Genesis of the Carpathian obsidians

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Abstract: Comprehensive study of the Carpathian obsidians reveals that these rocks as typical arc igneous products were derived by multistage processes with the primary basaltic magma formed due to melting of the lower crustal source at the mantle/crust border. Subsequent formation of melt reservoirs in the middle and upper crust, accompanied by secondary melting of the surrounding rocks with recurrent addition of an ascending melt, and repeated processes of assimilation and fractionation produced a suite of chemically variable lithology from basalt to rhyolites and obsidians before 12.0–11.4 Ma in the Carpathians.

Introduction

Obsidian is instantaneously solidified (quenched) igneous–volcanic rock, originated mainly from the acid rhyolitic melt, often referred to as "*natural volcanic glass*" with typical glassy lustre and usually dark jet-black, grey or brown colour. Generally, it is dominantly composed of amorphous, dark (opaque ± locally translucent) volcanic glass (≥95 volume %), with addition of various minerals like biotite, plagioclase, alkali feldspar, quartz, pyroxenes, amphiboles, magnetite, Fe–Ti oxides, zircon, apatite, monazite, pyrrhotite, pyrite, chalcopyrite, olivine, uraninite, ilmenite, hercynite and garnet. Obsidian was widely used for tool-making (stone industry) during prehistoric times, and played significant role in the evolution of Humankind and civilization. Volcanic glass was geologically known since the end of the 18th Century on our territory. It was archeologically documented in the 19th Century in the Zemplín–Tokaj area (on the both sides of present boundary between SE Slovakia and NE Hungary), the only natural volcanic glass region in Central Europe (see review: Biró 2006). The Carpathian obsidians (CO) were traded since the Aurignacien 28 000 yrs. BP.

Geological setting

The Carpathian obsidians from the studied Zemplín–Tokaj area belong to the Eastern Slovakian Neovolcanic Field (ESNF) in the SE Slovakia / NE Hungary, where the isolated Sarmatian volcanos penetrate the Miocene strata and pre-Cenozoic basement. The complicated geological setting of the Zemplínske vrchy Mts (ZVM) and their surroudning includes the evolution from the Paleozoic up to recent. The ZVM form typical tectonic horst surrounded by the East Slovakian Basin with several elevated volcanic bodies. Present architecture is a consequence of the back-arc extension, associated with the asthenosphere updoming accompanied by calc-alkaline volcanism and pull-apart opening during the Miocene, followed by the Pannonian to Quaternary late stage regional uplift and erosion. The Paleozoic basement rock sequences encompass various sedimentary and volcanic rocks of the Carboniferous to Permian age, whereas the high-grade metamorphic rocks (gneisses, amphibolites, and metagranites) can be found in deeper horizon. The Mesozoic cover is composed of conglomerates, sandstones, calcareous shales, dolomites, rarely with the evaporite intercalations of the Lower

Triassic in age. The Middle Triassic is formed mainly by carbonates (limestones and dolomites). The oldest Cenozoic sediments in the studied area are the Lower Miocene–Karpatian in age (claystones and of sandstones), followed by the Badenian basal conglomerates, sandstones, and grey calcareous claystones, that were overlaid by extrusive rhyodacite lava flow bodies and their tuffites and tuffs of the Upper Badenian age. The Lower–Middle Sarmatian rhyolite tuffs and tuffites are intercalated by clays and sandy claystones. The Middle–Upper Sarmatian rhyolite volcanism is represented by the dyke bodies, and an extrusion body with associated volcanoclastics in the Viničky broader area. The margins of the bodies are formed by perlitized obsidian, often in breccia development. The Upper Sarmatian is formed by calcareous sands and sandstones with interbeds of clays, tuffitic clays and tuffites. The sequence finished by the Pannonian lacustrine and river clays, silts with intercalations of sands, river gravels (Kobulský et al. 2014).

Mineralogy

Although the obsidians are dominated by the amorphous volcanic glass an important role play the rock-forming and accessory minerals from genetic point of view. The Carpathian obsidians consist of a broad association of minerals like plagioclase, biotite, alkali feldspar, quartz, pyroxenes, amphiboles, magnetite, Fe–Ti oxides, pyrrhotite, pyrite, olivine, zircon, apatite, monazite, uraninite, ilmenite, and garnet that are observable mainly under the microscope. These minerals can be present in the form of phenocrysts (having size 100~1000 μm), microlites (10~50 μm), and hair like trichites. Beside the autolithic origin of these minerals, sporadic xenoliths from the source and/or assimilated rocks can be also present. Commonly observed banded texture or alternation of dark and pale stripes is caused by minute microlites and trichites oriented in the direction of the melt flow. Although, the majority of described minerals have the primary magmatic origin, not all of them reflect their crystallization from a parent rhyolite melt. Plagioclases — most of the grains are subhedral microlites, although the phenocrysts in the size up to 450 μm are present locally as well. Generally, they are zoned with broad chemical composition (andesine–bytownite $An_{33–89}$) in the cores, whereas more acid oligoclase (An_{19-31}) and scarcely albite compositions were identified in the rime. K-fs's – are less frequent than Pl; sporadic anhedral grains up to 100 μm are mainly anortoclases, while high-temperature sanidines were found as well as.

Biotites — form mainly larger laths 100~850 μm in size, and/or smaller oval/anhedral flakes having brown pleochroic colour. Typical primary magmatic Fe-biotites have annite composition with $mg^\#=0.32~0.43$ and/or high TiO_2 content 3.2~4.6 wt. % indicating high-temperature origin. Elevated Fe content together with moderate Mg and Al contents show their peraluminous character influenced partly by calc-alkaline source. Generally, the low Fe^{3+} (ca 7 % from FeO^t) suggests for their crystallization at QFM buffer. Pyroxenes — form essentially euhedral and subhedral microlites and trichites, and locally anhedral grains in aggregates. Commonly, all of them belong to Ca–Fe–Mg group of pyroxenes. Pyroxenes are dominantly orthopyroxenes; clinopyroxenes are rare. Opx's are of enstatite compositon ($mg^\#=0.55~0.76$), some of them have pigeonite and ferosilite composition ($mg^\#=0.29~0.35$). Cpx's have augitic composition ($mg^\#=0.60~0.68$). Amphiboles — were identified as subhedral microlites, and/or anhedral grains in aggregates. They fit in to Mg–Fe–Mn group of amphiboles of grunerite and/or commingtonite composition ($Si_{(apfu)}=7.02~7.64$; and $mg^\#=0.31~0.58$). Magnetite — form mostly small anhedral grains and trichites, and/or subhedral/anhedral xenocrystic grains up to 45 μm with typical ilmenite lamellas in a few cases. Olivines — were locally found with pyroxene in xenocrystic aggregates as anhedral grains 5~100 μm of forsterite composition ($mg^\#=0.55~0.68$, and $fe^\#=0.32~0.49$), having tholeiitic character. Zircon — forms euhedral quadrate and prismatic grains 10~50 μm in size with low $HfO_2=1.33~1.88$ wt. % and low Th/U=0.11~0.46 distinctive for felsic fractionated igneous rocks. Apatites — form mainly euhedral and subhedral prismatic microlites in size of 20~55 μm. Typical fluor-apatites with increased fluorine content F=2.02~4.41 wt. % indicate igneous origin from fractionated melt. Monazites — were commonly found as subhedral grains 15~100 μm in size and/or oval grains with sign of magmatic corrosion. Studied monazites are commonly enriched in Th ($ThO_2 \leq 10.63$ wt. %) and depleted in uranium ($UO_2 \leq 0.75$ wt. %) or Si ($SiO_2 \leq 2.65$ wt. %) with both cheralite and huttonite substitutions. Primary magmatic monazites (Ce) yield normally the Cenozoic–Miocene ages (CHIME), although the Variscan restite ones (age 330 Ma) were identified as well as.

Geochemistry and dating

Geochemically studied samples of the Carpathian obsidians from ZVM belong to the volcanic peraluminous

rocks, and high potassium calc-alkaline rhyolite series (ASI=1.05~1.15). Their SiO_2 content varies in narrow interval from 76.4 to 77.5 wt. % reflecting their fractionation nature. Relatively elevated FeO^t values with simultaneous declination in MgO (wt. %) indicate their overall ferroan character. The Rb/Sr ratio=2.13~3.46 points to the distinct differentiation of these volcanic rocks, however this does not appear in most of the surrounding rocks. Based on the classical I/S-typology for felsic magmatic rocks, studied obsidians belong to typical mixed (hybrid) I/S-type igneous rocks. Normalized REE patterns show 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 are falling on the boundary between "hot-dry-reduced" and "cold-wet-oxidized" magmas (Bachmann & Bergantz 2008) reflecting genesis of magma from mantle and crust sources. The binary plots of CaO/Na_2O vs. Al_2O_3/TiO_2 respectively Rb/Ba vs. Rb/Sr clearly indicate that our samples fit the mixing trajectories with dominant crustal magma proportion and weak (30~10 %) contribution from mantle component. The Carpathian obsidians and their host rhyolite and dacite rocks represent a typical magmatic analogue of volcanic arc products from the geotectonic point of view (Kohút et al. 2018). Cl/F ratio of studied CO varies between 1~3.5 what is familiar to obsidians from the Mature Island Arcs and/or those originated at the Continental Margins (Macdonald et al. 1992).

WR Sr isotopic composition of studied obsidians with measured $^{87}Sr/^{86}Sr$ values in narrow interval 0.7114~ 0.7122 and $^{87}Rb/^{86}Sr$=7.3129~8.8110 are considerably more radiogenic than values from basaltic to rhyolitic rocks of the Central Slovakian Neovolcanic Field (CSNF) see Kohút et al. (2012). Generally, Sr isotopic composition of the CO suggests a crustal source little affected by sub-continental lithospheric mantle (SCLM). The Nd isotopic composition of the CO with $^{147}Sm/^{144}Nd$=0.1172~0.1271 and $^{143}Nd/^{144}Nd$=0.51225~ 0.51227 is more radiogenic comparing volcanic rocks of the CSNF. Indeed these values resemble those of the Western Carpathians orthogneisses with mainly crustal origin (Kohút et al. 2012). WR lead isotopes of the CO with $^{206}Pb/^{204}Pb$=18.87~19.88; $^{207}Pb/^{204}Pb$=15.683~ 15.687 and $^{208}Pb/^{204}Pb$=38.91~38.93 are higher than MORB and gently lower than common upper crustal rocks. However, Pb isotopic picture of the CO is akin to the Western Carpathians amphibolites and/or indicates derivation in the Arc from SCLM that was influenced by less radiogenic crustal source. WR Hf isotopic signature

of the CO with $^{176}Hf/^{177}Hf$=0.28263~0.28265; $^{176}Lu/^{177}Hf$= 2.023~2.026 and initial $\varepsilon Hf_{(12)}$=−4.7~−5.2 is familiar to common continental magmas characteristics. Whereas zircon initial values $\varepsilon Hf_{(i)}$=−1.4~−6.5 call for slight SCLM source contribution. The CO oxygen isotopic composition with $\delta^{18}O_{(VSMOW)}$=8.6~9.3 ‰ indicates rather mixed crustal/mantle origin. Again, no simple explanation can be offered yet. Closed system fractionation of basaltic magma is precluded by the $\delta^{18}O$ data of the CO, and also excluded simple crustal contamination with sedimentary rocks and/or granites+othogneisses as an important mechanism in the formation of hosting rhyolites, but allows the possibility of magma mixing as a partial cause of the isotope variations. Hydrogen composition of studied samples with $\delta^2H_{(VSMOW)}$ varying in −103.2~−109.0 ‰ is within standard obsidian values of primary magmatic residual H_2O remaining after volcanic degassing, and excluding exchange with meteoric water. Li isotope composition with δ^7Li=0.3 to 0.6 ‰, underscored by elevated Li contents of 60~70 ppm is similar to S-type granitic and/or common supra-crustal rocks. On the other hand boron isotopic composition with $\delta^{11}B$=+0.6~−2.1 ‰ and low B contents B=21~26 ppm is rather indicative for volcanic products generated from altered oceanic crust and/or I-type granitic rocks.

Dating of the CO was mostly associated with dating of host rhyolitic rocks in the past. The first K–Ar dating of biotites and WR provided a broad age range of 13.5 ± 2.5 Ma to 10.8 ± 0.5 Ma (see review Kohút et al. 2017). Direct dating of the Carpathian obsidians was performed by the Uranium Fission tracks method (FT) with the ages 14.2 ± 0.5 and 11.1 ± 0.8 Ma (Repčok et al. 1988), as well as Bigazzi et al. (1990) with higher ages from 17.8 ± 1.1 Ma to 13.7 ± 0.8 Ma. Latterly studied obsidians were also dated by WR K-Ar method with ages 15.0 to 11.1 Ma (Bačo et al. 2017). Our new FT dating of the CO glasses using the isothermal plateau fission track (ITPFT) method provided slightly younger ages in a narrow time range of 12.0~11.2 Ma. Noteworthy, that four of the five WR Rb/Sr isotopic analyses of our CO samples form a pseudo-isochron with an age 13.5 Ma and initial Sr ratio 0.7103 what is a bit older age as brought the ITPFT dating, but still within the age interval of older dating methods. There was applied Ar/Ar isotopic dating (glass and biotites) from our CO samples due to more accurately determine the age of rhyolite magmatism. The obtained ages for glass varying from 12.0 to 11.4 Ma are comparable to those of the ITPFT method, whereas the biotites provided slightly older ages (14.4~12.4 Ma). Albeit studied obsidians contain

mostly tiny zircons (10~25 μm in size), enough larger zircon grains suitable for spot age dating of the rhyolite/obsidian magmatism in the high temperature domain were separated. Unfortunately, the use of SHRIMP failed to achieve a sufficient amount of radiogenic Pb to obtain meaningful ages and/or isotopic ratios, whereas the use of LA MC-ICPMS provided representative ages. However, rather than direct dating of the magma crystallization beginning, we obtained data on the source rocks. The most zircon grains were restitic ones with ages 490~478 Ma (originating from orthogneisses), 354~352 Ma (Variscan granites), 283~278 (Permian magmatites) and 88~83 Ma (Rochovce granite). This is consistent with the isotopic characteristics of the source rocks, and/or structure of the pre-Cenozoic basement in the Western Carpathians, suggesting recycling of the older crustal igneous rocks. Merely the rare zircons with ages 15 and 13 Ma have confirmed the CO's Miocene age.

Conclusions

Summarizing the above presented like the high silica content of CO strictly suggesting their crustal affiliation; mineral composition with the presence of accessory minerals as olivine, pyroxene, amphibole and/or bytownite feldspar indicating their partial mantle-derived origin; isotopic characteristics with more radiogenic Sr–Nd isotopic composition, and elevated values of the stable isotopic O, H and Li signatures attesting their crustal-dominated source, in contrast their Pb, Hf and B isotopic systematics argumentative for a lower crustal metabasic source slightly influenced by sub-continental lithospheric mantle. Collectively, isotopic compositions of the Carpathian obsidians resemble the 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 reservoirs in the middle and upper crust, accompanied by secondary melting of the surrounding rocks, and recurrent mixing with an ascending lower crustal SCLM influenced melt, and/or repeated processes of assimilation and fractionation produced

a suite of chemically variable lithology from basalt to rhyolites and/or obsidians before 12.0~11.4 Ma in the Carpathians.

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