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The Carpathian obsidians – contribution to their FT dating and provenance (Zemplín, Slovakia)

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Abstract

The Carpathian obsidian samples from the Slovakian part of the Zemplín – Tokaj area have been studied by means of fission-track dating (FT) and geochemistry to better understand the provenance of the archaeological obsidians from the Central Europe realm. New FT obsidian ages obtained by the isothermal plateau method (ITPFT) are in a narrow time interval between 12.45 ±0.45 and 11.62 ±0.25 Ma, and indicate a short-time monogenic volcanic evolution rather than a long-lasting volcanism over the 16 ~ 10 Ma period, as was previously thought. Geochemically, these obsidians belong to the silica-rich, peraluminous, high-potassium, calc-alkaline rhyolite series volcanic rocks with a ferroan character which were derived by multi-stage magmatic processes from mixed mantle and crustal sources during subduction in a volcanic arc tectonic setting. Chemical composition of the Carpathian obsidians clearly exhibits a common similarity among all examined localities (Brehov, Cejkov, Hraň, and Viničky). A comprehensive provenance study, including physical properties of the obsidians, confirms a general congruence within the studied obsidians and the use of common provenance labelling, such as *Carpathian-1* (*C1*) for the Slovakian – Zemplín area obsidians, is recommended.

Keywords: Obsidian, FT dating, geochemistry, provenance, Western Carpathians

Introduction

Obsidian was widely used for tool-making (stone industry) during prehistoric times, and played a significant role in the evolution of humankind and civilization. Since obsidian is found in a limited number of volcanic districts, it is an ideal material for identification of sources and trade routes of the ancient populations (Cann and Renfrew, 1964; Durrani et al., 1971; Williams-Thorpe et al., 1984; Torrence et al., 2009; Freund, 2013) by using modern geochemistry and dating methods. Obsidian is instantaneously solidified (quenched) volcanic rock, originating mainly from an acid rhyolitic melt, but rarely from a basaltic melt, and is often referred to as "natural glass" with typical glassy lustre and usually dark jet-black, grey or brown colour. Generally, obsidian is dominated by amorphous, dark (opaque) volcanic glass (≥95 volume %), with addition of various fine accessory minerals, reflecting their embryonic crystallization from a melt, that are observable mainly under a microscope. These minerals can be present in the form of phenocrysts (having a size of 1000 – 100 μm), microlites (50 – 10 μm), and hair-like trichites. The commonly observed banded structure or alternation of dark and pale stripes is caused by concentrations of microlites and trichites oriented in the direction of the melt flow. Volcanic glass from the Zemplín – Tokaj area of SE Slovakia and NE Hungary has been known since the studies of Fichtel (1791) and Szabó (1867), whereas its archaeological importance was documented long ago by Rómer (1867) and Janšák (1935). The Carpathian obsidians from these localities were for a long time the only source of archaeological obsidian in Continental Europe (Biró, 2006). The extent of obsidian utilization by the Palaeolithic to Neolithic individual cultures was variable. Obsidian use in the Pannonian Basin and/or broad Carpathian realm is documented since the Middle Palaeolithic (e.g. Biró, 1984; Markó 2009, 2019). However, the first use on the Slovakian territory is known by the Aurignacian culture of the Upper Palaeolithic showing marginal usage only, whereas more extensive utilization of obsidian came with the Gravettian and Epigravettian cultures, especially in surroundings of the Zemplínske vrchy Mts. in the Eastern Slovakia (Bánesz, 1968; Kaminská, 1991; Bačo et al., 2017). Famous archaeological localities and workshop sites occur in Eastern Slovakia, for example: Košice-Barca, Kechnec, Kašov, Cejkov, Hrčeľ-Pivničky, Kysta, Zemplínske Jastrabie, Malá and Veľká Tŕňa (see Appendix map). Production of obsidian stone industry was more prominent in Middle Neolithic time when archaeological sites of the younger Eastern Linear Pottery culture and Bükk culture appear, usually repeatedly, in the surroundings of known settlements: Malá and Veľká Bara, Viničky, Zemplín, Streda nad Bodrogom, Zemplínske Jastrabie, Hraň, Novosad, Kysta, Hrčeľ and Kašov (see Appendix map) (Janšák, 1935; Šiška, 1991; Kaminská, 1987; Bánesz, 1991).

Archaeologists have increased understanding of these rocks by using geochemical analyses determined by OES and NAA, and, in so doing, identified major source areas of obsidians from the Zemplín – Tokaj area of Central Europe using natural outcrops as well as cores and artifacts at archaeological sites (e.g. Renfrew et al., 1965; Williams-Thorpe et al., 1984). Differences in chemical compositions enabled Williams-Thorpe et al. (1984) to designate the following obsidian groups: ***Carpathians 1*** (*C1*) represent samples from localities Viničky and Malá Tŕňa (the Zemplínske vrchy Mts. – SE Slovakia), whereas samples from the Tokaj Mts. of NE Hungary are designated as ***Carpathians 2a*** (*C2a*), consisting of localities Csepegő Forrás, Tolcsva, Olaszliszka and Erdőbénye. ***Carpathians 2b*** (*C2b*) consists of redeposited obsidians from Erdőbénye, and ones from Mád – Kakas-hegy, Bodrogkeresztúr – Tufabánya Mellett which partly coincides with the division of Biró et al. (1986) for *C2E* and *C2T* (see Appendix map). Archaeologists have systematically studied obsidians from the Zemplín – Tokaj area and the results of their chemical analyses can be found in the works of Oddone et al. (1999), Bigazzi et al. (2000), Biró et al. (2005), Rózsa et al. (2006), Rosania et al. (2008) and Kasztovszky et al. (2014). Because the Carpathian obsidians are the only known autochthonous source region in Central Europe, this prominent raw material of the Palaeolithic to Neolithic era (Stone Age) was the main source of archaeological obsidian in Continental Europe for long time. The Carpathian obsidians were identified in the various Palaeolithic to prehistoric sites (Stone, Copper and Bronze Age) not only in the Central European realm (Slovakia, Hungary, Ukraine, Romania, Bulgaria, Croatia, Serbia, Bosnia, Poland, Czech Republic and Austria) but were discovered in remote locations like Grotta Tartaruga (NE Italy), Mandalo (Greece) or Zealand (Denmark) as far as 1400 km from source (Williams-Thorpe et al., 1984; Kilikoglou et al., 1996; Biró, 2014). A number of publications with analytical results of the Carpathian obsidians have been published (beside above mentioned these are e.g. Elburg et al., 2002; Glascock et al., 2015; Burgert et al., 2016), but these results are not always comparable. The aim of the present contribution is to provide new FT age and geochemical data on obsidian samples from the Zemplín area with a discussion on the age of volcanic activity and archaeological classification, and their relevance to archaeological interests on provenance studies.

Geological setting

The Carpathian obsidians of the Zemplín area belong to the Eastern Slovakian Neovolcanic Field (ESNF) in SE Slovakia where isolated Sarmatian volcanoes penetrate Miocene strata and pre-Cenozoic basement (**Fig. 1a, b**). The geological setting of the Zemplínske vrchy Mts. (ZVM) and their surroundings is complicated because it embraces rocks from the Paleozoic up to Holocene. ZVM forms a typical tectonic horst surrounded by the East Slovakian Basin with several elevated volcanic bodies (**Fig. 1b**). The present architecture is a consequence of back-arc extension that is associated with asthenosphere updoming and is accompanied by calc-alkaline volcanism associated with pull-apart opening during the Miocene. These events are followed by the Pannonian to Quaternary late stage regional uplift and erosion (Baňacký et al., 1989; Vass et al., 1991; Lexa and Kaličiak, 2000; Pécskay et al., 2006).

The pre-Cenozoic basement represents the so-called Zemplinicum, a tectonic unit of the Central Western Carpathians (CWC) that was amalgamated into a block during youngest Neogene times in the study area. It consists of the Variscan crystalline basement (Carboniferous to Permian in age) and its Mesozoic cover. The Palaeozoic basement rock sequences encompass various sedimentary and volcanic rocks, the former being cyclic and rhythmically bedded fluvial and fluvio-lacustrine sediments. Grey conglomerates, sandstones and shales, calcareous shales, grey limestones, and locally thin black coal seams are interbedded in places with acidic volcaniclastic material (Kobulský et al., 2014).

The Zemplinicum’s Mesozoic cover is composed of conglomerates, quartzose sandstones, limestones, dolomites, and shales with gypsum all of which originated in a shallow marine environment (Kobulský et al., 2014). The ZVM territory was then weathered, eroded and peneplanated before sedimentation of the Neogene strata.

Neogene strata of Miocene age are divided into the Badenian plus Sarmatian marine and Pannonian freshwater formations. Both older formations consist mostly of shallow marine sandstones, siltstones and shales, although conglomerates are common at the margin of ZVM. Volcanic rocks are present in both formations, including lava and pyroclastic flows, tuffites, tuffs, and volcaniclastic deposits, which, in places, such as at Viničky, contain perlites and obsidians (see Borsuk body in **Fig. 1b**). During Pannonian time clays, silts, sands and gravels were deposited in freshwater lacustrine and fluvial environments (Baňacký et al., 1989; Vass et al., 1991; Kobulský et al., 2014).

Description of samples and methods used

Because the majority of archaeological obsidian occurrences have been redeposited into secondary positions in the Zemplín – Tokaj area, the search for primary magmatic sources has been an important task of the past research (Janšák, 1935; Šalát and Ončákova, 1964; Williams-Thorpe et al., 1984; Kaminská and Ďuďa, 1985; Bačo et al., 2017). Generally, obsidian findings in Eastern Slovakia are divided into: ***a***) primary – autochthonous, in magmatic rhyolite extrusive rocks e.g. Viničky, Malá Bara, and volcaniclastic tuffitic rocks in Streda nad Bodrogom; ***b***) secondary – allochtonous, in naturally displaced Quaternary accumulations as at Brehov and Cejkov; and/or ***c***) archaeological – human-relocated obsidian occurrences within the Palaeolithic/Neolithic localities and workshop sites as Hraň, Kašov, Malá Tŕňa, Cejkov, and Zemplín (see Appendix map) (Bačo et al., 2017). Noteworthy, volcanic rocks at the Hraň locality are pyroxene andesites and pyroxene-amphibole-bearing dacite lava flow complexes of the Lower Sarmatian age that generally do not contain obsidian. Obsidians at this locality have an anthropogenic source – they were transported to this area by Man. Janšák (1935) assumed that there was a temporary obsidian warehouse and/or workshop. However, the original autochthonous archaeological location (cultural bed) is totally deteriorated, because at present it is utilized agricultural land. During the secular tillage and other agricultural activities, the obsidian cores and/or obsidian industry were markedly degraded. In addition to obsidian cores, nuclei and other stone industry products, many unprocessed natural pieces were found there as well. Due to better characterization of obsidians from the Zemplín area, representative samples for the FT and geochemistry were chosen from the following localities: Viničky (primary – autochthonous), Brehov, Cejkov (secondary – allochthonous) and Hraň (human-relocated). Obsidians always occur along with perlite, usually as obsidian nodules in perlite environment in the Viničky primary locality. Due to weathering and transportation, obsidian nodules from the allochthonous localities are more rounded and covered partly by patina and surface sculpturing (**Fig. 2a**). Generally, the obsidians are dominated by the amorphous volcanic glass but an important role is played by the rock-forming and accessory minerals from a genetic point of view. Petrographically, these obsidians are typical glassy rocks with a hyaline–vitritic structure. The parallel alternation of pale and dark stripes filled by minute microlites and trichites form a banded texture (**Fig. 2b**) caused by a melt flow. The studied Carpathian obsidians consist of a broad association of accessory minerals like plagioclase, biotite (**Fig. 2c + e**), alkali feldspar, quartz, pyroxenes (**Fig. 2d**), amphiboles, magnetite, Fe–Ti oxides, pyrrhotite, pyrite, chalcopyrite, olivine, zircon, apatite, monazite, uraninite, ilmenite, hercynite and garnet. Trichites (pyroxenes and Fe–Ti oxides including magnetite + hematite) having a hairy shape, magnified up to 500x look like continuous linear alignments (5 ~ 10 μm in diameter) are actually discontinuous, triaxial, hieroglyphic formations, documenting the rapid quenching of the flowing melt in nano dimension (**Fig. 2d + f**). Beside the autolithic origin of crystallized minerals sporadic xenoliths from the source and/or assimilated rocks can be present.

Fission-track dating

The obsidian samples were gently crushed in a mortar and pestle and sieved to recover the 0.5 – 0.25 mm and 0.25 – 0.125 mm size fractions. The coarser fraction was used for fission-track (FT) dating. Obsidian fragments from each sample were split into two aliquots, one for determination of the spontaneous FT area density (ρs), the other for irradiation, following which the induced FT area density (ρi) can be determined. Samples were irradiated at the McMaster Nuclear Reactor, Hamilton, Ontario, Canada. Mounting the obsidian fragments on glass slides was done by placing a blob of epoxy resin on a non-sticking Tephlon surface and mixing the sample into it. A glass slide was then placed on top of the resin, which spreads out as the slide comes to rest on adjacent spacers. The epoxy-sample mix was left to harden for at least two days. Gentle grinding was done on a 600 corundum grit paper followed by polishing on a paper lap using a suspension of water and 0.3 μm alumina powder. The last stage involved polishing with 6 μm diamond paste to give linear scratches on the surface of the obsidian fragments to indicate an internal surface. Only fission tracks on an internal surface were counted. Two ρi slides and three ρs slides were made for each sample. Fission tracks were revealed by etching in 24% HF at room temperature. Etch time was designed to give an average of 6 – 8 μm for the long axis of the tracks. Slides for ρs and ρi were etched under identical conditions, that is, simultaneously in the same beaker. Counting was done using an optical microscope at x500 magnification and the area covered was determined by use of an eyepiece graticule, because the surface area of the obsidian fragments in all samples is large. Track size measurements were done with an image analyzer attached to the microscope using x1000 magnification (**Fig. 3**). These measurements are required to determine the correction factor for partial track fading (PTF) in samples dated by the diameter correction method (DCFT) (Sandhu and Westgate, 1995). A heat treatment of 150°C for 30 days fully corrects for PTF when the isothermal plateau method (ITPFT) is used (Westgate, 1989). The glass-FT dating method used in this study was the zeta calibration method, which is based on analysis of age standards (Hurford and Green, 1983; Wagner and Van den haute, 1992). The population – subtraction variant was used (Westgate, 2015) and the age standard used in this study was the Moldavite tektite glass with a ^{40}Ar/^{39}Ar age of 14.808 ± 0.021 Ma (2σ) (Schmieder et al., 2018). Ages were calculated using $\lambda_D = 1.551 \times 10^{-10}$ yr^{-1}. The zeta value is 311 ± 4 based on 7 irradiations at the McMaster Nuclear Reactor, using the NIST SRM 612 glass dosimeter and the Moldavite glass. The fluence was obtained by multiplying the muscovite track density by 0.53 x 10^{10} based on 9 determinations. An internal age standard has been used to monitor the accuracy of the fission-track ages; it is Huckleberry Ridge Tuff with a ^{40}Ar/^{39}Ar age of 2.003 ±0.014 Ma (2σ) (Gansecki et al., 1998).

Major-element analyses

The fragments of each obsidian sample were mounted in epoxy blocks and polished. Major-element analyses were performed at University of Toronto using a Cameca SX-50 electron probe microanalyzer (EPMA) at 15 kV accelerating voltage, 6 nA beam current, and a

10μm beam diameter. Standardization was achieved using mineral and glass standards and variation between different analytical runs was monitored with the Old Crow tephra glass shards (Preece et al., 2011).

Laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) analyses

Trace element analyses on individual fragments of obsidian were performed by LA-ICP-MS in the Department of Geography and Earth Sciences, Aberystwyth University, Wales, using a Coherent GeoLas ArF 193 nm Excimer LA system coupled to a Thermo Finnegan Element 2 sector field ICP-MS. Trace element data were collected using 20 μm ablation craters. Laser fluence was 10 Jcm^{-2} at a repetition rate of 5 Hz for a 24 second acquisition. The minor ^{29}Si isotope was used as the internal standard, with SiO_2 (determined by EMPA) used to calibrate each analysis, after normalization to an anhydrous basis. The NIST 612 reference glass was used for calibration, taking concentrations from Pearce et al. (1997). A fractionation factor was applied to the data to account for analytical bias related to the different matrices of the reference standard (NIST, a soda-lime synthetic glass) and the sample (natural rhyolites). For further explanation of this factor as well as ICP-MS and laser operating conditions see Pearce et al. (2011, 2014), and references therein. Ablation into phenocrystic material can be recognized by anomalous concentrations of particular elements (e.g. high Sr when ablating into feldspar, high Zr from zircon) and where these were noted data have been edited to leave only the analyses of pure glass phases following methods described by Pearce (2014) and Pearce et al. (2014). For both LA-ICP-MS instruments, the MPI-DING reference glass ATHO-G (Jochum et al., 2006) was analysed as an unknown under the same operating conditions at the same time on four separate days. The Aberystwyth ATHO-G data shows that the accuracy of these analyses is typically within ±3–5 % and precision is between ±5–10 % based on analyses of ATHO-G conducted over several days at the same time as the analyses of the Carpathian obsidians in November 2015. Precision generally varies with concentration (worse at lower concentrations) as is expected.

Results

Fission-track data

The fission track ages shown in **Table 1** are based on three separate irradiations. Size-frequency plots of the long-axis of fission tracks are shown in **Fig. 4**. Ages obtained on the internal standard, included in each can, are within 1σ of its ^{40}Ar/^{39}Ar age and indicate an acceptable estimate was obtained for the age of each sample, including the neutron fluence that each sample received during the irradiation. Four samples have been corrected for partial track fading (PTF) by the ITPFT method (size-frequency curves for the spontaneous and induced fission tracks are coincident; $D_s/D_i = 1.00$**, Table 1**) and two samples by the DCFT method, the presence of PTF being demonstrated by the offset between the spontaneous and induced fission tracks **(Fig. 4 a, b**).

Three of the ITPFT samples date an interval of rhyolitic volcanism in the Zemplín area at 12.45 ± 0.40 to 11.62 ± 0.25 Ma (**Table 1**). These FT ages are younger than previously obtained FT ages (17.8 – 13.7 Ma) from the Zemplín area, but they partially overlap the younger ages (16.6 – 12.1 Ma) obtained on obsidian samples from the southern Tokaj region (Bigazzi et al., 1990, 2000). On the other hand, these ITPFT ages compare well with age estimates on co-existing biotite and whole rock K-Ar ages (see review paper Pécskay et al., 2006, and citations therein; and/or Bačo et al., 2017) and suggest a considerably tighter age interval of rhyolitic volcanism in the Zemplín – Tokaj region compared to that which is commonly presented, specifically, 16 – 10 Ma (Pécskay et al., 2006).

Two obsidian samples from Cejkov were dated, involving three separate irradiations and two different approaches to correction for PTF. All ages are significantly younger than the obsidian samples from Hraň, Viničky, and Brehov and range from 5.49 ± 0.14 to 8.34 ± 0.20 Ma. They are considerably younger than previously published K-Ar ages for Cejkov rhyolites and obsidian (see Discussion). Interestingly, the size-frequency curves for Ce-1 and Ce-2 (**Fig. 4 a, b**) are unimodal, showing no secondary peaks that would indicate a complex thermal history. These facts can be explained by the complete resetting of the fission-track clock of the Cejkov obsidian samples sometime after emplacement of its lava flow. The timing of this resetting event is given by their FT ages (**Table 1).** The culprit in this case is most likely a large wildfire during which temperatures can exceed 500°C, enough to anneal fission tracks in obsidian in a single day if placed at or near the ground surface (Westgate et al., 2021).

Obsidian sample UT2422 (Br-1) could not be dated by the FT methods used in this study because of the bimodal size distribution of its spontaneous tracks (**Fig. 4c**), which suggests that the obsidian sample was subjected to a thermal event subsequent to its solidification. This bimodality could be explained by a lava flow burying an older flow and in the process heating and partially annealing latent fission tracks in the older lava flow. Alternatively, because sample Br-1 has been reworked into Quaternary surface deposits, the heat source may again be a large forest fire.

Composition of obsidians

New chemical analyses on the Carpathian obsidian samples are given in **Table 2**. Because geologists have overlooked the importance of obsidians over the past 45 years, and because archaeologists have analysed only an eclectic set of elements in their provenance studies, a comprehensive geochemical study focused on their genesis is still not available. Major-element analysis sets have been published (Šalát and487Ončáková, 1964; Kaminská and Ďuďa, 1985) but are incomplete and not considered in this study. Some representative analyses of the surrounding rocks of the ZVM (Konečný, 2010) are compared to the obsidian analyses of this report.

Geochemically, the ZVM obsidians belong to typical volcanic calc-alkaline rocks with high potassium (**Fig. 5a**). Their SiO_2 content varies in a narrow range from 76.4 to 77.5 wt.%, while the surrounding host rocks (rhyolites, dacites ± andesites) have silica contents from 65.9 to 77.4 wt.% which reflects their fractional character. The chemical composition of the obsidian samples, recalculated for the normative values of Q (quartz), P (plagioclase) and A (K-feldspar), confirms their rhyolitic composition in the classification diagram QAP of Streckeisen (1976) (**Fig. 5b**). The normative composition of the host rocks shows a wider compositional range from rhyolites to dacites, mirroring prevalence of plagioclase within some of the samples. Calculated Aluminum Saturation Index (ASI – molar ratio $Al_2O_3/(CaO+Na_2O+K_2O)$ = 1.05 ~ 1.15) indicates their mildly peraluminous character and possible limited coexistence of hornblende and pyroxene with peraluminous magma which is in accordance with microscopic observations (**Fig. 5c**). The values of the ratio Rb/Sr = 2.13 ~ 3.46 indicate a significant differentiation of these volcanic rocks, which is not so pronounced in most of the surrounding rocks which have Rb/Sr = 0.57 ~ 1.12. Evolved, differentiated nature of the ZVM rhyolite/obsidian magma with qualified homogeneous composition of the studied obsidians is well documented in the TAS diagram (Total Alkali Silica; Cox et al., 1979; Middlemost, 1994) where projection points of the average values form a narrow field within the most fractionated rhyolites, while the host rocks scattered over the broad dacite – rhyolite area (**Fig. 5d**). The ZVM obsidians are classified as a typical mixed I/S-type volcanic rock having a crustal/mantle origin, which is detectible in the Na_2O vs. K_2O classification diagram where their projection points fall on the interface of the I/S-type mixed magmatites (Chappell and White, 1992). The relatively increased values of FeO^t (0.76 ~ 0.89 wt.%) along with decreased values of MgO (0.03 ~ 0.07 wt.%) in the ZVM obsidians, as well as the surrounding host rocks, indicate their general ferroan character in the sense of Frost et al. (2001). The trace elements composition of the ZVM obsidians is well documented in Zr/TiO_2 vs. Nb/Y diagram, which is essentially a proxy for the TAS classification diagram, where Nb/Y is a proxy for alkalinity (Na_2O+K_2O) and Zr/TiO_2 is a proxy for silica (Pearce, 1996). All analysed obsidian samples lie in the evolved acidic rhyolitic rocks field, sub-alkaline character, whereas part of host rocks has an affinity with the intermediate rocks. Normalized REE patterns of studied samples show a uniform distribution trend with a pronounced negative Eu anomaly, La_N/Yb_N = 3.43 ~ 7.17 and partially elevated HREE values compared to surrounding rhyolite and dacite rocks. Their C1 chondrite normalized REE patterns fall on the boundary between "hot-dry-reduced" and "cold-wet-oxidized" magmas (Bachmann and Bergantz, 2008) reflecting genesis of magma from mantle and crust sources (**Fig. 5e**). The Carpathian obsidians and their host rhyolite and dacite rocks represent typical products of a volcanic arc.

Discussion

Obsidian dating

In the past, the age of the ZVM obsidians was mostly interpreted on the basis of the isotope dating results from volcanic rhyolite and rhyodacitic rocks. Naturally, there exist common lithostratigraphic and/or biostratigraphic determinations from sedimentary sequences within the surrounding East Slovakian Basin (Baňacký et al., 1989; Vass et al., 1991). Authors compiled traditional lithostratigraphic columns of the sedimentary deposits, including intercalated tuffitic layers, but because the Zemplínske vrchy Mts. form a tectonic horst, correlation from the basin to the ZVM is sometimes unclear. K-Ar dating of biotites and whole rhyolite rocks (WR) provided a wide age interval ranging from 15.3 ±2.0 Ma to 10.6 ±2.0 Ma (Bagdasarjan et al., 1968, 1971; Vass et al., 1971, 1978). These age estimates were obtained during the basic mapping study of the East Slovakian Basin on the Slovakian side of the Zemplín – Tokaj area. Authors have suggested there is either a long-lasting volcanism of Langhian to Tortonian (Badenian to Sarmatian) age or two separate volcanic phases. Recent direct dating of obsidians using the K-Ar method (Bačo et al., 2017) did not shed light on this problem. These authors presented the following ages: Brehov obsidian 12.45 ±0.92 Ma; Cejkov obsidian 13.48 ±0.72 Ma; Hraň obsidian 13.51 ±0.78 Ma; Viničky obsidians 13.52 ±0.81 Ma and 11.04 ±0.34 Ma (perlitized obsidians 12.12 ±0.47 Ma and 11.19 ±0.53 Ma). K-Ar ages of the rhyolitic rocks (on biotites and WR) brought more or less a comparable age spectrum from 14.6 ±0.8 Ma to 10.5 ±0.4 Ma for the Miocene volcanics of the Tokaj Mts. of NE Hungary (Balogh and Rakovics, 1976; Balogh et al., 1983; Pécskay et al., 1986, 2006). Interestingly, the rhyolites from the obsidian locality Erdőbénye yielded very similar ages of 12.2 ±0.4 Ma and 11.5 ±0.5 Ma (Pécskay et al., 1986) which fit well with the obsidian FT dates of this study.

Pioneer work dealing with the application of obsidian fission-track dating as an aid to locate provenance (Durrani et al., 1971) presented obsidian FT data from an archaeological locality at Borsod in NE Hungary. The obtained ages (3.86 ±0.24 Ma and 3.37 ± 0.27 Ma) have no geological importance because it is believed that the Pliocene was a time of volcanic quiescence in the subject area, and the nearest alkali basalt volcanism with a comparable age is more than 130 km to the west in the Nógrád-Southern Slovakia area (Pécskay et al., 2006), and/or these young ages probably reflect partial annealing (heat effect). Due to the absence of compositional data on the Borsod obsidians, little can be said about their relation to the standard classification of Carpathian obsidians in the Zemplín – Tokaj area. The first FT obsidian data from the ZVM was published by Repčok (1977) with the Viničky obsidian age of 11.1 ±0.8 Ma. Later Repčok et al. (1988) published FT age of 14.2 ±0.5 Ma for Hraň obsidian. Systematic work on the FT age of obsidians from most of the geological and archaeological localities of the Zemplín – Tokaj area (Bigazzi et al., 1990, 2000) resulted in varied age intervals. The obtained ages are: ***1***) in the Zemplín area ages range from 17.83 ±1.13 to 13.71 ±0.82 Ma with main peak at 15.5 Ma; ***2***) in the Tokaj area obsidians ages range from 16.63 ±1.35 to 12.15 ±0.73 Ma with the main peak at 15.2 Ma. Another age data set gives a younger interval of 10.38 ±0.77 to 8.27 ±0.69 Ma with a peak at 9.5 Ma. Bigazzi et al. (1990, 2000) accepted that general agreement with the K-Ar ages of the associated rhyolites is poor, though there are some exceptions. However, a benefit was that they confirmed an "archaeological" Upper Paleolithic age (ca 28 000 years BP) related to human activity by FT dating artifacts belonging to the obsidian stone industry, previously documented by radiocarbon dating. Noteworthy, is the identification of an enigmatic thermal event before 8.8 ~ 8.3 Ma which probably reflects resetting of magmatic age due to the effect of a large wildfire (possibly the same event that affected Ce-2 = UT2423, **Table 2**).

Composition and provenance

The geochemical provenance of obsidian artefacts has long been an effective method to improve understanding of the trade routes and socioeconomic context of past populations (Cann and Renfrew, 1964; Williams-Thorpe et al., 1984; Torrence et al., 2009; Freund, 2013; Orange et al., 2017; and citations therein). Since archaeologists began an extensive use of obsidian geochemistry for sourcing studies, the number of works dealing with the Zemplín – Tokaj area obsidians has increased. The early work of Renfrew et al. (1965) provided the first study on the characterization of the Carpathian obsidian geochemical provenance. These authors compared Carpathian obsidian samples from archaeological localities at Derekegyhaza, Herpaly and Vinca to those present in their Aegean study area and noted that "*geochemical analyses give no grounds whatever for distinguishing between the Carpathians obsidians and those from Melos, or those of south Anatolia…*". The Carpathian obsidian sources were successfully discriminated in this way by Williams-Thorpe et al. (1984). These authors distinguished and graphically displayed provenance sources such as: "*Carpathian-1*" originating from the Viničky (Szöllöske) and Malá Tŕňa = Zemplín localities; "*Carpathian-2a*" coming from the occurrences at Csepegő Forrás, Tolcsva, Olaszliszka and Erdőbénye located in the southern Hungarian – Tokaj sector; and "*Carpathian-2b*" representing redeposited obsidians from Erdőbénye. Samples in this study fall within the Carpathian-1 and Carpathian-2 interface of Williams-Thorpe et al. (1984) (**Fig. 6**). Due to the congruent and homogeneous composition of the studied obsidians, their projection points form a small well-defined field in this plot, as they do on all the geochemical diagrams (Fig. 5). The increasing number of analysed archaeological and geological obsidian samples from the various Zemplín – Tokaj localities enabled a more detailed distinction of the source localities based on their trace elements contents. Rosania et al. (2008) proposed two Harker diagrams, namely Sr vs. Zr and U vs. Rb for this purpose, where samples from Viničky were determined as a separate group *Carpathian-1a* (***C1a***) and samples from Cejkov as *Carpathian-1b* (***C1b***). Authors (Rosania et al., 2008) have confirmed the legitimacy of the separation of groups C2a and C2b from the Hungarian Tokaj area, the obsidians from Rokosovo in the Ukraine, labelled as *Carpathians-3* (*C3*), the Central Slovakia Neovolcanic Field obsidians from Szabova skala are classified as *Carpathians-4* (*C4*), and the obsidians from Tokaj Bodrogkeresztur as *Carpathians-5* (*C5*). Noteworthy, that *C4* and *C5* obsidians have not been used in the stone industry because of their hydrated perlite character and/or small size (tiny shards). However, in this study ICPMS analyses of the ZVM obsidians demonstrate the compatibility of analytical determinations for strontium, rubidium and zirconium but not uranium and thorium analyses, which were done by XRF or NAA (Rosania et al., 2008) (**Fig. 7**). Prompt Gamma Activation Analysis (PGAA) is currently a very effective and non-destructive technique applied to the Carpathian obsidians, especially for archaeological artefacts where preservation of exhibited show-pieces is a matter of principle. Useful data from the the Zemplín – Tokaj obsidians can be found in Kasztovszky et al. (2014, 2018). Published analyses of the Viničky and Cejkov obsidians (Kilikoglou et al., 1996; Oddone et al., 1999; Bigazzi et al., 2000; Orange et al., 2016; Rózsa et al., 2006) are provided in Fig. 7 for comparison purposes. Although there is some variability of these trace elements analyses (especially in Th and U) due to different methods used (XRF, NAA and ICP MS) and inter-laboratory bias, it is obvious that the Slovakian (*C1*) obsidians are different from the Hungarian (*C2*) ones. Furthermore, data from this study do not allow discrimination between *C1a* and *C1b,* as proposed by Rosania et al. (2008), because the individual analyses have trace element contents that overlap each other within one standard deviation. Bonsall et al. (2017) proposed a simple ternary (Zr-Sr-Rb) provenance discrimination diagram for sourcing archaeological obsidian artefacts from the northern Balkan Peninsula on the basis of evaluation of the chemical composition of Carpathian obsidians (cf. Rosania et al., 2008). The composition of samples defined in this study fit well with the Carpathian-1 (*C1*) obsidians, and confirms the correctness of the defined *C1* field for the unknown obsidians assigned by Bonsall et al. (2017) (**Fig. 8**). Orange et al. (2016) published a new optimized LA-ICP-MS protocol for sourcing obsidians using the Carpathian obsidian data. Their analyses compare favourably with those of this study, and although they did not distinguish in detail the individual Carpathians sources (*C1*, *C2*, *C3*), personal communication and localization of their analysed samples allowed the separation of *C1*, *C2* and *C3* sources (**Fig. 9**). Because the data presented in this study do not show any major differences in composition of the obsidians, it is recommended that the common provenance label *Carpathian-1* (*C1*) be used for all the studied localities given the current state of knowledge. In addition, there is congruency not only in the chemical composition of the obsidians, but also in the results of a comprehensive physical study, including µCT scanning, X-ray spectroscopy, Raman spectroscopy, Mössbauer spectroscopy, positron annihilation lifetime spectroscopy (PALS), thermogravimetric analysis (DTA), Fourier-transform infrared spectroscopy (FTIR), magnetic susceptibility, including thermomagnetic properties, electron (spin) paramagnetic resonance (ESR/EPR), and SQUID magnetometry. A high degree of uniformity exists amongst these obsidians (Kohút et al., 2019).

Conclusions

Newly obtained isothermal plateau fission-track ages of the Carpathian obsidians (localities: Brehov, Hraň and Viničky) define a narrow age interval of 12.45 ±0.45 to 11.62 ±0.25 Ma for rhyolitic volcanism in the ZVM. These ages differ from the commonly assumed larger age range of 16 ~ 10 Ma. This short-time period of 12 ± 0.5 Ma suggests a monogenic volcanic evolution in the ZVM area. Geochemically, the ZVM obsidians belong to the acid, fractionated volcanic peraluminous rocks of the high potassium calc-alkaline rhyolite series, having a ferroan character. The Carpathian obsidians and their host rocks represent typical magmatic products of a volcanic arc. They originated through multi-stage magmatic processes involving mixed mantle and crustal sources. The chemical compositions of the ZVM obsidians are very similar; no essential differences exist that would justify a distinction between the Viničky (formerly assigned as *C1a* provenance) and Cejkov (*C1b*) obsidian localities as separate sources for the archaeological stone industry. Given the general uniformity within the Slovakian obsidians from the Zemplín area it is recommended that the common provenance label ***C1*** be used without any additional sourcing specification.

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Figure captions and Table explanations

Fig. 1: Simplified geological maps and positions of studied samples. **a**) Position of the ESNF and studied area within the Western Carpathians in Slovakia. *Abbreviations*: CWC – the Central Western Carpathians, OWC – the Outer Western Carpathians, CSNF – the Central Slovakians Neovolcanic Field, ESNF – the Eastern Slovakian Neovolcanic Field; Red lines denote tectonic lines dividing three principal tectonic units (Tatricum, Veporicum and Gemericum) in CWC. **b**) Simplified and modified geological map of the ZVM based on the published map by Vass et al. (1991).

Fig. 2: Macro and micro view of the studied obsidian samples; **a**) typical shape of obsidian nodule from the Brehov-2 (Br-2) locality, scale bar 5 cm; **b**) banded texture in sample Br-1; **c**) phenocryst of biotite surrounded by parallel alignment of trichites in sample V-1, view from polarised microscope; **d**) trichites and fine microlites in sample Br-1; **e**) large phenocryst of biotite in sample Hr-1, back scattered electrons image (BSEI) from electron micro probe (EMP); **f**) linear alignment of trichites in sample V-1, BSEI.

Fig. 3: Induced fission tracks in the studied Carpathian obsidians, as seen using an optical microscope. **a**) sample UT2400 (V-1) the mean track diameter is 6.53 ± 0.07 μm; **b**) sample UT2401 (Br-2), the mean track diameter is 6.38 ± 0.07 μm. Samples are etched in 24% HF to give an average for the long dimension of the fission tracks in the range of 6 to 8 μm. Areal FT density is determined at a magnification of 500x and measurements for the partial track fading correction are made at a magnification of 1000x.

Fig. 4: Size-frequency plots of the long-axis of fission tracks in obsidians from the Carpathians demonstrating partial track fading; the spontaneous tracks are smaller than the induced tracks. All samples have not been subjected to any heat pre-treatment. With the exception of Br-1, they show unimodal curves suggesting a simple thermal history – no heating event affected them since their solidification. This is true of samples **d**, **e**, and **f** but not **a,** and **b**, whose spontaneous fission tracks have been totally reset (see text). DCFT ages were not determined for samples **d**, **e**, and **f**; ITPFT ages are available for these samples (**Table 1**). Sample UT2422 (Br-1) indicates a more complex thermal history (see text).

Fig. 5: Diagrams for geochemical categorization of the studied obsidians and their rhyolitic host rocks. **a**) AFM diagram [alkali (Na_2O+K_2O) – total iron FeO^t – magnesium MgO] after Irvine and Baragar (1971) documenting affiliation of the ZVM obsidians to calk-alkaline rhyolitic series; **b**) QAP classification diagram (Streckeisen, 1976) based on the normative content of quartz – alkali feldspar – plagioclase; **c**) molar values A/NK = $Al_2O_3/(Na_2O+K_2O)$ vs. A/ANK = $Al_2O_3/(CaO+Na_2O+K_2O)$ [commonly referred to as the Aluminum Saturation Index – ASI] show mild peraluminosity of the ZVM obsidian; **d**) TAS diagram (Cox et al.,

1979; Middlemost, 1994) indicate their fractionated rhyolitic character; **e**) The C1 chondrite normalized spider diagram of the ZVM obsidians and host rocks.

Fig. 6: Discrimination diagram for the Carpathian, other European and Near Eastern obsidians after Williams-Thorpe et al. (1984). *Explanation:* Acıgöl obsidian localities are known today as: Bogazköy obsidian, Kocadag obsidian, Güneydag obsidian, Korudagi obsidian and/or Kuzay and Kaleci obsidian deposits (Druitt et al., 1995), whereas the Çiftlik obsidians come from Göllü Dağ (Göllüdağ) massif representing various localities: 1- Bozköy Ilbiz-Meneninyeri; 2- Gösterli; 3- Büyük Göllü; 4a- Birtlikeler; 4b- Ekinlik - Kaletepe deresi 3; 5- Kaletepe dere 2 Eriklidere; 6- Bozköy Boztepe; 7- Sırca Deresi, and Kayırlı that were distributed in the Fertile Crescent (Binder et al., 2011).

Fig. 7: Bivariate plots after Rosania et al. (2008) for detail discrimination of the Carpathian obsidians. **a**) Sr vs. Zr and **b**) U vs. Rb. *Abbreviations: C1a* – Viničky, *C1b* – Cejkov, *C2a* – Erdőbénye, Tolcsva, *C2b* – Mád, Bodrogkeresztur, *C3* – Rokosovo, Rakovets (Ukraine), C4 – Szabova skala (Central Slovakia Neovolcanic Field), *C5* – Tokaj - Bodrogkeresztúr. LA-ICP-MS data from this contribution do not confirm defined *C1a* and *C1b* fields in general.

Fig. 8: Ternary Zr – Sr – Rb diagram according Bonsall et al. (2017). *Abbreviations: C1* – Slovakia, *C2* – Hungary, *C3* – Ukraine. Data from this study approve legitimacy of suggested discrimination.

Fig. 9: Binary plot log(Sr/Nb) vs. log(Cs/Nb) after Orange et al. (2016) for the Mediterranean area and the Carpathian obsidians. Noteworthy is the fact that data from identical methods (LA-ICP-MS) show excellent conformity.

Table 1: Fission-track ages of Carpathian obsidians from the Zemplín area, Slovakia

Table 2: Average chemical composition of studied Carpathian obsidians from the Zemplín area, Slovakia

Appendix:

AF-1 Schematic map with localization of the archaeological and geological obsidian localities from the Zemplín – Tokaj area. *Abbreviation*: ZJ – Zemplínske Jastrabie.

GPS localization of studied samples.

Sample	locality	Latitude (°N)	Longitude (°E)
Br-1	Brehov–1	48°29′40.70″	21°47′50.10″
Br-2	Brehov–2	48°29′42.40″	21°48′15.00″
Ce-1	Cejkov–1	48°28′14.60″	21°47′12.50″
Hr-1	Hraň–1	48°31′08.60″	21°47′14.60″
V-1	Viničky–1	48°24′04.90″	21°44′16.70″

Fig. 1

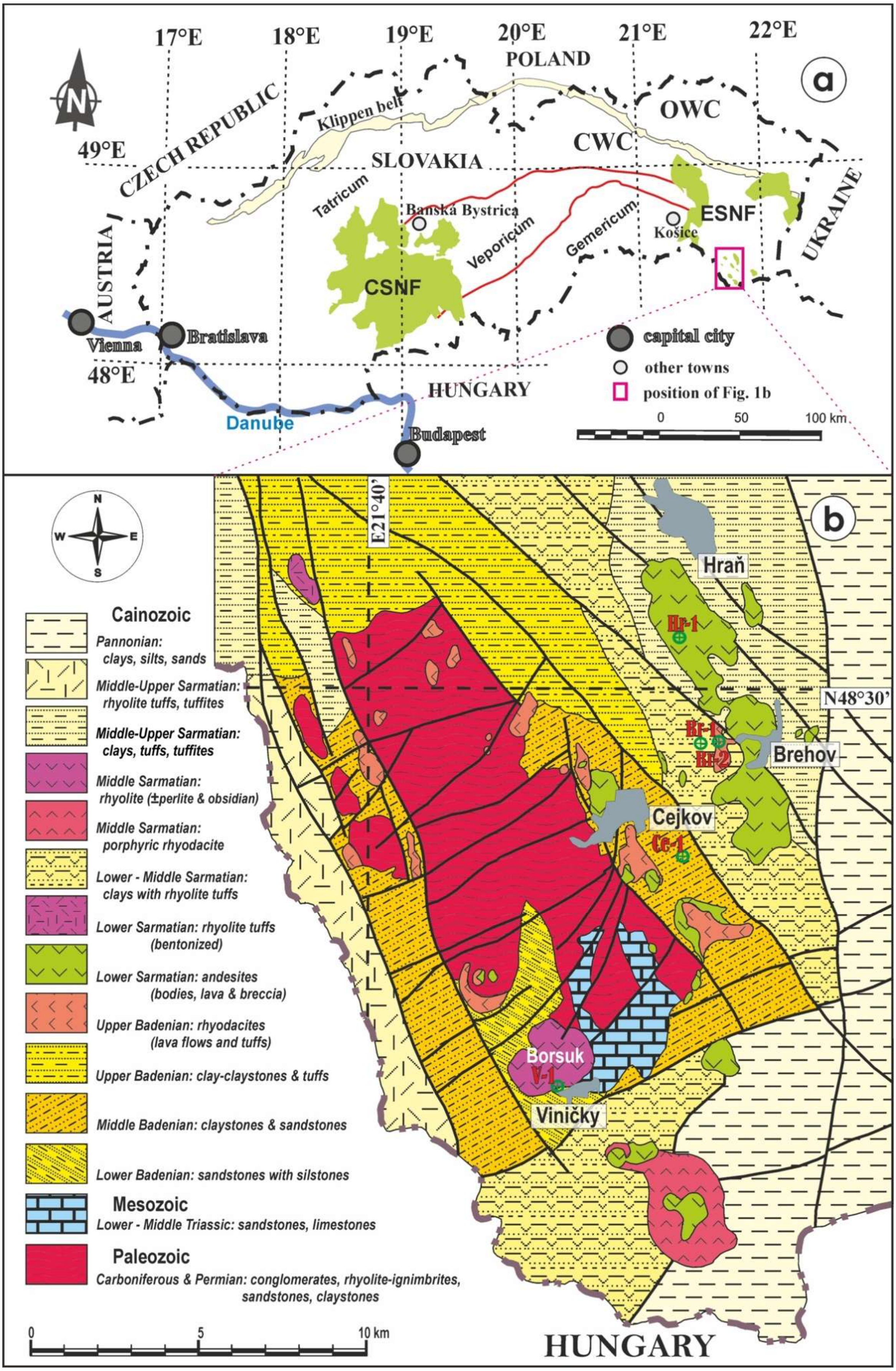

a
17°E
18°E
19°E
20°E
21°E
22°E
49°E
48°E
N
POLAND
CZECH REPUBLIC
Klippen belt
OWC
CWC
SLOVAKIA
Tatricum
Banska Bystrica
Veporicum
Gemericum
Košice
ESNF
UKRAINE
AUSTRIA
CSNF
Vienna
Bratislava
HUNGARY
Danube
Budapest
capital city
other towns
position of Fig. 1b
0
50
100 km
b
N
W
E
S
E21°40'
N48°30'
Hraň
Hr-1
Hr-1
Hr-2
Brehov
Cejkov
Ce-1
Borsuk
V-1
Viničky
Cainozoic
Pannonian: clays, silts, sands
Middle-Upper Sarmatian: rhyolite tuffs, tuffites
Middle-Upper Sarmatian: clays, tuffs, tuffites
Middle Sarmatian: rhyolite (±perlite & obsidian)
Middle Sarmatian: porphyric rhyodacite
Lower - Middle Sarmatian: clays with rhyolite tuffs
Lower Sarmatian: rhyolite tuffs (bentonized)
Lower Sarmatian: andesites (bodies, lava & breccia)
Upper Badenian: rhyodacites (lava flows and tuffs)
Upper Badenian: clay-claystones & tuffs
Middle Badenian: claystones & sandstones
Lower Badenian: sandstones with silstones
Mesozoic
Lower - Middle Triassic: sandstones, limestones
Paleozoic
Carboniferous & Permian: conglomerates, rhyolite-ignimbrites, sandstones, claystones
0
5
10 km
HUNGARY

Fig. 2

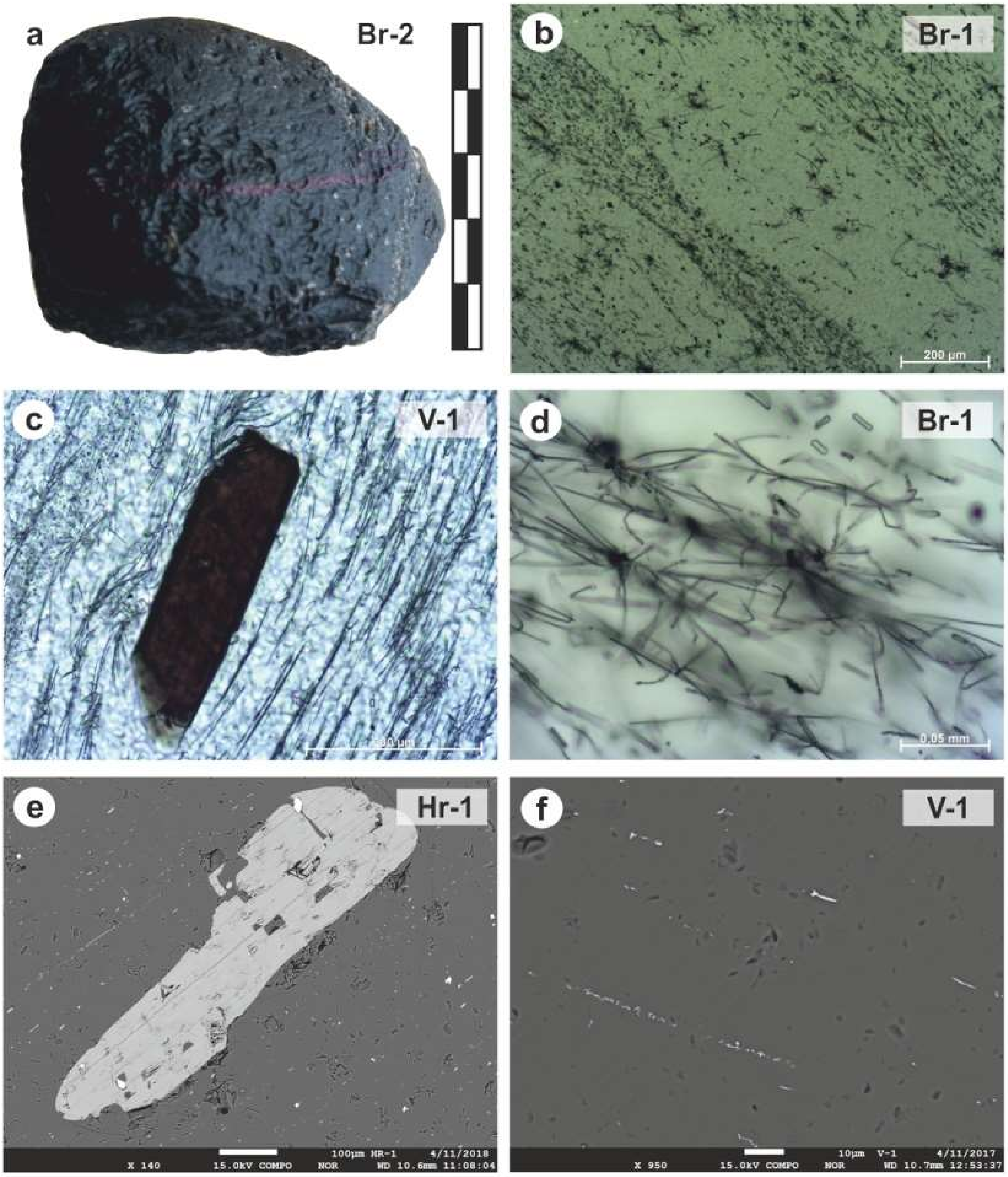

a
Br-2
b
Br-1
200 µm
c
V-1
d
Br-1
0.05 mm
e
Hr-1
100µm HR-1 4/11/2018
X 140 15.0kV COMPO NOR WD 10.6mm 11:08:04
f
V-1
10µm V-1 4/11/2017
X 950 15.0kV COMPO NOR WD 10.7mm 12:53:37

Fig. 3

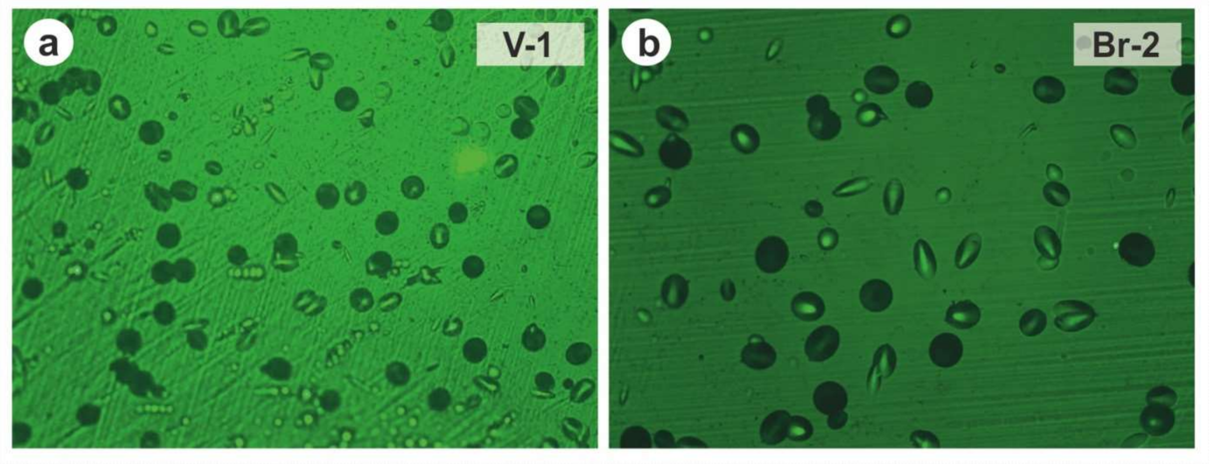

a
V-1
b
Br-2

Fig. 4

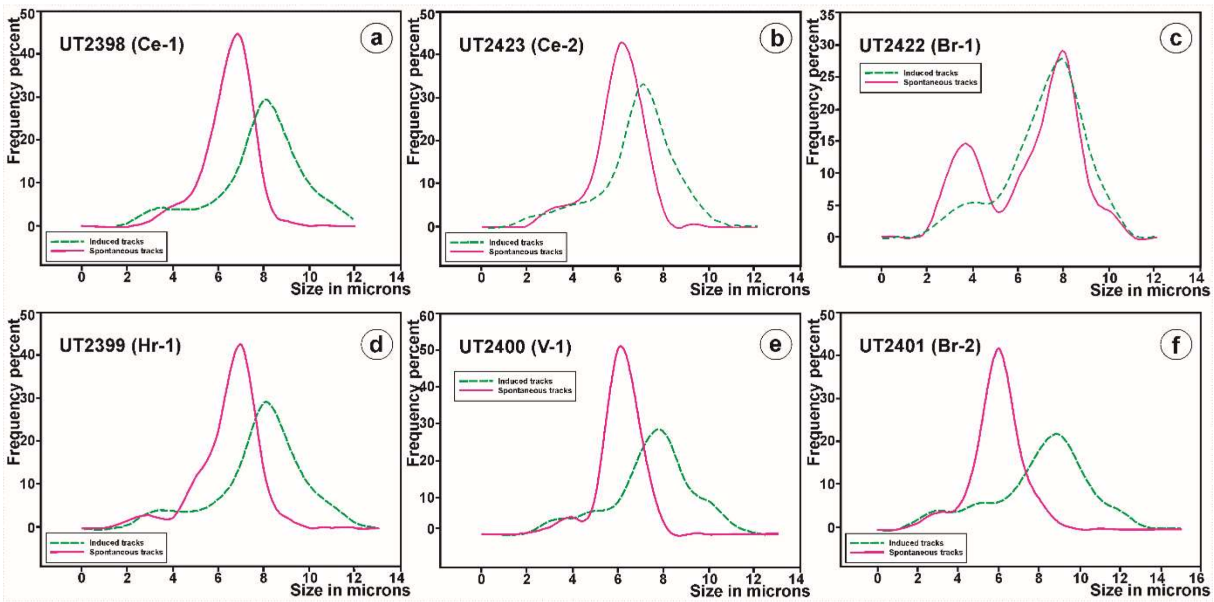

UT2398 (Ce-1)
a
UT2423 (Ce-2)
b
UT2422 (Br-1)
c
UT2399 (Hr-1)
d
UT2400 (V-1)
e
UT2401 (Br-2)
f
Frequency percent
Size in microns
Induced tracks
Spontaneous tracks
0
2
4
6
8
10
12
14
16
0
5
10
15
20
25
30
35
40
50
60

Fig. 5

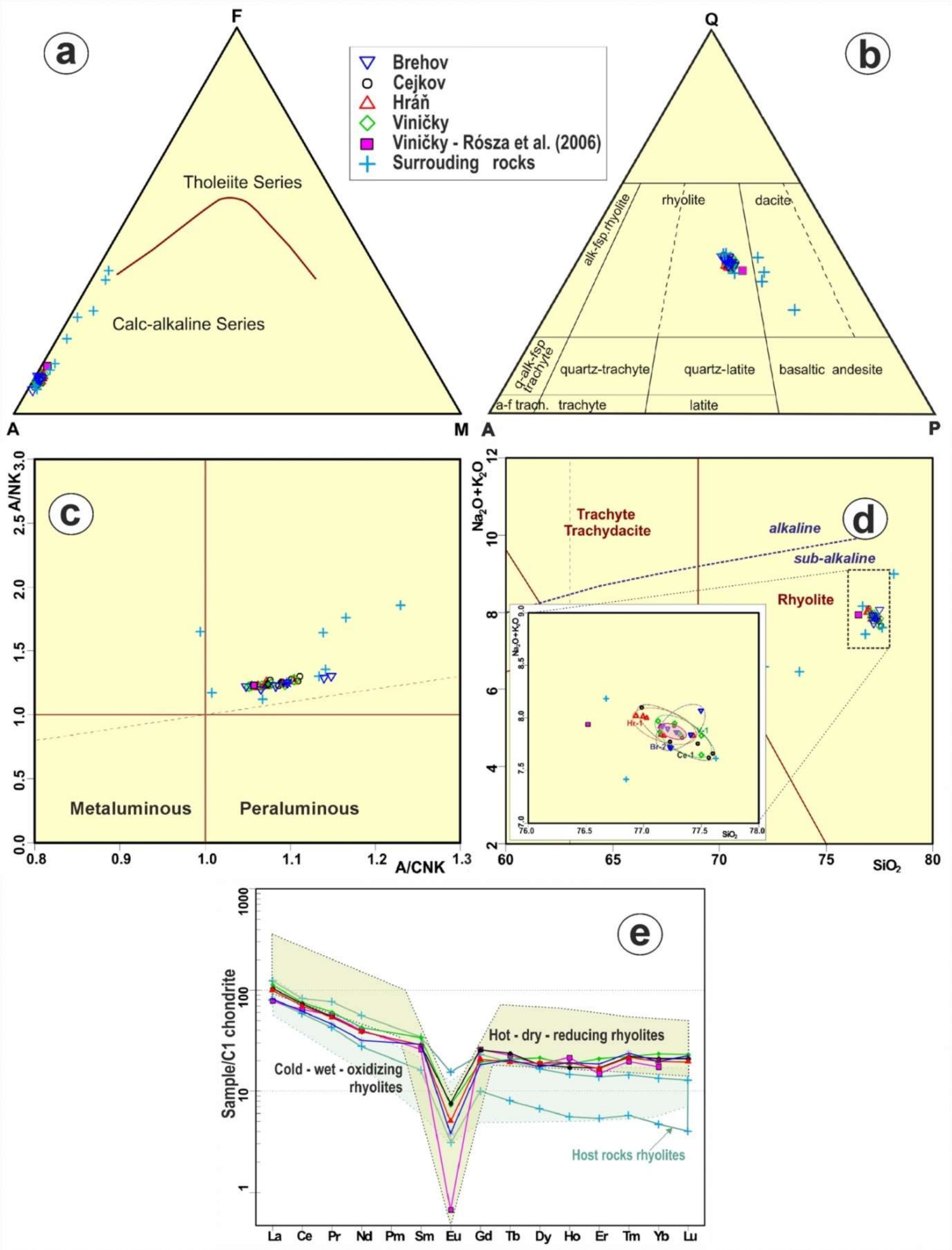

a
b
c
d
e
F
A
M
Q
P
Brehov
Cejkov
Hráň
Viničky
Viničky - Rósza et al. (2006)
Surrouding rocks
Tholeiite Series
Calc-alkaline Series
alk-fsp.rhyolite
rhyolite
dacite
q-alk-fsp trachyte
quartz-trachyte
quartz-latite
basaltic andesite
a-f trach.
trachyte
latite
A/NK
A/CNK
Metaluminous
Peraluminous
Na2O+K2O
SiO2
Trachyte Trachydacite
alkaline
sub-alkaline
Rhyolite
Hr-1
Br-2
Ce-1
V-1
Sample/C1 chondrite
Hot - dry - reducing rhyolites
Cold - wet - oxidizing rhyolites
Host rocks rhyolites
La Ce Pr Nd Pm Sm Eu Gd Tb Dy Ho Er Tm Yb Lu

Fig. 6

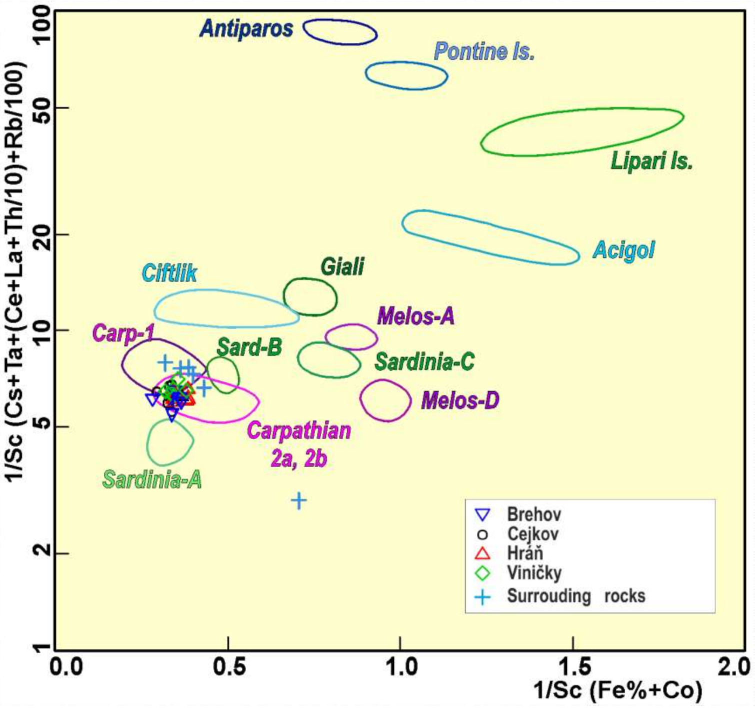

Antiparos
Pontine Is.
Lipari Is.
Acigol
Ciftlik
Giali
Melos-A
Carp-1
Sard-B
Sardinia-C
Melos-D
Carpathian 2a, 2b
Sardinia-A
Brehov
Cejkov
Hráň
Viničky
Surrouding rocks
1/Sc (Cs+Ta+(Ce+La+Th/10)+Rb/100)
1/Sc (Fe%+Co)
1
2
5
10
20
50
100
0.0
0.5
1.0
1.5
2.0

Fig. 7

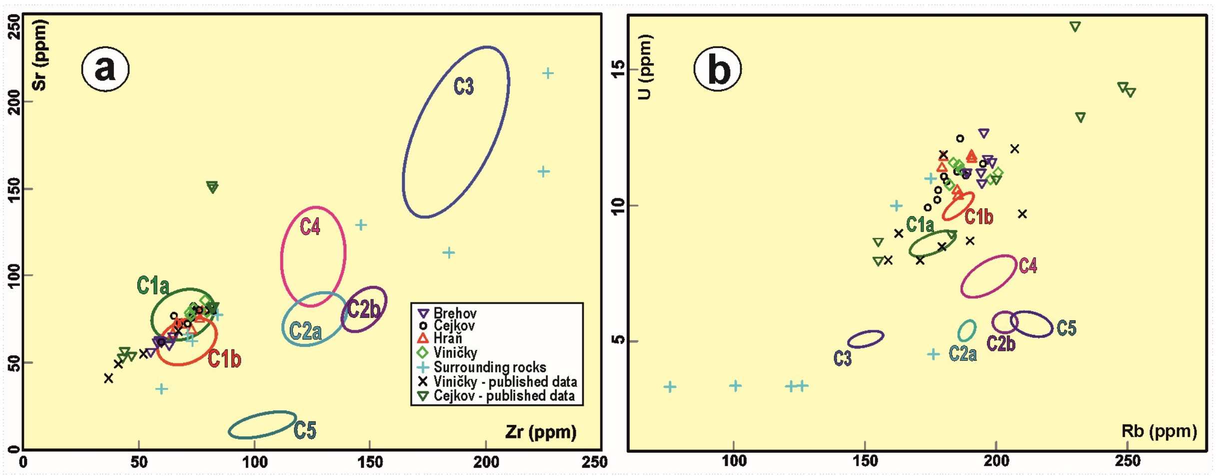

a
Sr (ppm)
Zr (ppm)
C1a
C1b
C2a
C2b
C3
C4
C5
Brehov
Cejkov
Hraň
Viničky
Surrounding rocks
Viničky - published data
Cejkov - published data
0
50
100
150
200
250
b
U (ppm)
Rb (ppm)
C1a
C1b
C2a
C2b
C3
C4
C5
5
10
15
100
150
200
250

Fig.8

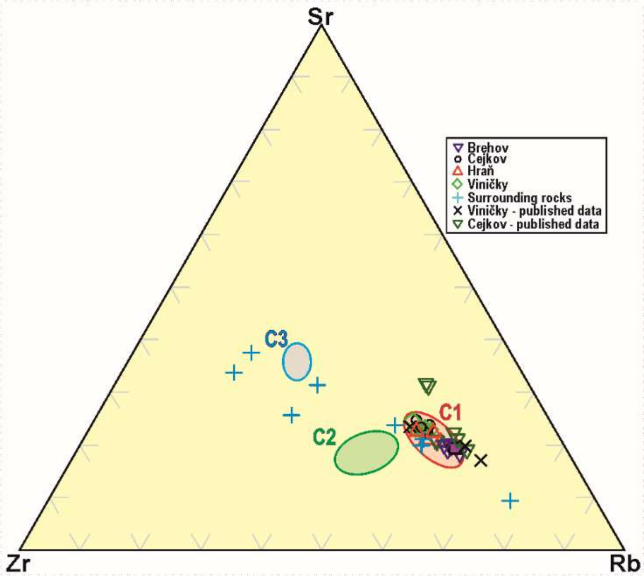

Sr
Zr
Rb
Brehov
Cejkov
Hraň
Viničky
Surrounding rocks
Viničky - published data
Cejkov - published data
C1
C2
C3

Fig. 9

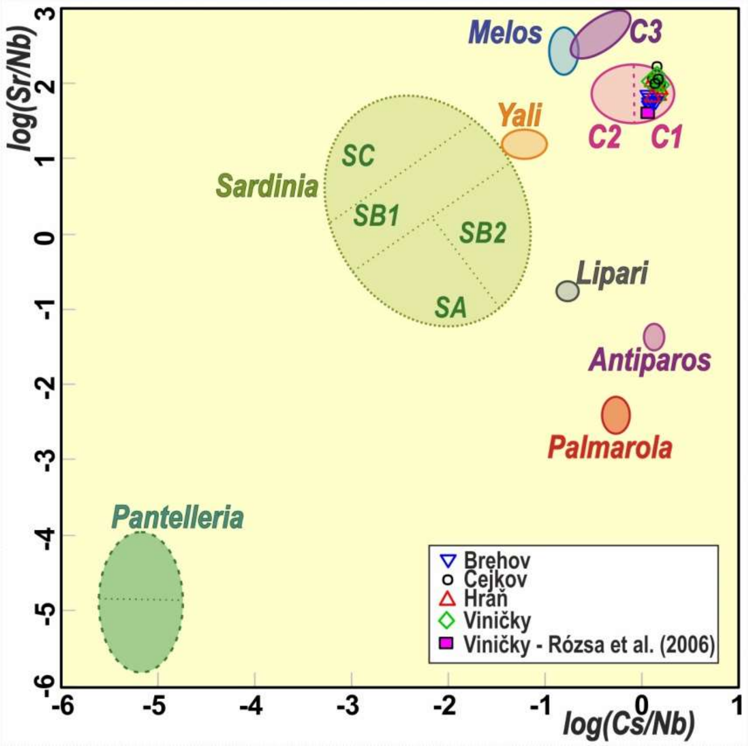

log(Sr/Nb)
log(Cs/Nb)
3
2
1
0
-1
-2
-3
-4
-5
-6
-5
-4
-3
-2
-1
0
1
Melos
C3
Yali
C2
C1
Sardinia
SC
SB1
SB2
SA
Lipari
Antiparos
Palmarola
Pantelleria
Brehov
Cejkov
Hraň
Viničky
Viničky - Rózsa et al. (2006)

Table 1

Table 1. Fission-track ages of some Carpathian obsidians from the Zemplin area, Slovakia

Sample number	Field number	Irradiation can	Correction method for partial track fading	Spontaneous track density (10^4 t/cm^2)	Corrected spontaneous track density (10^4 t/cm^2)	Induced track density (10^4 t/cm^2)	Track density on muscovite detector over dosimeter glass (10^5 t/cm^2)	Etching conditions HF:temp:time (%: ^{o}C: s)	D_s (µm)	D_i (µm)	D_s/D_i or $D_i/D_s$$^{\#}$	Age ± 1σ (Ma)
UT2398	Ce-1	Can 15-1	ITPFT	1.57 ± 0.05 (1111)		42.70 ± 0.48 (7968)	5.44 ± 0.05 (13928)	24: 23: 250	6.87 ± 0.10 [151]	6.67 ± 0.06 [764]	1.03 ± 0.02	6.21 ± 0.21
UT2398	Ce-1	Can 15-3	DCFT	1.48 ± 0.05 (932)	1.71 ± 0.06 (932)	54.20 ± 0.52 (10692)	5.05 ± 0.04 (12929)	24: 20: 230	6.00 ± 0.06 [255]	6.93 ± 0.07 [777]	1.16 ± 0.02$^{\#}$	4.96 ± 0.18
									Weighted mean and error of Ce-1			5.49 ± 0.14
UT2399	Hr-1	Can 15-1	ITPFT	3.73 ± 0.11 (1133)		50.70 ± 0.43 (14030)	5.44 ± 0.05 (13928)	24: 23: 250	7.27 ± 0.12 [202]	7.06 ± 0.08 [511]	1.03 ± 0.02	**12.45 ± 0.40**
UT2400	V-1	Can 15-1	ITPFT	2.90 ± 0.05 (3513)		40.30 ± 0.56 (5226)	5.44 ± 0.05 (13928)	24: 21: 270	6.53 ± 0.16 [117]	6.53 ± 0.07 [508]	1.00 ± 0.03	**12.19 ± 0.21**
UT2401	Br-2	Can 15-1	ITPFT	3.20 ± 0.05 (4170)		46.50 ± 0.55 (7075)	5.44 ± 0.05 (13928)	24: 21: 250	6.76 ±0.11 [204]	6.38 ± 0.07 [501]	1.06 ± 0.02	**11.62 ± 0.25**
UT2423	Ce-2	Can 16-1	DCFT	2.48 ± 0.05 (2708)	2.85 ± 0.05 (2708)	53.60 ± 0.61 (7695)	5.04 ± 0.04 (12887)	24: 22: 180	5.43 ± 0.08 [212]	6.24 ± 0.06 [737]	1.15 ± 0.02$^{\#}$	8.34 ± 0.20
Huckleberry Ridge Tuff, internal standard												
UT1366		Can 15-1	ITPFT	0.24 ± 0.01 (411)		21.80 ± 0.12 (35495)	5.44 ± 0.05 (13928)	24: 20: 180	6.24 ± 0.11 [105]	6.13 ± 0.07 [409]	1.02 ± 0.02	1.90 ± 0.16
UT1366		Can 15-3	DCFT	0.41 ± 0.01 (1413)	0.52 ± 0.01 (1413)	43.40 ± 0.26 (28695)	5.05 ± 0.04 (12929)	24: 19: 170	6.00 ± 0.08 [192]	7.69 ± 0.08 [589]	1.28 ± 0.02$^{\#}$	1.89 ± 0.19

Notes: The population-subtraction method was used (Westgate, 2015). Ages calculated using the zeta approach and $\lambda_D = 1.551 \times 10^{-10}$ yr^{-1} .
Zeta value is 311 ± 4 based on 7 irradiations at the McMaster Nuclear Reactor, Hamilton, Ontario, using the NIST SRM 612 glass dosimeter and the Moldavite tektite glass with an ^{40}Ar/^{39}Ar age of 14.808 ± 0.021 Ma (2σ) (Schmieder et al., 2018). Number of tracks counted is given in parentheses; number of tracks measured is given in square brackets.The fluence is obtained by multiplying the muscovite track density by 0.53×10^{10} based on 9 determinations. Age determinations are corrected for partial track fading using the isothermal plateau method (ITPFT) (Westgate, 1989) or the diameter correction (DCFT) method (Sandhu and Westgate 1995). Ds = mean long-axis of spontaneous tracks; Di = mean long-axis of induced tracks. ^{40}Ar/^{39}Ar age of Huckleberry Ridge Tuff is 2.003 ± 0.014 Ma (2σ) (Gansecki et al., 1998).

Table 2

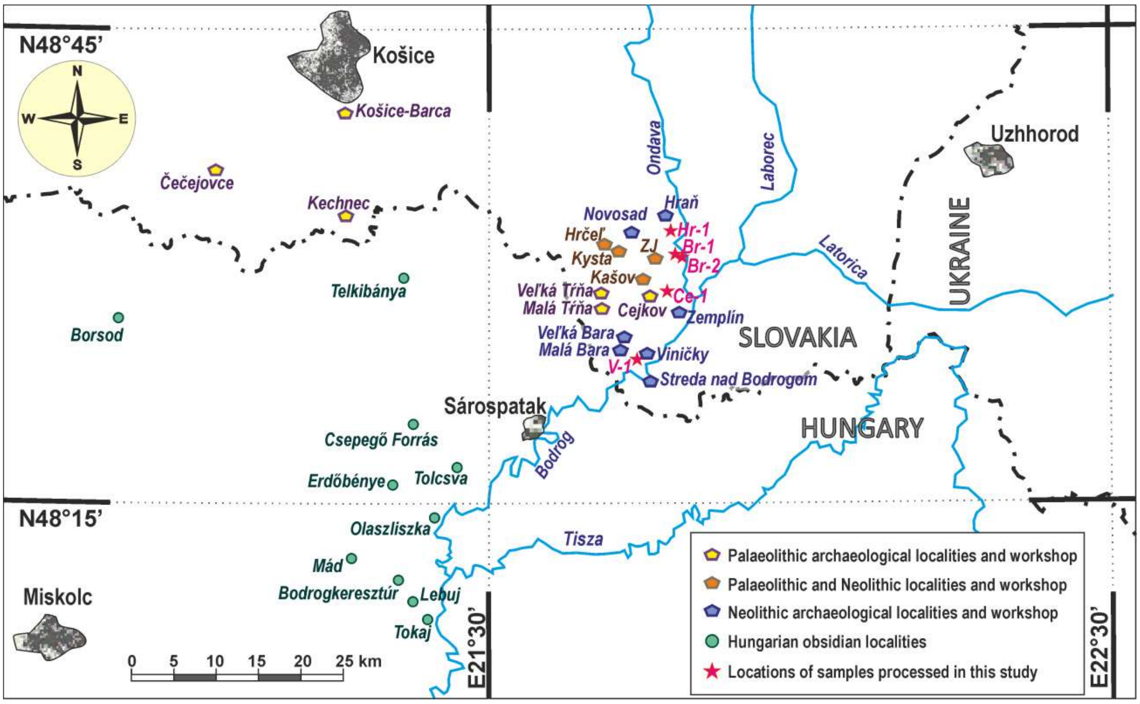
Table 2. Average composition of some Carpathian obsidians from the Zemplin area, Slovakia

	Cejkov (Ce-1)	Cejkov (Ce-2)	Brehov (Br-1)	Brehov (Br-2)	Viničky (V-1)	Hraň (Hr-1)
	UT2398	UT2423	UT2422	UT2401	UT2400	UT2399
SiO_2	77,30 ± 0,24	77,01 ± 0,17	77,06 ± 0,16	77,26 ± 0,15	77,30 ± 0,17	77,16 ± 0,18
TiO_2	0,10 ± 0,06	0,11 ± 0,03	0.10 ± 0,02	0,06 ± 0,04	0,04 ± 0,02	0,05 ± 0,03
Al_2O_3	13,00 ± 0,08	13,11 ± 0,09	13,18 ± 0,11	13,03 ± 0,13	12,98 ± 0,07	12,99 ± 0,09
FeOt	0,76 ± 0,06	0,84 ± 0,06	0,83 ± 0,05	0,80 ± 0,11	0,82 ± 0,08	0,89 ± 0,08
MnO	0,06 ± 0,02	0,05 ± 0,03	0,04 ± 0,03	0,11 ± 0,03	0,06 ± 0,04	0,08 ± 0,03
CaO	0,86 ± 0,08	0,89 ± 0,03	0,76 ± 0,04	0,79 ± 0,08	0,87 ± 0,07	0,86 ± 0,06
MgO	0,07 ± 0,03	0,06 ± 0,02	0,03 ± 0,01	0,06 ± 0,03	0,07 ± 0,02	0,07 ± 0,02
Na_2O	3,39 ± 0,13	3,42 ± 0,14	3,38 ± 0.10	3,45 ± 0,13	3,52 ± 0,08	3,46 ± 0,05
K_2O	4,42 ± 0,07	4,45 ± 0,08	4,56 ± 0,07	4,41 ± 0,08	4,33 ± 0,09	4,46 ± 0.01
Cl	0,07 ± 0,06	0,06 ± 0,02	0,06 ± 0,02	0,05 ± 0,04	0,05 ± 0,02	0,06 ± 0,04
H_2O_d	0,71 ± 0,39	0,74 ± 0.40	0,97 ± 0,41	0,60 ± 0,27	0,84 ± 0,38	0,17 ± 0,08
n	7	16	15	6	6	7
Rb	181 ± 5	nd	nd	195 ± 3	189 ± 8	185 ± 5
Sr	78,0 ± 3,5			61,4 ± 3,0	80,2 ± 3,0	72,2 ± 4,7
Y	37,2 ± 2,1			34,3 ± 3,0	37,8 ± 1,5	36,4 ± 1,7
Zr	72,8 ± 5,9			60,0 ± 3,5	75,9 ± 3,6	71,1 ± 5,3
Nb	10,1 ± 0,8			10,5 ± 0,6	10,8 ± 0,7	10,9 ± 0,5
Cs	7,43 ± 0,57			8,88 ± 0,50	7,92 ± 0,65	8,16 ± 0,78
Ba	546 ± 33			467 ± 24	567 ± 22	533 ± 26
Sc	3,62 ± 0,11			3,48 ± 0,10	3,58 ± 0,11	3,56 ± 0,12
Co	0,39 ± 0,04			0,51 ± 0,04	0,45 ± 0,05	0,50 ± 0,05
La	32,4 ± 1,8			25,4 ± 2,0	35,0 ± 1,7	30,8 ± 1,0
Ce	59,4 ± 3,5			49,5 ± 3,0	60,7 ± 1,6	56,1 ± 2,4
Pr	6,61 ± 0,59			5,61 ± 0,38	7,37 ± 0,77	6,54 ± 0,25
Nd	23,4 ± 3,5			19,0 ± 1,8	25,7 ± 2,8	23,2 ± 1,3
Sm	5,59 ± 1,33			5,66 ± 1,49	6,59 ± 0,88	5,54 ± 1,00
Eu	0,56 ± 0,25			0,28 ± 0,12	0,48 ± 0,28	0,37 ± 0,16
Gd	6,69 ± 1,26			4,72 ± 1,24	5,05 ± 0,80	5,36 ± 1,37
Tb	1,13 ± 0,33			0,97 ± 0,29	0,98 ± 0,19	0,92 ± 0,15
Dy	5,88 ± 1,27			5,62 ± 0,72	6,90 ± 1,61	6,10 ± 0,91
Ho	1,24 ± 0,14			1,38 ± 0,23	1,33 ± 0,29	1,37 ± 0,40
Er	3,54 ± 0,5			3,89 ± 0,72	4,40 ± 1,02	3,50 ± 0,53
Tm	0,71 ± 0,23			0,77 ± 0,13	0,71 ± 0,19	0,70 ± 0,18
Yb	4,40 ± 0,73			4,11 ± 0,98	4,89 ± 0,50	4,13 ± 0,85
Lu	0,68 ± 0,15			0,72 ± 0,24	0,74 ± 0,15	0,63 ± 0,17
Hf	3,35 ± 0,29			3,33 ± 0,65	3,43 ± 0,66	2,79 ± 0,71
Ta	1,92 ± 0,54			2,24 ± 0,36	1,89 ± 0,26	1,78 ± 0,22
Pb	50,9 ± 3,6			57,7 ± 1,9	54,7 ± 3,2	51,3 ± 2,6
Th	20,6 ± 1,3			16,9 ± 1,7	21,4 ± 0,9	19,0 ± 1,4
U	10,9 ± 0,9			11,6 ± 0,6	11,2 ± 0,3	11,3 ± 0,6
n	6			6	6	6

Notes: Oxide concentrations in wt %, anhydrous analyses, trace elements in ppm, nd is "not determined". Mean and standard deviation are given for each element. Control on accuracy is specified in text.

Appendix:

AF-1 Schematic map with localization of the archaeological and geological obsidian localities from the Zemplín – Tokaj area. *Abbreviation*: ZJ – Zemplínske Jastrabie.



GPS localization of studied samples.

Sample	locality	Latitude (°N)	Longitude (°E)
Br-1	Brehov–1	48°29´40.70″	21°47´50.10″
Br-2	Brehov–2	48°29´42.40″	21°48´15.00″
Ce-1	Cejkov–1	48°28´14.60″	21°47´12.50″
Hr-1	Hraň–1	48°31´08.60″	21°47´14.60″
V-1	Viničky–1		