**Day 1 (27 May)**

**11:40-12:50: lectures**
**Session II - Formation and geology of obsidian**

11:40-12:00
Kohút, M. - Anczkiewicz, R. - Danišík, M. - Erban, V. - Gerdes, A. - Halton, A. - Kirkland, Ch. - Kochergina, Y. - Magna, T. - Milovsky, R. - Pearce, N. - Recio, C. - Sherlock, S. - Westgate, J. - Bačo, P.: Progress in geological understanding of the Carpathian obsidians

12:00-12:20
Szepesi, J. - Vona, A. - Fintor K. - Buday T. - Scarani, A. - Harangi, Sz.: Cooling and hydration of the Carpathian obsidian, a differential scanning calorimetry (DSC), thermogravimetry (DTA) and infrared spectroscopy (FTIR) study

12:20-12:40
Lexa, J.-Bačo, P.-Bačová, Z.-Konečný, P.-Konečný, V.†-Németh, K.-Pécskay, Z.: Viničky rhyolite volcano: one of the sources of obsidian in Eastern Slovakia

12:40-12:50
General discussion on session II

# Progress in geological understanding of the Carpathian obsidians

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**Session II - Formation and geology of obsidian**
**Form of communication**: oral
Day 1 (27 May) 11:40-12:00

The Carpathian obsidians from the Zemplín – Tokaj area (SE Slovakia and NE Hungary), the only natural volcanic glass region in Central Europe, have been studied by geological and archaeological methods for long time (see review: Biró, 2006). However, modern geological investigation was missing. Chemical analyses of obsidians performed by archaeological survey often contain only eclectic set of elements that cannot be used for geological purposes (e.g., rock typology, and/or genesis determination). Therefore, comprehensive and systematic study including Electron Probe Micro-Analysis of glass and minerals, bulk analysis of the major and trace elements, determination of radiogenic (Sr, Nd, Pb, Hf) and stable (O, H, B, Li) isotope compositions, Ar/Ar dating of glass and biotite, fission track dating of glass, U–Pb zircon and (U–Th)/He zircon has been undertaken. Although the obsidians are dominated by amorphous volcanic glass with high silica content (up to 76–77 wt.% $SiO_2$) strictly suggesting their crustal affiliation, the presence of accessory minerals like olivine, pyroxene, amphibole and/or bytownite feldspar indicate their partial mantle-derived origin. Some isotopic characteristics of these obsidians with more radiogenic Sr–Nd isotopic composition, and elevated values of the stable isotopic O, H and Li signatures attest to crustal-dominated source; in contrast their Pb, Hf and B isotopic systematics points to a lower crustal metabasic source slightly influenced by sub-continental lithospheric mantle. Collectively, isotopic compositions of the Carpathian obsidians resemble arc igneous products derived by multi-stage processes with the primary basaltic magma formed due to melting of the lower crustal source at the mantle/crust boundary. Subsequent formation of a melt reservoir in the middle crust, accompanied by secondary melting of the surrounding rocks, and/or repeated process of assimilation and fractionation produced a suite of chemically variable lithology from basalt to rhyolites and/or obsidians before 12.1–11.4 Ma in the Carpathians.

**Keywords**: Carpathian obsidians, geology, isotopic composition, dating

# Cooling and hydration of the Carpathian obsidian, a differential scanning calorimetry (DSC), thermogravimetry (DTA) and infrared spectroscopy (FTIR) study

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**Session II - Formation and geology of obsidian**
**Form of communication**: oral
Day 1 (27 May) 12:00-12:20

The low temperature water diffusion is very common in the rhyolitic glasses but the interpretation of the cooling and hydration process on a relative effusion timescale is very controversial in the literature. The primary occurrences of the calc-alkaline Miocene (13-11.2Ma) Carpathian obsidian frequently associated with perlite deposits in variable eroded lava dome and flow edifices. The samples have been obtained from Lebuj, Erdőbénye outcrops (Tokaj Mountains) and Viničky (Zemplín Hills). Differential scanning calorimetry (DSC) measurements performed in order to evaluate the glass transition temperature ($T_g$) related to cooling history.

The controlled cooling/heating cycle behavior has been determined at 5, 10 and 25K/min. Thermogravimetric analysis (TGA, 25-1000°C, heating rate: 10°C $min^{-1}$) was used to quantify the total volatile content (TVC). The textural heterogeneity in the water concentration evaluated by Fourier transform infrared spectroscopy (FTIR) on double polished thin sections (MCT detector, range 400-6000 $cm^{-1}$).

The peak glass transition temperatures lie in the range of 670-780°C, which slightly shifts with controlled cooling/heating rates. The estimated natural cooling rates are generally <25K/min.

The measured TVC of the obsidian varied between 0,1-0,5% and elevated above 3% in the perlites. The FTIR revealed a very heterogenous water concentration profile. The hydration rinds (2-3% $H_2O$) transition rapidly (30-50 μm) to non-hydrated obsidian cores. The results confirmed that rhyolitic lava have been quenched from temperatures of 850-760°C (based on original water content). Using a mean $T_g$ (760 °C) the first 90°C of cooling of these lavas occurred above the glass transition in a plastic state, which followed by a longer period in solid-state (glassy) to ambient temperature. The TVC analysis confirm that majority of the magmatic water was lost during the effusive degassing. The textural water diffusion happened

below the glass transition. The glassy shells of the perlitic cracking formed in the response to hydration induced stress. The relict obsidian grains support the theory that the fast but incomplete, temperature dependent hydration process could possibly occur during the post eruptive cooling or later at ambient temperature.

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**Keywords:** obsidian, perlite, hydration, glass transition temperature

# Viničky rhyolite volcano: one of the sources of obsidian in Eastern Slovakia

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**Session II - Formation and geology of obsidian**
**Form of communication:** oral
Day 1 (27 May) 12:20-12:40

Four essential volcanic units have been recognized in the late Middle Miocene rhyolite complex at the southern side of the Zemplín horst next to the village Viničky, well exposed in galleries of a wine cellar: distal facies tuffs and paleosoil, proximal facies of phreatomagmatic pyroclastic ring, roots of a rhyolite dome and a thick rhyolite flow at the top of the succession. Obsidians associate with the last two units. Roots of the extrusive dome, exposed in the eastern side of the wine cellar, are formed of almost fully perlitized glass of a rhyolite composition. Perlite is of grey to dark grey colour with typical perlitic bulbous jointing. The cross section shows a lateral development of the glass and its subsequent perlitization. At the margin, in thickness up to 10-15 m, perlite shows a fluidal structure parallel to the body margin. In the central part perlitized glass is massive, including marekanite with obsidian cores of black colour. Their size ranges from a few mm to 10 cm, very rarely larger. In fragments of dimensions up to 0.5 cm obsidian is variably translucent or opaque. Weathered out obsidians from this primary source occur on the recent surface in eluvial and deluvial deposits at the southern slope of the Borsuk hill, having the local name Zajačí skok (Hare Jump).

The second obsidian occurrence in the Viničky area is related to the southern marginal and basal parts of a thick rhyolite lava flow covering older volcanic units. Its source is at the Borsuk hill extrusive dome 1.5 km northeastward. The basal part of the flow with obsidian crops out in galleries in the northern part of the wine cellar. It is formed of strongly perlitized glass breccia with distinctly fluidal texture. Breccia is formed of angular fragments to blocks of dimensions up to 3 m with matrix of grey-pinkish disintegrated perlitic matter. Obsidians, similarly as in the first case, are a part of perlite blocks, showing a marekanite character. Black obsidian cores are usually smaller, up to 5 cm in diameter. A possibility that obsidians from this primary source occur at the current surface is less likely.

**Keywords**: obsidian, perlite, marekanite, rhyolite dome, rhyolite dome-flow