky Gyula már 1886-ban a fajsúlyuk alapján jellemezte a különböző – fekete, áttetsző, zöldesvörös – obszidián változatokat. A mágneses szuszceptibilitás mérésével az obszidiánok megkülönböztethetők a velük összetéveszthető modern salaküvegektől, amelyek terepbejárásokon gyakran kerülnek elő.*

*A bemutatott kísérleti módszereket a fizikai jellemzőik szerint tárgyaljuk, azaz, hogy milyen típusú információ nyerhető a vizsgálat segítségével. Elemi- vagy izotópösszetétel, felszíni vagy tömbi összetétel adatot kapunk? Mely kémiai elemek mérhetőek, elég érzékenyek az említett technikák nyomelemek kimutatására? Melyek az egyes módszerek előnyei és hátrányai? A minták roncsolásának kérdését, továbbá a vizsgálatok gazdaságosságát (gyorsaság, költség) is tárgyaljuk. Néhány irodalmi példán mutatjuk be az egyes módszerek alkalmazását a kárpáti obszidiánok provenancia kutatásában.*

KEYWORDS: OBSIDIAN, PETROGRAPHY, NAA/PGAA, XRF, ICP-AES/MS, DATING

KULCSSZAVAK: OBSZIDIÁN, KŐZETTAN, NAA/PGAA, XRF, ICP-AES/MS, KELTEZÉS

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**Fig. 1.:** The geographical occurrence of the Carpathian 1a, 2 and 3 types obsidian

**1. ábra:** A kárpáti 1a, 2 és 3. típusú obszidiánok földrajzi előfordulásai

### Introduction

Obsidian is one of the most popular raw materials used for chipped stone production in the prehistoric times. It is a volcanic glass formed from rhyolitic lava during quenching process (Taylor 1976). One of the important questions in the archaeological research is to determine the possible geographical locations of the raw material sources that have been used for production of tools. Fortunately, because of the specific conditions of its formation, the geochemical composition of the obsidian can be associated with the provenance with high confidence, as it has shown as early as in the 1960's and 1970's (Cann & Renfrew 1964, Gordus et al., 1968, Bowman et al., 1973).

In addition, the number of geological obsidian sources over the world is limited (Pollmann 1999), which makes the assignation of historical outcrops easier.

In this study, we focus on the Carpathian obsidian, as the main obsidian raw material type used in the prehistory of the Carpathian basin and in its surroundings. The utilization of Carpathian obsidian has been studied already in the 19<sup>th</sup> century (Rómer 1867, 1878, Szabó 1867, 1878, Szádeczky 1886) and later, in the early 20<sup>th</sup> century (Janšák 1935, Roska 1934, 1936, Gábori 1950, Vértes 1953).

By now, it is agreed between the scientists (Williams Thorpe et al. 1984, Rosania et al. 2008, Biró 2014) that basically three major types of Carpathian obsidian exist. The C1 (Slovakian) types are 11–15 Ma old (K-Ar dating and fission tracks ages are summarized by Bačo et al. 2017) and they can be found in the Zemplín Hills (south-eastern Slovakia). Comparing the Tokaj – Zemplén Mountains in Hungary, it is another geological and geomorphological unit with Palaeozoic central part and Tertiary volcanic rocks only on its margins. In the south we can distinguish an area of primary obsidian sources around a rhyolite body of Borsuk (267.3 m) with localities Viničky, Malá Bara, Velká Bara and with two different groups from the standpoint of K-Ar ages (older group approximately in the range 13.5 – 11.6 Ma and the younger one with the age a little bit above 11 Ma). Macroscopically similar obsidians probably only shortly transported at Streda nad Bodrogom yielded the third different group of ages between 14.32 – 14.95 Ma (see Bačo et al. 2017). Obsidian from the southern part of Zemplín Hills can be characterized as black, non-translucent, with polyedric shape and smooth surface without sculpture (source Carpathians 1b). Its utilisation in prehistoric times is still a matter of question.

In the north-eastern part of Zemplín Hills there exists a large secondary source of obsidian (fluvial and deluviofluvial deposits, about 6 km<sup>2</sup>) near the

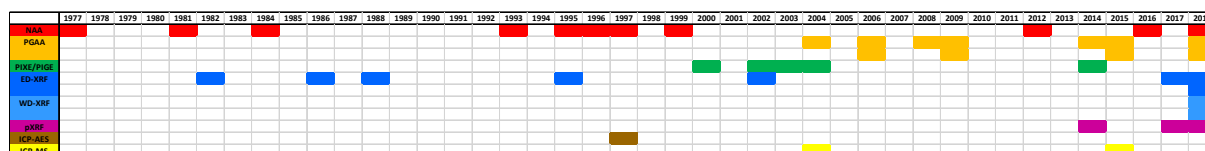
Ošva River. The obsidian is usually translucent, partly in the form of pebbles or rounded pieces up to 20 cm with expressively sculptured surface (source Carpathians 1a) and its K-Ar dating varies between 12 – 13.5 Ma. Because of the best quality it was the most popular prehistoric obsidian raw material in the Carpathian region (Přichystal & Škrdla 2014, Bačo et al. 2017).

Radiometric ages for silicic volcanism in the southern part of Tokaj – Zemplén Mountains, it means Hungarian continuation of the Slanec (Slanské) Mountains in Slovakia, are between  $12.8 \pm 0.5$  and  $10.6 \pm 0.5$  Ma (Pécskay et al. 1987, Szepesi & Kozak 2014), so the C2 (Hungarian) type obsidian has the same age. It can be divided in two sub-types, the C2E is from Mád-Erdőbénye, the C2T is from Tolcsva. Its colour is typically grey or brownish, but there exists a unique mahogany coloured variant of the Tolcsva type, which is labelled as C2Tr. Hungarian obsidians from the primary sources have smooth surface without sculpture.

Finally, there is a C3 type Carpathian obsidian, which can be found in the Vinohradiv Mountains, the Tolstoi-Tupoi volcano in Transcarpathian Ukraine (Fig. 1.). The Carpathian 3 obsidian is black with pitch lustre, non translucent, its surface can be sculptured by sharp grooves filled with red clay. C3 is considered the poorest type local material of the three, rarely used as raw material for

tools. Plagioclase phenocrysts up to 2 mm are visible by naked eye. The whole-rock K-Ar age of surrounding pyroxene dacite is  $10.6 \pm 0.5$  Ma (Pécskay et al. 2000).

In our paper, we discuss the modern analytical methods applied on the Carpathian obsidian samples for provenance research purposes, starting from the 1960s. Certainly, besides of the archaeometry, pure geochemistry might also be interested in the investigation of obsidian composition. These studies aim to answer questions regarding the geological age, formation mechanism, genetics, coloured variants, etc., but this research is out of our scope. We classify the methods according to their physical features, i.e. how the information obtained, elemental-, isotopic- or structural analysis, bulk or surface methods. We examine what elements can be measured, are they sensitive enough for trace element analysis, what are the advantages and limitations. Question of the non-destructivity, as well as economic aspects, i.e. the speed and costs of the analysis are also considered. Some examples of the provenance research of Carpathian obsidians are shown. Further detailed annotated bibliography of the Carpathian obsidian research can be found in this volume. The dates of significant publications about a novel application of a new analytical method on obsidian research are shown in Table 1.



**Table 1.** Appearance of various analytical techniques in the studied literature about Carpathian obsidian. The total number of the papers studied is about 50. Each coloured cell represents one publication.

**1. táblázat:** A különböző analitikai módszerek alkalmazásainak első publikáció a kárpáti obszidiánok irodalmában - Kb. 50 cikk alapján. Minden színes téglalap egy publikációt jelöl.

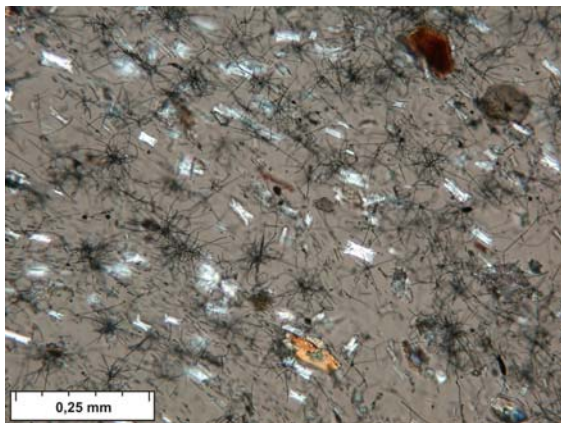
## Overview and discussion

### Petrographic studies and investigation of physical properties

Before using modern geochemistry on a large scale, the determination of physical properties (specific gravity, refractive index) represented important non-destructive and cheap methods to characterise individual sources of the Carpathian obsidian and to distinguish archaeological obsidian from pseudoartefacts made of artificial glassy slag. That is why a chapter using these methods for mineralogical investigation of the Carpathian obsidian appeared in the classical comprehensive book of Š. Janšák (1935). The chapter has been

written by F. Ulrich, professor of mineralogy at Charles University in Prague. The same methods and determination of the main oxides by wet analysis were used by J. Štelcl (1973) when looking for provenance of Neolithic obsidians in Moravia (eastern part of the Czech Republic). He measured specific gravity and refractive index on 29 obsidians from three Neolithic localities in Moravia. He concluded to be a homogenous group belonging to rhyolite obsidian and because of different refractive index on obsidian from Viničky (at that time believed the only one natural occurrence of obsidian in Slovakia), he supposed origin of Moravian archaeological obsidians in Hungary.





**Fig. 2.:** Characteristic mineral inclusions (biotite microphenocrysts, plagioclase microliths, clusters of hair-like trichites) in thin section of obsidian from Malá Bara, Slovakia. Photo by A. Přichystal.

**2. ábra:** Jellegzetes zárványok (biotit mikrofenokristályok, plagioklász mikrolitok, hajszál-szerű trichit-csomók) obszidián vékonycsiszolatában (Kisbár, Szlovákia). A. Přichystal felvétele.

Classic petrographic studies of thin sections under polarising microscope revealed usually hyaline fluidal texture with various proportions of microphenocrysts (plagioclase, biotite), microlites (plagioclase, magnetite, ilmenite, zircon, monazite, pyroxene, olivine, garnet, apatite) and hair-like blackish trichites (**Fig. 2.**). Such clusters or fluffs of microlites seem to be typical for dark obsidians from the Borsuk rhyolite body in Slovakia while in the Hungarian non-translucent obsidian sources the microlites form many simple individual small bars arranged in almost parallel orientation. R. Ďud'a (in Kaminská & Ďud'a 1985) estimated the contents of microlites in Slovakian obsidians from the Borsuk rhyolite body between 10–25% of the rock volume. Substantial progress in petrography of the Carpathian obsidians is connected to the application

of microprobe. E. Švecová (2009) or M. Kohút et al. (2018) studied Slovakian obsidians (Carpathians 1 type). Plagioclases are usually zoned with Ca-rich cores (bytownite) and a higher content of Na in their rims (oligoclase). Biotites correspond to Fe-annites. As pyroxenes are concerned, orthopyroxenes of enstatite composition substantially prevail.

Y. Suda et al. (2014) and B. Rác et al. (2016) investigated Transcarpathian obsidians (Carpathians 3) from the area of Rokosovo. The first group of authors studied in detail plagioclases (with and without zonal structure), orthopyroxenes, olivine and amphibole. Presence of three types of glomeroporphyritic aggregates (the olivine and the orthopyroxene bearing varieties, the third one is composed of only plagioclase) seems to be a characteristic sign for the Transcarpathian obsidians as well.

Petrographic description of Hungarian volcanic glasses was partly a subject of two PhD theses at University of Debrecen. Z. Elekes (2001) studied phenocrysts in obsidian glasses from Armenia, Greece, Slovakia and Hungary as well. He mentioned in detail zircon, pyroxene a biotite from two Hungarian samples (Erdőbénye, Sima). J. Szepesi (2009) focussed his attention on acid lava sequences in NE Hungary including their K/Ar dating and volcano-facies investigation.

At Masaryk University in Brno E. Švecová (2011) studied Carpathian obsidians from all three main sources (Slovakia, Hungary, Transcarpathian Ukraine). Using microprobe, she investigated also obsidians from Olaszliszka, Erdőbénye and Mád and she found plagioclases, orthopyroxenes, biotites, zircons, apatites, magnetites, ilmenites, rarely chalcopryrite (Olaszliszka) or olivine (Mád) among mineral inclusions.

	What is measured?	Bulk / Surface?	Sensitivity?	Accuracy	Sampling?	Speed?	Price?
<b>NAA</b>	Some major, more trace elements (Rb, Sr, Zr, REE); isotopes	Bulk; average for the sample	Sensitive	Good	10-100 mg	Slow (cooling)	Expensive (Reactor)
<b>PGAA</b>	Most major, some trace (B, Cl, H)	Bulk; average for a few cm <sup>3</sup>	Medium for traces 1-10 ppm	Good	No (large objects!)	Slow (spectrum evaluation)	Expensive (Reactor)
<b>PIXE/PIGE</b>	Major and traces, >Al	Near surface 10-100 um	Sensitive	Good	No	Fast	Less expensive (accelerator)
<b>ED-XRF</b>	Major and traces, >Mg	Near surface some 10 um	Sensitive 0.1-1 ppm	Good	Yes or No	Fast	Less expensive
<b>WD-XRF</b>				Moderate			
<b>pXRF</b>	Traces	Bulk for the sample	Very sensitive: <<ppm	Very good	Yes	Slow (Calibration)	Expensive
<b>ICP-AES</b>							
<b>ICP-MS</b>							

**Table 2.:** The major characteristics of the analytical methods most frequently applied in obsidian research

**2. táblázat:** Az obszidián kutatására általánosan használt módszerek összehasonlítása

### Determination of finger-printing chemical elements

As it was mentioned earlier, the geochemical composition, i.e. the concentrations of the major, minor and trace elements is characteristic for the location of the obsidian source. This means that sources of two different geographical locations are significantly different in chemical composition. Furthermore, samples within one geographical source can be considered homogeneous, at least within the uncertainty of the given analytical method. It implies that an analytical technique, which is capable to measure the “finger-printing” chemical element with high precision will be useful in provenance studies. Since many times valuable archaeological objects are studied, non-destructive methods are preferred. The various chemical methods are summarized according to their basic features (i.e. the size of the analysed sample, sensitivities, accuracy, speed and costs), in **Table 2**.

#### Neutron activation methods

In general, the various neutron activation analytical methods are based on the physical phenomenon, that an atomic nucleus emits characteristic gamma radiation, following the capture of a neutron.

From the 1960s, in parallel with the development of spectroscopic instrumentation, neutron activation analysis (NAA) has become a routine analytical tool to determine a few major and a series of trace elements in obsidian, and also in other geological samples. The chemical elements that can be easily measured by NAA are: Na, K, Sc, Cr, Fe, Co, Ni, Zn, As, Se, Br, Rb, Sr, Zr, Ag, Cd, Sb, La, Hf, Ta, W, Ir, Au, Th, U and the rare-earth elements. From these elements, mostly Na, K, Fe, Rb, Sr and Zr are used in the obsidian provenance research. Kilikoglou et al. was able to differentiate between the Mediterranean (Antiparos, Adamas, Demenegaki, Giali) and the Carpathian 1 – mentioned as “Slovakian” obsidian, based on INAA measurements (Kilikoglou et al., 1996). Williams-Thorpe et al. have applied Principal Component Analysis on the concentration data measured by NAA and were able to distinguish even between the various Carpathian sources (Williams-Thorpe et al., 1984).

The NAA method was the most popular technique applied in the obsidian archaeometry in the 1970’s and 1980’s, at the heyday of the research reactors. When NAA chosen, it must be considered that it requires samples of 10-100 mg to analyse. Furthermore, due to the high neutron flux in the reactor core, the sample will stay radioactive for several days, and cannot be returned to the owner.

Another, less known neutron activation method is called Prompt Gamma Activation Analysis (PGAA). The physical phenomenon is the same as

in the case of NAA, but the object is irradiated in an external beam of thermal or cold neutrons, and the characteristic photons are detected at the same time. The use of external beam allows the scientist to omit the sampling. On the other hand, since the so-called prompt photons are detected, the method is sensitive for different chemical elements. Typically, the major geochemical components, i.e. H, Na, K, Ca, Mg, Al, Si, Ti, Mn, Fe and some minor and trace elements, i.e. B, Cl, Sc, V, Nd, Sm, Gd and Eu can be detected with PGAA. Since neutrons can travel deep into the irradiated object, the result is representative for the whole irradiated volume, i.e. the method is a “*bulk*” analytical method.

Until now, only the Budapest PGAA laboratory at the Budapest Neutron Centre applied the method for systematic provenance research of obsidians (Kasztovszky et al., 2008). They have successfully determined the provenance of archaeological obsidian from Hungary (Kasztovszky et al., 2014), from Croatia (Kasztovszky et al., 2009) from Poland (Kabacinski et al., 2015) and from Romania (Kasztovszky et al., 2018a). They have compared the applicability of PGAA, the handheld XRF and the INAA methods for obsidian provenance research and have shown that the B, Cl and Ti concentrations measured by PGAA are perfectly applicable finger-prints (Kasztovszky et al., 2018b).

#### X-ray fluorescence methods

In another large group of the methods, the analytical information is obtained by detection of characteristic X-ray photons emitted by the electrons of the atoms. The electrons of the atoms in a sample can be excited with various kinds of incident radiation that can be produced by an X-ray (XRF)-, electron (SEM-EDS)- or proton (PIXE) source. The characteristic radiation is detected in energy dispersive (ED) or wavelength dispersive (WD) modes. For all these mentioned methods, the sensitivity is proportional to the atomic number of a given element, and the lightest detectable element is Mg. We must mention that with some portable XRF instrument using He-flush, the detection of Na is also possible. When evaluating the analytical results provided by any of the X-ray fluorescence methods, we must remember that the penetration depth of the exiting radiation is in the order of 10–100 µm, thus the result is representative for the bulk composition, if the sample is homogeneous and the surface is free of any layer of different composition. Furthermore, the result is reliable only if the analyse surface is flat and smooth. In case of laboratory based XRF instruments, homogenized samples are produced by melting the original geological pieces. R. E. Hughes and D. Werra (2014) applied the XRF method to find the provenance of Late Mesolithic obsidians from central Poland. Similarly, this method together with LA-ICP-MS determination of Rb and Zr was used

to analyse Late Palaeolithic/Mesolithic and Neolithic obsidians from Bohemia, western part of the Czech Republic (Burgert et al. 2016). Rózsa et al. (2006) have applied comparative fluorescence spectroscopic methods (i.e. PIGE and LA-ICP-MS) for geochemical studies of obsidian samples from various localities (Carpathian Mts., Mexico, Armenia, Iceland and Turkey).

Despite the above disadvantages, the XRF methods, especially the portable ones are widespread, because they are cheap, fast and easy to handle. Marina Milić has shown that the analytical data provided by handheld XRF are as precise as those provided by laboratory-based ED-XRF, PIXE or ICP-MS instruments. Furthermore, based on the well detectable Rb, Sr and Zr concentrations, obsidians from various sources are well separable (Milić 2014).

Although Proton Induced X-ray Emission (PIXE) Spectroscopy in principle does not differ from the XRF methods, in practice it is considered as a “large scale facility” since it requires a Van de Graaf accelerator to generate a proton beam, and therefore associated with significantly higher operational costs, compared to the portable XRF. Using PIXE and PIGE, however, it is possible to measure fingerprinting chemical elements, such as Ti, Mn, Rb and Sr, based on which discrimination of obsidian sources can be done (Elekes et al., 2000; Bugoi et al., 2004; Constantinescu et al., 2002, 2014.). It can be seen from **Table 1**, that PIXE and PIGE are mostly used in the archaeometry of the Carpathian obsidian from the 2000’s and performed by the laboratories of Debrecen, Hungary and Bucarest, Romania. Rózsa et al (2003) have applied micro-PIXE method to map the distribution of phenocrysts in obsidian, mainly in Carpathian ones for provenance purposes.

#### ***Plasma spectroscopy methods***

In case of the third large group of analytical methods, the elemental or isotopic composition of the samples is determined by the means of plasma spectroscopy. A tiny amount of the sample is combusted in a high frequency plasma torch, and the atomized components are analysed by the detection of characteristic electromagnetic radiation (AAS, AES, ICP-AES) or by mass spectrometry (ICP-MS). When the analysed material is vaporized by a laser beam (LA-ICP-MS), the smallest, practically invisible destruction is done on the object. The method was used to analyse a large collection of 46 obsidians from three basic geological sources in the Carpathians, from natural occurrences in Turkey or Greece and archaeological artefacts from Moravia, Slovakia, Italy, Nicaragua, Mexico, Iraq and Syria (Prokeš et al. 2015).

On the other hand, the Inductively Coupled Plasma Spectroscopic (ICP) methods represent the most

sensitive and most accurate techniques applicable in geochemistry, specifically in the obsidian provenance research. Almost every chemical element – except hydrogen, the halogens and noble gases – can be measured in a concentration as low as ppb (ng/g) level. These methods are also applicable to determine isotopic composition of the samples that is even more effective tool to identify the geological origin of obsidian (Orange et al., 2016).

#### ***Structural studies (Electron Microscopy, Mössbauer Spectroscopy, Small Angle Neutron Scattering)***

Although only a few studies dealt with the topic, it is believed that – as a consequence of the formation process – not only the elemental composition, but also some structural information might refer to the location of a given obsidian source. In a recent study (Kasztovszky et al., 2018c), geochemical reasons of the formation of the rare mahogany obsidian, and the possibilities of source identification was discussed. Black and mahogany obsidians from Tolcsva, as well as mahogany obsidian from Bogazköy have been analysed by Electron Microscopy, Mössbauer Spectroscopy and Small Angle Neutron Scattering (SANS). With the help of SANS, anisotropy, porosity, etc. can be investigated on a 10-100 nm scale by detecting the elastic scattering pattern by cold or thermal neutrons.

SANS measurements at the Budapest Neutron Centre have determined that the so-called fractal exponents (3.28 for Tolcsva black and 3.60 for Tolcsva mahogany) are the “measure” of the surface roughness. Smoother or rougher surface features could be linked to the different genetic conditions of the samples (such as composition, temperature, pressure, cooling rate etc.) With the help of Transmission Electron Microscopy (TEM), agglomerated iron-oxide nanocrystallites were identified as scattering objects. The isotropic scattering of the Tolcsva sample originated from randomly oriented nanocrystallites, while anisotropic scattering originated from nanocrystallites with a preferred orientation, aligned during their formation. Finally, Mössbauer Spectroscopy has identified disordered hematite in the mahogany samples.

#### ***Dating methods (Fission Track Dating & Hydration Dating)***

Two different kinds of dating are applied to study the provenance of archaeological obsidian. Fission Track Dating (FTD) is based on the counting of microscopic tracks caused by the fission of natural uranium content of obsidian. This method aims to determine the geological age, i.e. the date of formation of obsidian. With the help of FTD,

Bigazzi et al. was able to distinguish between the younger “Tokaj” (i.e. C2 type) and the older “Zemplin” (i.e. C1 type) obsidians (Bigazzi et al., 1990). In a later study (Bigazzi et al., 1993) it is shown that with combination of FTD and NAA, Anatolian and Carpathian obsidians were possible to distinguish with high efficiency.

The Hydration Dating (HD) is based on the phenomenon that on a fresh surface of obsidian, a thin hydration layer starts to grow. The thickness of the layer is typically in the order of 10 µm, and it grows proportionally with the ½ exponent of time. With the help of HD, one can determine the approximate time of the elaboration of the archaeological obsidian (Bíró & Pozsgai 1982).

### Conclusions

In this study, we aimed to give a brief overview of the modern analytical methods that can be used in the archaeometrical studies of obsidian. We have demonstrated, that not only the elemental composition, but also some structural information as well as the dating of obsidian samples might help to determine the provenance of the object, i.e. to localise the geographical source of its raw material.

Apparently, when one must choose one or more analytical techniques, more arguments has to be considered. Every analytical method has advantages and disadvantages, too. Speaking of objects of the Cultural Heritage, non-destructive and non-invasive methods are absolutely preferred. Optimisation of costs vs. benefit (i.e. the abundance and usefulness of the provided information), as well as of speed and accuracy of the investigations are natural demands.

In many cases, combination of complementary methods may lead to more successful research. But we have to draw the attention to the adequate interpretation of the analytical results that are obtained with inherently different methods.

To help the analyst to choose the best combination of method, we summarize the most important features of the techniques discussed here.

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