Accessory minerals of Permian volcanites of South Gemeric Unit and Bôrka Nappe

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Introduction and aims of work

The goal of this study was to summarize and complete the results from the study of acid metavolcanites and their accessory minerals (Zircon Zr_2SiO_4, Monazite $CePO_4$ and Xenotime YPO_4) from the Southern Gemericum Unit and from the Bôrka Nappe. The acid metavolcanites and their accessory minerals were observed of the modern analytical methods.

The late Variscan, post-orogenic overstep sequence of the Southern Gemeric Unit is represented only by the Permian continental and near-shore, lagoonal-sabcha volcano-sedimentary complexes. They unconformably overlap their Lower Paleozoic basement, the volcano-sedimentary deep-water turbidites of the Gelnica Group and Štós Formation (defined in the Variscides as the Gelnica Terrane [1]. Generally, the sediments of the Gočaltovo Group represent the relic of rift-related sedimentary basin fillings, which originated with the initial stage of the post-Variscan extension and crustal relaxation. The whole sequence is subdivided into two lithostratigraphic units: the basal Rožňava Formation and the upper Štítnik Formation [2]. The studied volcanites are an integral part of the basal Rožňava Formation. The characteristic lithotype of the Rožňava Formation is the oligomictic, quartzose conglomerate. Conglomeratic horizons are connected with rhyolite-dacite subareal volcanism [3]. Zircon populations from two samples of volcanogenic horizons of the Rožňava Formation rock complexes have been analysed. The magmatic zircons documented the Kungurian age of Permian volcanic activity of the Southern Gemeric basin. The age interval of these zoned magmatic zircons is from 267 to 287 Ma with Th/U ratios in the range of 0.39-0.75, with the average concordia ages of 273.3±2.8 Ma and 275.3±2.9 Ma [4]. The evidence for the Early Permian magmatic event at 276 ± 25 Ma in the Rožňava Formation volcanites was the first time recorded in the corroded monazite cores [5]. The majority of these monazites show an two-phase Alpine tectonothermal overprinting at 167±12 Ma and 136±10 Ma [5].

The high-pressure Bôrka Nappe rock complex represents a relic of the accretionary prism originated as a result of the Jurassic subduction of the oceanic bottom and thinned continental margin of the Meliata Ocean [6]. The Permian metasediments of the Bôrka Nappe, which were defined as the Bučina Formation and Jasov Formation [6], consist of siliclastic sediments associated with the huge mass of rhyolite-dacite volcaniclastics and volcanites in places. Their relationship to the underlying Lower and Uper Paleozoic rock complexes of the Southern Gemericum is tectonic in all sections. Chemical monazite dating from the Permian metavolcanites and metavolcaniclastics of the Bôrka Nappe records the Late Jurassic and Early Cretaceous tectonothermal overptinting [5].

Analytical methods

All rocks samples were analysed for major and trace elements content including REE. Their chemical composition was determined by ICP/ICP SM Acme Laboratories Ltd. in Canada.

The Monazites and xenotimes were analyzed with using of electron microprobe Cameca SX-100 in the Department of microanalysis at State Geological Institute of Dionýz Štúr (Geological Survey) in Bratislava. The analytical conditions were as follows 15 KV accelerating voltage which is sufficient for REE, Th, U, Pb lines excitation,; Pb was measured 130 s, Th 35 s, U 65 s, REE 25 s and all other elements 15 s; high beam current 100 nA was used to achieve sufficient counts for counting statistic. Natural minerals and chemical compounds were used for the calibration: Al-Al_2O_3, Si-SiO_2, P-apatite, Ca-wollastonite, REE-(REE)PO_4, Pb-PbS, U-UO_2 and Th-ThO_2. Th, U, Pb, Y, P were measured with LPET, REE with LLIF and Si, Al with TAP analyzing crystal. X-ray Kα lines were used for Si, Al, Ma lines for Th, Pb, Mb line for U, La or Lb line for REE elements. Existing interferences between REE elements and $PbM\alpha$□-$YL\gamma_1$ and $UM\beta$□-$ThM\gamma_1$ were corrected with an empirical correction factor. Chemical monazite analyses were recalculated to the ages using statistical model developed by [7]. A program DAMON developed by P. Konečný (during 2004-2006) was used for recalculation procedure as well as age histogram and isochrone construction. More detailed information on measurement conditions and recalculation method is given in [8].

The zircons have been separated from rocks by standard grinding, heavy liquid and magnetic separation analytical procedures. The internal zoning structures and shapes of the half-sectioned zircon crystals mounted in epoxy resin puck with chips of the TEMORA (Middledale Gabbroic Diorite, New South Wales, Australia) and 91500 (Geostandard zircon) reference zircons, were first imaged by BSE and CL, in order to reveal surface features for analytical spots positioning. *In situ* U-Pb analyses were performed on a SHRIMP-II in the

Center for Isotopic Research (CIR) at VSEGEI in St.-Petersburg, Russia. Each analysis consisted of 5 scans through the mass range, the diameter of each spot was about 25 μm, and primary beam intensity was about 6 nA. The data have been reduced in a manner similar using the SQUID Excel Macro. The Pb/U ratios have been normalized relative to a value of 0.0668 for the $^{206}Pb/^{238}U$ ratio of the TEMORA reference zircons, equivalent to an age of 416.75 Ma. Uncertainties given for individual analyses (ratios and ages) are at the 1σ level; but the uncertainties in calculated concordia ages are reported at 2σ levels. The concordia plot has been prepared using ISOPLOT/EX.

CAMECA SX-100 electron microprobe at Slovak Geological Survey, Bratislava was used for element concentration analyses. Si and Zr together with elements such as Hf, Y, U, Th, P and REE have been analysed. La was below the detection limits. The operating conditions were as follows: 15 kV accelerating voltage, 40 nA beam current, beam diameter 1—5 μm; standards – zircon (Zr, Si), HfO_2 (Hf), apatite (P), $YbPO_4$ (Yb), wollastonite (Ca), CePO4 (Ce), ThO_2 (Th), YPO_4 (Y), Gd_2O_3 (Gd); connecting period at 30 s (Si, Zr), 50 s (Hf), 110 s (Y) and 140 s (U, Th).

Results and Discussion

The Southern Gemeric Permian and Bôrka Nappe metavolcanites and metavolcaniclastics have dominant felsitic and vitroclastic character. Related metavolcaniclastics contain a little amount of deformed relics of β-quartz, perthitic alkali feldspars and scarce biotite as well as abundant fragments of felsites and recrystallized volcanic glass. Volcaniclastics from Rožňava Formation are characteristic with distinct preservation of ignimbrite structure, with relics of deformed "fiamè". Newly formed metamorphic mineral assemblage is represented by the fine-grained aggregate of quartz + phengite ± chlorite ± albite. Zircon, monazite, xenotime, apatite, rutile and Fe-Ti oxide are present as accessory minerals. Chemical composition of the acid metavolcanites largely falls into rhyolite-dacite peraluminous suite. Very high K_2O/Na_2O ratio is a result of secondary alteration processes. Volcanic rocks are generally characterized by extremely low CaO (0.01—0.03 wt. %), MgO (from 0.39 to 0.66 wt. %) and relative low Fe_2O_3t (from 0.73 to 2.46 wt. %) contents. The chondrite-normalized trace-elements variation diagram for the studied samples reflects strong negative anomalies of Ba, Nb, Sr and Ti, and enrichment in Rb, Th, K, La, Ce, Nd, Hf and Y. These broadly indicate their A-type affinity. Similarly, based on the chondrite-normalized REE distribution the rhyolites are enriched in light REE, and have relatively unfractionated heavy REE with Σ(La/Yb)n= 3.5 and Σ(Gd/ Lu)n = 1.6. These features, together with the distinct negative Eu-anomaly (Eu/Eu*= 0.48) are typical for A-type magmatites. Based on Y/Nb ratio, which ranges from 2.3 to 2.6 in all studied samples, the metavolcanites correspond to non-orogenic A_2-subtype, which could indicate the post-collisional magmatic environment [5,9,10] . At the petrological and geochemical composition, the Bučina Formation metavolcanites and metavolcaniclastics as well as zircon typology show a distinct similarity with the southgemeric metarhyolite-metadacite volcanism [9]. Both represent a rift-related post-collisional A_2-subtype magmatism [10] connected with the Variscan post-orogenic extension and thermal relaxation. This coincides with former results of [11] based on zircon typology.

The analysed zircons exhibit composition zonation trends of increasing HfO_2 and (UO_2 + ThO_2) concentrations and decreasing ZrO_2/HfO_2 ratios from the core to the rim of the crystals. The HfO_2 abundance of these zircons range from 0.77 to 2.03 wt. % and the mean of 1.29 wt. % falls in the field of Hf (wt. %) variation in the zircon associations of acid magmatic rocks. The variation of the ZrO_2/HfO_2 ratios in the zircon assemblage ranges from 86 to 57 in the core and from 78 to 42 in the rim. The Th/U ratios are high, ranging from 0.42 to 0.89, typical for magmatic rocks. Based on chemical composition of studied zircons, the dominant substitution was probably the simple mechanism (Hf^{4+}= Zr^{4+}) combined with coupled substitution “xenotime” mechanism [$(Y, REE)^{3+}+P^{5+}= Zr^{4+}+Si^{4+}$], which is reflected in variations of Y contents (from 0.1 to 0.8 wt. %) and ΣREE abundance (0.15—1.31 wt. %). Zircon populations from the metavolcanites were dated from the Rožňava Formation. A typical feature of the majority of the studied zircon population is the presence of well developed oscilatory growth zoning and less with sector zoning. Euhedral zircons with fine oscillatory zoning, typical of magmatic origin, gave an avarage concordia ages from 267 to 287 Ma (Probability of concordance = 0.90; MSWD of concordance = 0.016; n= 10) with Th/U ratios within the range of 0.44 to 0.73. The Permian ages ranging from 266 to 287 Ma were determined in the wider zoned or unzoned central parts of the zircon crystals, as well as in their fine growth oscillation zoned rims. [5].

Monazite, a REE bearing phosphate, is largerly distributed in the studied rocks. Its grain size varies from 1 to 20 μm, while the crystal about 5-10 μm prevail. The monazites are mostly surrounded by the metamorphic white mica–phengite. Most grains are angular, hypidiomorphic in composition, although small size prevents a detailed observation of the zonality in BSE. Some zonality is observed only in few larger grains

The chemical composition between grains has quite substantial variability. Most of the chemical changes are attributed to the thorium. ThO_2 varies from very low concentrations 0.9 wt. % up to 14.5 wt. % (5.1 wt. % in average). The uranium content is quite low; the UO_2 concentrations are between 0.023 and 0.735 wt. % (0.278 wt. % in average. The chemical composition of the monazite from all samples recalculated to end-members. The major solid solution part of the crystal structure is filled by monazite-(Ce). The brabantite and huttonite content is even less. Monazite-(Ce) content is relatively high, 94.2 mol % in average (from 85.1 to 99.1 mol. %). Almost pure monazite- (Ce) end-members are also present. Average huttonite content is low (1.5 mol. %). Few monazites can contain up to 7.5 mol. %. Brabantite content is higher than huttonite, reaching 4.3 mol. % in average with the range from 0 to 13.2 mol. %. Ytrium concentration in majority of studied monazites is relatively low (between 0.3-0.5 wt.% Y_2O_3) suggesting subordinate xenotime-type substitutions. The Majority of the monazites from the Permian acid metavolcanic rocks record an Alpine tectonothermal event around ca. 148±8 Ma. Alpine age data divided according to the statisticalmodeling present two successive sub-events yielding ages of 167±12 and 136±10 Ma. The evidence for the Early Permian magmatic event at 276±25 Ma in the Rožňava Formation recorded in the corroded monazite cores is presented for the first time [6].

Conclusion

The obtained in situ U-Pb (SHRIMP) zircon ages 273±2.8 or 275±2,9 Ma from Rožňava Formation of the Southern Gemericum Unit correspond to the Kungurian, the latest Ciuralian stage [5]. The similar age 276±25 Ma, has been determinated by chemical dating from the monazite cores of these volcanites [6]. The both of dating clearly document the timing of post-Variscan extensional rifting in the internal zone of the Variscan Western Carpathians. The Late Jurassic (average age at 167±12 Ma) and Early Cretaceous (average age at 136±10 Ma) events recorded in the rim of the Permian monazite as well as within the newly formed monazite grains have been interpreted as a strong reworking of the Permian rock complexes linked to the subduction/accreation processes and the successive compression. Polyphase Alpine tectonic evolution connected with the gradual Cretaceous collision and indentation is also confirmed by the youngest age data set 100±11 Ma [6].

Acknowledgements

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