

First evidence for Permian-Triassic boundary volcanism in the Northern Gemericum: geochemistry and U-Pb zircon geochronology

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Abstract: Several magmatic events based on U-Pb zircon geochronology were recognized in the Permian sedimentary succession of the Northern Gemeric Unit (NGU). The Kungurian magmatic event is dominant. The later magmatism stage was documented at the Permian-Triassic boundary. The detrital zircon assemblages from surrounding sediments documented the Sakmarian magmatic age. The post-orogenic extensional/transtensional faulting controlled the magma ascent and its emplacement. The magmatic products are represented by the calc-alkaline volcanic rocks, ranging from basaltic metaandesite to metarhyolite, associated with subordinate metabasalt. The whole group of the studied NGU Permian metavolcanics has values for the Nb/La ratio at (0.44–0.27) and for the Nb/U ratio at (9.55–4.18), which suggests that they represent mainly crustal melts. Magma derivation from continental crust or underplated crust is also indicated by high values of Y/Nb ratios, ranging from 1.63 to 4.01. The new ²⁰⁶U–²³⁸Pb zircon ages (concordia age at 269 ± 7 Ma) confirm the dominant Kungurian volcanic event in the NGU Permian sedimentary basin. Simultaneously, the Permian-Triassic boundary volcanism at 251 ± 4 Ma has been found for the first time. The NGU Permian volcanic activity was related to a polyphase extensional tectonic regime. Based on the new and previous U-Pb zircon ages, the bulk of the NGU Permian magmatic activity occurred during the Sakmarian and Kungurian. It was linked to the post-orogenic transpression/transtension tectonic movements that reflected the consolidation of the Variscan orogenic belt. The Permian-Triassic boundary magmatism was accompanied by extension, connected with the beginning of the Alpine Wilson cycle.

Key words: zircon (SIMS) ages, acid to intermediate volcanites, North Gemeric Permian basin, Western Carpathians.

Introduction

The Northern Gemeric Unit (NGU) Permian volcanic-sedimentary succession overlaps unconformably with eroded relics of the Carboniferous sedimentary sequences as well as the two pre-Carboniferous crystalline basement complexes, the Rakovec and Klátov Complexes. These Paleozoic complexes, in the northern and north-eastern part of the Slovenské Rudohorie Mts, are located in a very complicated Alpine synclinorium structure, in which the system of folds, tectonic slivers and fold faults is cut by younger transversal tectonics (Bajaník et al. 1983, 1984; Biely et al. 1996a and references therein). As the Permian sedimentation proceeded from continental arid to semiarid climatic conditions, they lack or are deprived of relevant faunal and floral age evidence. In addition, the Alpine deformation and anchi- to low-grade metamorphic recrystallization destroyed the majority of possibly pre-existing biostratigraphically relevant fossil remains. Because a distinct part of the Permian sequence is formed by acidic to intermediate metavolcanic rocks and their volcanoclastics, they could be used to prove the age of these volcanic horizons, as well as for age estimation of the adjoining sediments.

The first U-Pb dating from the U-bearing volcanogenic horizon within the Novoveská Huta ore deposits gave the

age of 240 ± 30 Ma, that was interpreted as the age of mineralization (Arapov et al. 1984). Monazite ages prove the Cisuralian age of 278 ± 10 Ma in the metarhyolite tuff from the same locality (Rojkovič & Konečný 2005). The newest U-Pb (SHRIMP) magmatic zircon ages from the NGU Permian volcanic suite (in the vicinity of Krompachy) yielded the concordia age of 272 ± 7 Ma for basaltic metaandesite, and the concordia age of 275 ± 4 Ma for metarhyodacite (Vozárová et al. 2012). These results also correspond to the Cisuralian Epoch, in the time span of the Kungurian Stage. Consequently, the acquired ²⁰⁶Pb/²³⁸U zircon age data document nearly a contemporaneous manifestation of the acid and basic volcanic activity within the NGU Permian basin.

Therefore, our investigation focuses on the continuation of magmatic zircon radiometric dating in order to confirm the stratigraphic specification and position of the subdivided lithostratigraphic units. The method of *in situ* U-Pb SHRIMP zircon dating (performed at the A.P. Karpinsky Russian Geological Institute (VSEGEI), Laboratory of Isotopic Research, St.-Petersburg) has been applied, with the main target of determining the age of volcanism and specifying the stratigraphic position of the adjoining sediments. In this study, we follow the time-scale calibration of the International Stratigraphic Chart 2014 (International Commission on Stratigraphy, drafted by Cohen et al. 2014) in order to

compare geochronological data from the studied volcanics with the fossil-bearing strata. The main goal of this study was to bring new isotopic and geochemical data on the sources of magma generation, in order to infer the relationship with the geotectonic setting of the studied area.

Geological setting

The NGU belongs to the pre-Gosau northward stacking crustal scale nappe system of the Western Carpathians (Biely et al. 1996a and references therein). The NGU fits into the innermost part of the internal zone of the Alpine Western Carpathians, and as a whole it clearly overthrusts the Veporicum Unit in its footwall, along the Alpine thrust nappe contact recognized as the Lubeník-Margecany Line (Andrusov 1959). Similarly, further to the south, the tectonic contact of the NGU with the neighbouring Southern Gemeric Unit is represented by the Hrádok-Železník Line (defined by Abonyi 1971), which continues the system of thrust faults to the east (Fig. 1). Extreme Early Cretaceous shortening due to nappe stacking is characteristic for the innermost part of the Western Carpathians. Due to this fact, the complexes preserved in the NGU synclinorium (Mahel' 1954; Mahel' & Malkovský 1984) structure are generally specified by the strong tectonic reduction and shortening.

The NGU zone encloses relics of the Variscan collision suture, represented by the thrust wedges of the two pre-Carboniferous complexes (the higher-grade Klátov and low-grade Rakovec Terranes; in the sense of Vozárová & Vozár 1996), and fragments of Mississippian deep-water turbidite sequences (Fig. 1).

The NGU Mississippian turbidite wedges (the Ochtiná Group divided into the Hrádok, Črmeľ and Lubeník Formations in the sense of Vozárová 1996), supposedly disposed by the Variscan suture, represent the intra-suture remnant of the ocean basin fill. The turbidite deposition (the Hrádok and Črmeľ Formations) was followed by the deposition of Viséan/Serpukhovian shallow water clastics and carbonates (the Lubeník Formation). The Tournaisian-Viséan fore-deep and remnant ocean basins have been correlated across the whole Alpine-Carpathian realm (Nötsch-Veitsch-Northgermeric Zone — Neubauer & Vozárová 1990; Veitsch/Nötsch-Szabadbattyán-Ochtiná Zone — Ebner et al. 2008). They are partly syn-orogenic, and partly also post-date the Late Devonian-Mississippian climax of the Variscan orogeny.

Post-Variscan deposition includes Pennsylvanian (Bashkirian-Lower Moscovian) fan delta/shallow-marine to proximal delta (Upper Moscovian-Kasimovian) and continental Permian sequences (Rakusz 1932; Rozložník 1935; Rozložník 1963; Bajanič et al. 1981, 1983; Vozárová & Vozár 1988; Vozárová 1996 and references therein).

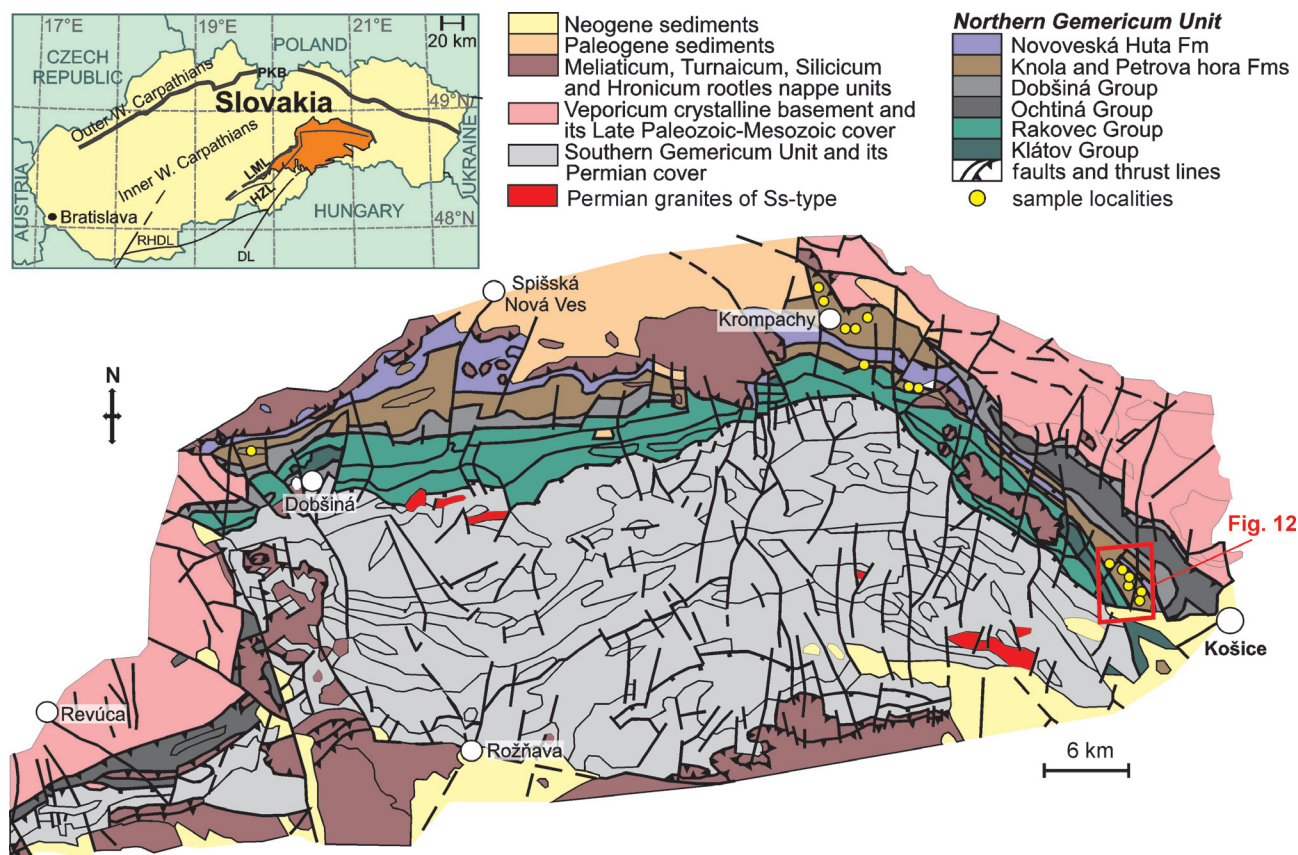


Fig. 1. Schematic geological map of the NGU showing the volcanic rock sampling localities (modified from the Geological map of Slovakia, 1:500,000, Biely et al. 1996b). The red line squared field designs the area of zircon collecting. For more details see Fig. 12.

Shallow-water to paralic Upper Bashkirian-Moscovian formations overstepped unconformably both, the NGU pre-Carboniferous crystalline complexes (Klátov and Rakovec T.) as well as, the Mississippian syn-orogenic Črmeľ Formation in the eastern part of the occurrences (a part of the Veitsch/Nötsch-Szabadbattyán-Ochtiná Zone; Ebner et al. 2008). Important indications are two breaks of sedimentation. The first was during the Early Pennsylvanian (Bashkirian) and the second in the Late Pennsylvanian (Kasimovian-Ghzelian). Both hiatus were connected with gradual reconstruction of the NGU sedimentary realm, at the first stage in a transpressional and the second in a transtensional tectonic setting (Vozárová et al. 2009a). This assumption is documented by a different pre-transgressive erosion step of individual pre-Pennsylvanian sequences and by their reworked detrital material. The marine post-orogenic sequence (8–170 m thick) started with delta-fan boulder to coarse-grained polymict conglomerates (the Rudňany Formation), with rock fragments derived from all the pre-Pennsylvanian complexes of the NGU zone. The 370–380 Ma $^{40}\text{Ar}/^{39}\text{Ar}$ cooling age data from sandstone clastic white mica and gneiss pebble metamorphic mica, as well as the detrital zircon ages (Vozárová et al. 2005, 2013) indicate perfectly the first step of the Variscan collisional suturing in NGU realm. After initial rapid sedimentation, the littoral to shallow-neritic limestones and fine-grained siliciclastic sediments were associated with basalts and their volcanoclastics. This succession was formerly defined as the Zlatník Formation (ZF) by Bajaník et al. (1981). The lower part of the ZF is well biostratigraphically fixed, based on brachiopods, bryozoans, crinoids, gastropods, corals, ammonites and mainly trilobites (Rakusz 1932; Bouček & Příbyl 1960), plant debris (Němejc 1953) and conodonts (Kozur & Mock 1977).

Ivan & Méres (2012) separated the complex of basic metavolcanites and metavolcanoclastics, associated with small amounts of metapelites and fine-grained metapsammites from the lower part of the ZF. The metabasalts of E-MORB, N-MORB and BABB types in this complex and chemical differences in these rocks were considered to be the basis for the separation of these metabasalts from the lower part of the ZF. The authors defined this new lithostratigraphic unit as the Zlatník Group. However, this name expression was firstly used for the biostratigraphically well assessed ZF (Bajaník et al. 1981). This strongly contradicts the priority rule of the stratigraphic code (see the International Guide to Stratigraphic Classification; Hedberg 1976 and others; Slovak Stratigraphic Guide, Michalík et al. 2007). According to the definition of the new lithostratigraphic unit rule, as defined by Ivan & Méres (2012), the detailed field distinction of the Zlatník Group and, above all, its relationship to underlying and overlying rock complexes (tectonic or primary position etc.) are missing. Though the schematic map was presented, it seems that the authors included in the Zlatník Group even some parts of the Rakovec Group and the Rudňany Formation rock complexes. For the solving of this problem, further structural and geological field studies are badly needed. In any case, only the geochemical data cannot form the basis for such distinction. The submitted work is not going to form any arguments for further solving of this problem, as the ZF succession in the eastern part of the NGU is not present.

The termination of this Late Bashkirian-Moscovian peripheral basin is reflected by cyclical paralic sedimentation (the Hámor Formation).

The continental Permian deposits (Krompachy Group; Bajaník et al. 1981) overlap the slightly deformed Pennsylvanian and Mississippian sedimentary rocks, as well as both NGU pre-Carboniferous crystalline rock complexes. The basal Knola Formation (KF) contains poorly sorted polymict conglomerates of variable thickness (Fig. 2), with pebbles derived from the directly underlying rock complexes. Acid to intermediate/basic volcanism associated with the red-beds of fluvial, fluvial-lacustrine and playa facies is characteristic of the Petrova hora Formation (PHF) (Fig. 2). The existing monazite and U-Pb SHRIMP zircon ages yield a Cisuralian age (Artinskian-Kungurian) for both, the acidic and basic vol-

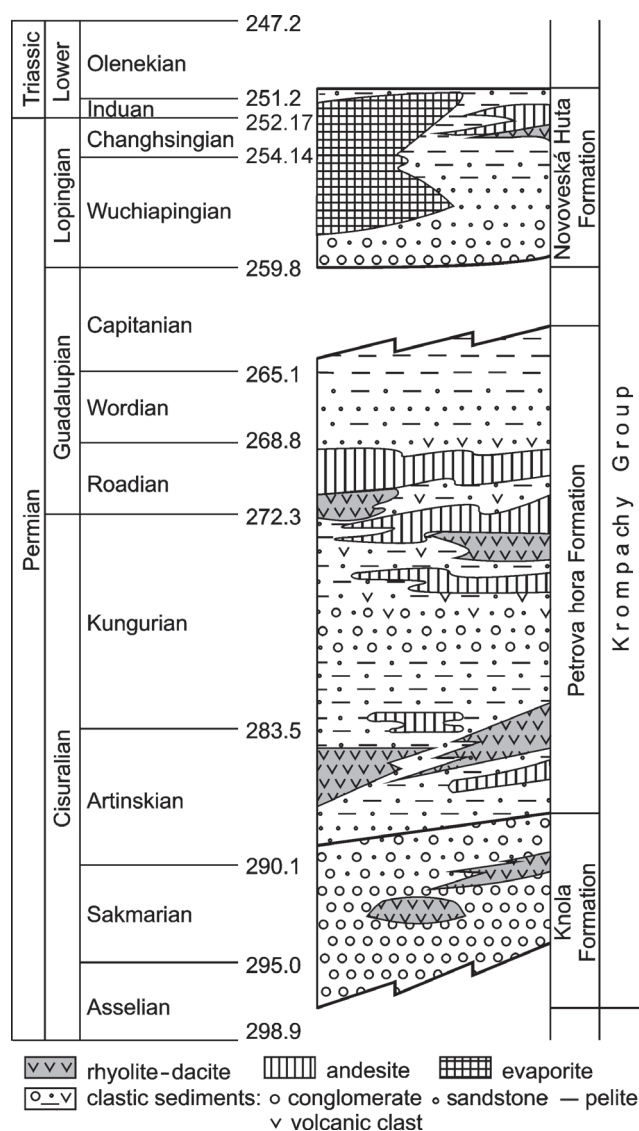


Fig. 2. Schematic lithostratigraphic column of the NGU Permian sequence (modified after Bajaník et al. 1981; Vozárová 1996 and this study). The time-scale calibration follows the International Stratigraphic Chart (International Commission on Stratigraphy, drafted by Cohen et al. 2014).

canic members (Rojkovič & Konečný 2005; Vozárová et al. 2012). The acidic volcanism produced the huge mass of pyroclastic rocks, mainly in the eastern part of the NGU. Two regional pulses of volcanic activity correspond to the large-scale sedimentary cycles triggered by the extensional regime. Based on these two independent volcanogenic horizons, some authors determined two separate lithostratigraphic members within the PHF: i) the older Novoveská Huta volcanic complex, and ii) the younger Pátrov Grúň volcanic complex (Novotný & Mihál 1987; Mihál 1990 in Rojkovič & Mihál 1991). The PHF volcanism was usually dominated by the metarhyolite-dacite volcanic rocks, associated with metaandesite and basaltic metaandesite (Ivanov 1953, 1957; Maheľ 1954; Rojkovič & Vozár 1972; Václav & Vozárová 1978; Novotný & Mihál 1987; Rojkovič & Mihál 1991; Vozárová et al. 2012).

The top of the Permian succession (Fig. 2) consists of the Novoveská Huta Formation (NHF) red-beds that prograded upwards and across to near-shore sabkha/lagoonal evaporite facies.

Analytical methods

Zircons have been separated from rocks by standard grinding, heavy liquid and magnetic separation 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, Black et al. 2003) and 91500 (Geostandard zircon, Wiedenbeck et al. 1995) reference zircons, were imaged by optic microscopy, BSE and CL, in order to guide analytical spots positioning. *In situ* U-Pb analyses were performed on a SHRIMP-II in the Centre of Isotopic Research (CIR) at VSEGEI in St.-Petersburg, Russia.

Each analysis consisted of 5 scans through the 196–254 AMU (atomic mass range); primary beam diameter was about 25 µm, with intensity of ca. 6 nA. The data have been reduced in a manner similar to that described by Williams (1998 and references therein), using the SQUID Excel Macro of Ludwig (2000). The Pb-U ratios have been normalized relative to a value of 0.0668 for the $^{206}\text{Pb}/^{238}\text{U}$ ratio of the TEMORA reference zircons, equivalent to an age of 416.75 Ma (Black et al. 2003); common lead was corrected using measured $^{204}\text{Pb}/^{206}\text{Pb}$ (Stacey & Kramers 1975). Age calculations and plotting were done with ISOPLOT/EX (Ludwig 1999). Uncertainties given for individual analyses (ratios and ages) are at the one σ level; however, the uncertainties in calculated Concordia ages are reported at the two σ levels.

The chemical composition of the rocks was analysed at the ACME Analytical Laboratories (Vancouver, Canada). Major elements were determined by inductively coupled plasma — optical emission spectrometry (ICP-OES). Concentrations of trace elements and rare earth elements (REE) were determined by ICP mass spectrometry (ICP-MS). The analytical accuracy was controlled using geological standard materials and is estimated to be within a 0.01% error (1 σ , relative) for major elements, within a 0.1–0.5 ppm error range (1 σ , relative) for trace elements and 0.01–0.05 ppm for REEs. Fur-

ther details are accessible on the web page of the ACME Analytical Laboratories (<http://acmelab.com/>).

Sample characteristics

Petrography

The acidic members of the PHF volcanics represent a relatively huge volcanic succession related to subaerial fissure eruptions. Pyroclastic tuffs and ignimbrites are dominant with subordinate lava flows. The huge aerial eruptions are also documented by mixing of large redeposited volcanoclastic detritus with the surrounding non-volcanic sediments. The acidic volcanics are characterized by the prevalence of vitric matrix and less preserved phenocrysts of β -quartz, K-feldspar and Na-plagioclase. Relics of deeply altered biotite are scarce. A relative strong Alpine reworking is manifested by distinct foliation and preferred orientation of the newly-formed aggregates of muscovite + albite + quartz \pm chlorite.

The PHF intermediate to basic volcanic members are represented by metaandesites and basaltic metaandesites, less metabasalts. They are fine-grained violet or dark-green rocks with dominant glassy, microofitic or vitroporphyrlic texture. Lathes of plagioclases are the dominant phenocrysts. Albitized plagioclases with inclusions of chlorite/illite were also observed. Magmatic mafic minerals are completely decomposed and replaced by Fe-Mg chlorite and Fe-Ti oxides. Magnetite and ilmenite belong to the primary mafic minerals. Ilmenite was partially decomposed to rutile and hematite. The strong Alpine deformation and recrystallization are reflected in the fine-grained aggregates of chlorite + Fe-Ti oxides + calcite + epidote \pm albite, which crystallized along the foliation planes. The acidic volcanics are dominant in the northern and north-eastern part of the Slovenské Rudohorie Mts and more basic volcanics in its eastern part, mainly at the localities of Krompachy and Jahodná.

Three samples have been collected, GZ-32, GZ-33 and GZ-34, for zircon dating, all from the vicinity of Jahodná, northwest from Košice. Among them, only two samples (GZ-32 and GZ-33) were suitable for dating. The first, GZ-32 sample (GPS: N 48°45' 810", E 21°09' 000"; 607 m above sea level; ca. 250 m east of the Kurišková (622 m) elevation point) represents the acid variety, corresponding to the fine-grained metarhyolite or metadacite pyroclastic rock, beige in colour. No phenocryst relics are preserved and thus, due to the very strong Alpine deformation and recrystallization, it is difficult to distinguish if the original rock was primary aphanitic volcanic or felsic pyroclastic rock. A very strong foliation is also reflected in the distinct preferred orientation of the newly formed metamorphic minerals in the texture (muscovite + albite + quartz \pm chlorite). Irregular dispersed Fe-Ti oxide grains are preserved in the fabric.

The second sample, GZ-33 (GPS: N 48°45' 411", E 21°09' 746"; 551 m above sea level; ca. 350 m NW from the Kamenný hrb (559 m) elevation point), corresponds to a dacite/andesite composition. The studied volcanic rock is dark, dark-violet in colour and with microporphyrlic texture. It is fine-grained, macroscopically with small whitish plagioclase

clase phenocrysts, which are deformed and cataclastized within the foliated matrix. An intersertal or fluidal texture, dominated by lathes of plagioclase (albite), was partly identified in the basaltic andesite rocks (sample *GZ-34*). Spaces between plagioclase lathes are filled with fine-grained chlorite and chlorite/muscovite masses after primary glassy material. The plagioclase grains are strongly albitized. The metaandesites and basaltic metaandesites are characterized by plentiful grains of Fe-Ti oxides within the fine-grained matrix, and less frequent phenocrysts of magnetite and ilmenite.

Geochemistry

The NGU Permian volcanic rocks include a wide range of compositions, ranging from basaltic andesite, andesite to dacite and rhyolite. Representative major- and trace-elements

including rare earth elements of whole-rock analyses are given in Tables 1 and 2. The list of the analysed volcanic rocks and sample localities is specified in Table 3. The NGU Permian volcanic rocks vary from peraluminous to metaluminous intermediate to acid volcanic suite. The loss on ignition (LOI) suggests the variable degrees of post-magmatic alteration (3.9–2.6 wt. % of volatiles). The degree of secondary alkali metasomatic alteration has been considered by reference to the variation of total alkali content to potash/total alkali ratio (Hughes 1973, 1982). Generally, the NGU metaandesites and basaltic metaandesites, associated with a part of the metarhyodacites (Group I.) belong to the unaltered or slightly Na-metasomatically altered volcanic rocks ($\text{Na}_2\text{O} + \text{K}_2\text{O}$ ranging from 6.3 to 8.3; $\text{K}_2\text{O}/(\text{Na}_2\text{O} + \text{K}_2\text{O}) \cdot 100$ ranging from 21 to 55). A second part of the metarhyodacites (Group II.) is indicated by their lower total alkali content ($\text{Na}_2\text{O} + \text{K}_2\text{O}$ ranging from

Table 1: Chemical composition of the Group I volcanic rocks, basaltic andesite-rhyolite suite with $\text{Eu}/\text{Eu}^* > 0.5$. Analysis 16 sm has been selected from Vozárová et al. (2012). **PH** — Petrova hora Formation, **NV** — Novoveská Huta Formation.

Fm		Andesites						Rhyolites-dacites			
		PH	PH	PH	PH	PH	NV	PH	PH	PH	NV
Sample		14 sm	16 sm	20 sm	21 sm	41 sm	GZ-34	15 sm	17 sm	GZ-32	GZ-33
SiO ₂	%	60.26	55.94	57.1	55.51	58.19	60.76	68.31	68.54	66.98	64.31
TiO ₂		0.97	1.19	1.08	1.15	1.03	1.00	0.32	0.27	0.22	0.44
Al ₂ O ₃		16.45	16.07	15.85	15.82	18.02	16.66	15.99	16.17	15.26	15.82
Fe ₂ O ₃		7.66	9.02	8.96	9.47	8.25	6.20	4.18	4.59	4.38	6.53
MnO		0.11	0.09	0.11	0.11	0.04	0.04	0.03	0.12	0.04	0.02
MgO		1.97	1.85	1.99	2.01	3.45	3.75	0.86	0.35	3.27	2.26
CaO		1.79	3.58	3.48	4.19	0.62	0.58	0.21	0.33	0.22	0.31
Na ₂ O		5.28	4.91	4.49	4.78	5.38	7.14	5.99	4.27	0.60	4.15
K ₂ O		2.32	1.75	2.15	1.50	1.42	0.42	2.36	2.97	5.16	3.02
P ₂ O ₅		0.395	0.604	0.560	0.596	0.420	0.440	0.147	0.088	0.130	0.210
Cr ₂ O ₃	ppm	n.d.	n.d.	n.d.	n.d.	0.002	n.d.	n.d.	n.d.	n.d.	0.005
LOI		2.7	5.0	4.2	4.9	3.0	2.9	1.5	2.2	3.6	2.7
sum		99.89	100.03	99.99	100.02	99.81	99.86	99.87	99.88	99.85	99.8
Rb		91.3	59.8	67.5	50.3	51.3	16.7	81.8	105.5	146.6	106.9
Cs		5.0	2.1	2.7	1.5	2.8	0.9	4.2	3.4	8.5	4.5
Ba		453	209	283	153	113	69	320	283	158	147
Sc		13	15	15	16	15	13	9	9	7	12
Y		43.0	46.4	44.6	46.2	34.5	41.5	66.8	60.1	54.2	58.2
La		27.8	35.8	36.7	37.8	23.3	35.3	64.6	77.5	47.0	76.2
Ce		63.5	79.5	80.7	82.4	57.5	78.8	132.1	138.7	109.6	179.1
Pr	ppm	8.45	10.55	10.54	10.71	6.91	9.13	16.84	18.03	13.01	20.87
Nd		36.5	44.0	43.0	43.6	29.7	37.9	67.4	66.5	52.9	77.0
Sm		7.92	9.00	8.73	8.99	7.42	8.36	12.91	11.41	12.98	15.59
Eu		1.84	1.98	2.02	2.22	1.55	1.92	2.51	2.23	2.10	2.91
Gd		8.05	8.87	8.4	8.64	7.54	8.38	12.38	10.57	10.66	13.8
Tb		1.34	1.42	1.38	1.43	1.25	1.16	2.00	1.64	1.44	1.71
Dy		7.60	8.20	8.11	7.98	6.95	7.78	11.42	9.00	9.74	12.5
Ho		1.59	1.67	1.60	1.64	1.36	1.42	2.35	1.93	1.76	2.14
Er		4.39	4.64	4.47	4.60	3.72	4.24	6.82	5.64	5.39	6.27
Yb		4.11	4.45	4.34	4.36	3.50	3.91	6.78	5.27	5.10	5.84
Lu		0.64	0.70	0.66	0.67	0.50	0.61	1.10	0.86	0.75	0.96
Th	ppm	8.7	9.7	9.0	8.9	10.0	7.3	19.4	19.7	11.7	17.7
U		2.6	2.4	2.5	2.4	3.2	2.8	4.8	3.1	2.6	4.0
V		72	57	43	52	89	68	9	n.d.	n.d.	n.d.
Co		12.9	13.5	12.5	13.8	14.0	15.6	1.7	1.4	2.7	3.2
Ni		1.5	1.5	1.8	0.8	1.6	1.1	1.1	1.6	0.7	2.7
Zr		232	279	276.3	268.6	296	239.4	568.4	478.4	314.8	569.4
Nb		11.8	14.1	13.0	13.1	14.8	11.7	22.8	14.1	13.5	20.3
Hf		6.4	7.6	7.4	7.0	8.3	6.3	14.6	12.0	8.4	13.3
Ta		0.8	0.9	0.8	0.9	1.1	0.9	1.4	0.9	1.1	1.3
Ga		20.9	20.3	18.4	18.0	24.4	22.2	21.2	22.5	22.5	23.6
Pb		2.0	0.9	6.7	0.9	2.3	0.8	3.1	0.8	0.7	1.1
Eu/Eu*		0.702	0.675	0.719	0.767	0.699	0.631	0.605	0.618	0.544	0.604

Table 2: Chemical composition of the Group II volcanic rocks, rhyolite-dacite suite with $Eu/Eu^* > 0.5$. Analyses 38 sm and 38 sm-b have been chosen from Vozárová et al. (2012). **PH** — Petrova hora Formation.

Fm		Rhyolites-dacites							
		PH	PH	PH	PH	PH	PH	PH	PH
Sample		19 sm	25 sm	33 sm	34 sm	36 sm	38 sm	38 sm-b	39 sm
SiO ₂	%	74.93	80.69	71.62	72.11	79.55	82.50	80.95	71.54
TiO ₂		0.17	0.44	0.30	0.05	0.06	0.12	0.12	0.12
Al ₂ O ₃		12.52	9.17	12.79	15.99	12.23	8.75	11.02	13.88
Fe ₂ O ₃		3.16	3.42	3.04	1.08	1.59	2.25	2.22	1.53
MnO		0.01	0.01	n.d.	n.d.	0.04	n.d.	0.03	0.04
MgO		3.03	0.51	2.82	3.31	0.74	1.71	0.30	2.30
CaO		0.11	n.d.	0.04	0.02	n.d.	0.04	0.07	1.43
Na ₂ O		0.19	0.07	0.06	0.19	0.26	0.06	0.18	0.15
K ₂ O		2.78	3.63	5.28	3.92	3.27	2.52	3.22	4.42
P ₂ O ₅		0.079	0.04	0.04	0.03	0.03	0.05	0.07	0.06
Cr ₂ O ₃		n.d.	0.006	0.005	n.d.	0.004	0.005	0.005	0.005
LOI		3.1	1.9	2.8	3.2	2.1	1.9	1.7	4.4
sum		100.03	99.91	99.81	99.89	99.93	99.87	99.9	99.88
Rb	ppm	119.7	108.0	232.9	140.4	115.7	91.3	150.4	137.9
Cs		6.9	4.1	12.3	4.3	10.9	11.8	9.3	16.0
Ba		196	130	209	142	110	395	275	189
Sc		6	7	10	3	3	3	4	4
Y		20.8	28.0	42.0	13.9	15.9	16.8	17.0	24.2
La		20.6	41.7	55.6	11.4	9.9	19.4	27.0	20.6
Ce		44.2	91.4	121.3	25.0	24.0	42.2	63.1	50.7
Pr		5.50	11.77	13.64	2.95	2.66	4.60	7.15	5.91
Nd		22.3	47.1	53.1	10.7	10.1	16.9	26.9	22.8
Sm		4.31	9.80	9.72	2.74	2.51	4.18	5.65	5.31
Eu		0.53	1.52	0.96	0.38	0.33	0.58	0.70	0.67
Gd		3.16	8.79	8.38	2.17	2.33	3.90	4.30	4.77
Tb		0.54	1.05	1.39	0.37	0.43	0.65	0.63	0.84
Dy		3.26	6.62	7.67	2.20	2.67	3.34	3.31	4.56
Ho		0.68	1.10	1.50	0.44	0.54	0.61	0.58	0.87
Er		1.96	2.99	4.17	1.28	1.48	1.67	1.48	2.21
Yb		2.00	2.82	3.93	1.45	1.49	1.37	1.28	2.01
Lu		0.32	0.43	0.57	0.20	0.19	0.19	0.17	0.26
Th		7.8	13.4	16.5	7.2	6.3	12.2	9.7	9.1
U		6.5	2.3	2.5	3.8	2.3	0.9	2.4	3.1
V		18	36	25	n.d.	n.d.	11	17	n.d.
Co		22.5	3.1	5.0	1.2	3.5	4.0	3.5	2.4
Ni		16.7	21.7	4.9	1.9	19.7	9.3	6.5	1.9
Zr		96.1	378.8	344.1	43.1	56.5	73.5	79.8	63.6
Nb		7.6	13.0	18.5	8.9	6.0	8.6	10.4	14.2
Hf		3.1	10.5	9.9	2.3	2.7	2.5	3.1	2.5
Ta		0.9	1.0	1.3	1.1	0.9	0.6	0.9	1.5
Ga		14.7	12.7	10.9	12.8	15.6	10.9	12.8	15.6
Pb		1.8	1.4	0.9	2.3	0.5	0.7	0.6	0.6
Eu/Eu*		0.437	0.499	0.324	0.475	0.415	0.437	0.432	0.405

2.6 to 5.3) and high potash/alkali ratio ($K_2O/Na_2O + K_2O^*100$ ranging from 94 to 97) which is typical for K-metasomatism. In order to minimize the effect of post-magmatic alteration, interpretation is mainly based on the immobile elements. The NGU metavolcanics are classified on the basis of incompatible elements Zr/Ti vs. Nb/Y (after Pearce 1996). They assemble a continuous volcanic suite from the metarhyolite and metadacites to metaandesite and basaltic metaandesites and plot in the subalkaline field ($Nb/Y < 0.70$; Fig. 3). The Mg-numbers of the NGU metaandesites and metarhyodacites have

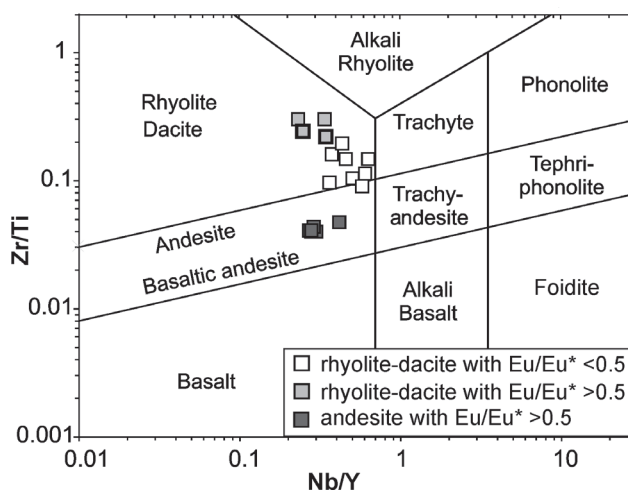
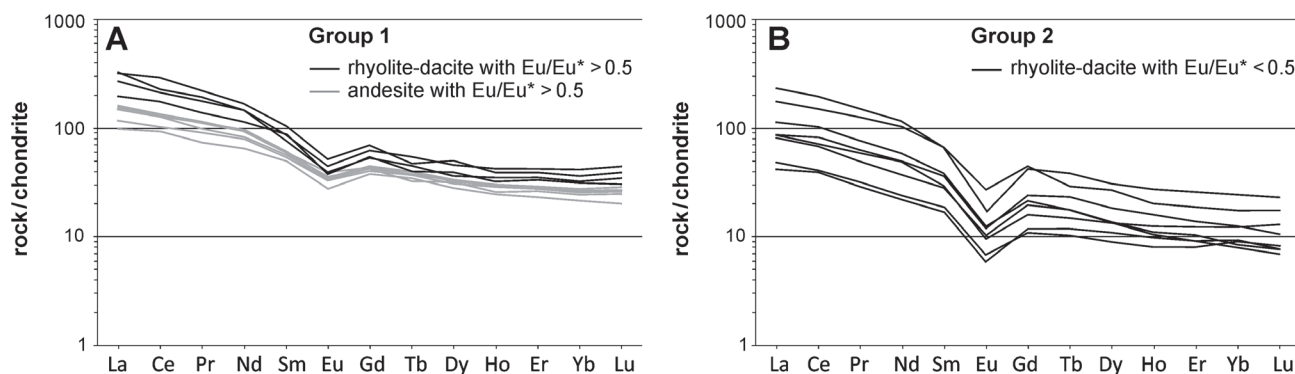


Fig. 3. Zr/Ti vs. Nb/Y diagram (Pearce 1996) corresponding to the NGU Permian volcanic rocks. The zircon-dated samples are designated by bold bordered symbols.

Table 3: List of chemically analysed volcanic rock sample localities.

Sample	Lithostratigraphic unit	Sample locality	GPS coordinates
14 sm	Petrova hora Formation	1.1 km south from Jahodná, 572 m a.s.l.	N 48°46'113" E 21°08'295"
15 sm	Novoveská Huta Formation	NW from Kamenný Hrb height, 530 m a.s.l.	N 48°45'590" E 21°09'500"
25 sm	Novoveská Huta Formation	NW from Kamenný Hrb height, 530 m a.s.l.	N 48°45'590" E 21°09'500"
19 sm	Petrova hora Formation	Čierna Hora height, NW from Dobšiná	N 48°85'836" E 20°34'497"
20 sm	Petrova hora Formation	SE from Kropachy, 445 m a.s.l.	N 48°55'074" E 20°53'818"
21 sm	Petrova hora Formation	SE from Kropachy, 445 m a.s.l.	N 48°55'074" E 20°53'818"
33 sm	Petrova hora Formation	Kolínovce village, 388 m a.s.l.	N 48°55'688" E 20°51'470"
34 sm	Petrova hora Formation	North from Richnava village, 372 m a.s.l.	N 48°55'799" E 20°54'256"
36 sm	Petrova hora Formation	West from Jaklovce village, 396 m a.s.l.	N 48°52'408" E 20°58'404"
39 sm	Petrova hora Formation	West from Jaklovce village, 361 m a.s.l.	N 48°52'160" E 20°58'723"
41 sm	Petrova hora Formation	Southeast from Košická Belá, 390 m a.s.l.	N 48°47'740" E 20°07'072"
GZ-32	Petrova hora Formation	East of Kurišková height, 607 m a.s.l.	N 48°45'810" E 21°09'000"
GZ-33	Novoveská Huta Formation	350 m NW from Kamenný Hrb height, 551 m a.s.l.	N 48°45'411" E 21°09'746"
GZ-34	Novoveská Huta Formation	NW from Kamenný Hrb height, 603 m a.s.l.	N 48°45'393" E 21°09'754"

**Fig. 4.** Chondrite-normalized REE patterns of the NGU Permian volcanic rocks. The chondrite normalizing values come from McDonough & Sun (1995). **A** — Group I volcanics, **B** — Group II volcanics.

the widest range values of 22–60. Based on the $\text{FeO}_{\text{tot}}/\text{MgO}$ ratios compared to the SiO_2 contents (Miyashiro 1974), the studied andesite-rhyolite metavolcanites plot in the field of calc-alkaline suite, with a slight tholeiite trend in basaltic metaandesites. On the whole, they display chondrite-normalized rare earth element (LREE) enrichment and moderate to pronounced negative Eu-anomalies, with no significant heavy rare earth element (HREE) fractionation (Fig. 4). The REE diagram shows apparently two different patterns: Group I — is represented by the basaltic andesite-rhyolite suite, with a slight enrichment in LREE ($\text{La}_N/\text{Yb}_N = 4.51\text{--}9.99$) and Eu anomaly (Eu/Eu^* ranging from 0.54 to 0.71), and Group II — the rhyolite-dacite suite, with decreasing contents of all the REEs compared to Group I and higher enrichment in

LREEs relative depletion of HREEs $\text{La}_N/\text{Yb}_N = 14.33\text{--}9.61$ and a distinct Eu anomaly (Eu/Eu^* ranging from 0.40 to 0.46). Fractionation of plagioclases and titanomagnetites is responsible for the higher Eu and Ti anomalies and for depletion of Sr and V in the Group II rocks. The high Rb/Sr ratios of the Group II rhyolite-dacites, which are >3 , are also consistent with the fractional crystallization of plagioclases.

In a primitive mantle-normalized multi-element variation diagram (Fig. 5), the basic/intermediate and felsic metavolcanites show similar enrichment and depletion trends. These rocks are enriched in Rb, K, Th and U, and strongly depleted in Ba, Sr, Nb, Ta and Ti. Compared to these, the basaltic metaandesites are slightly enriched in Ti and depleted in U. Enrichment in LILE and LREE with troughs at Ta-Nb and Ti, is a distinctive feature considered typical of subduction-

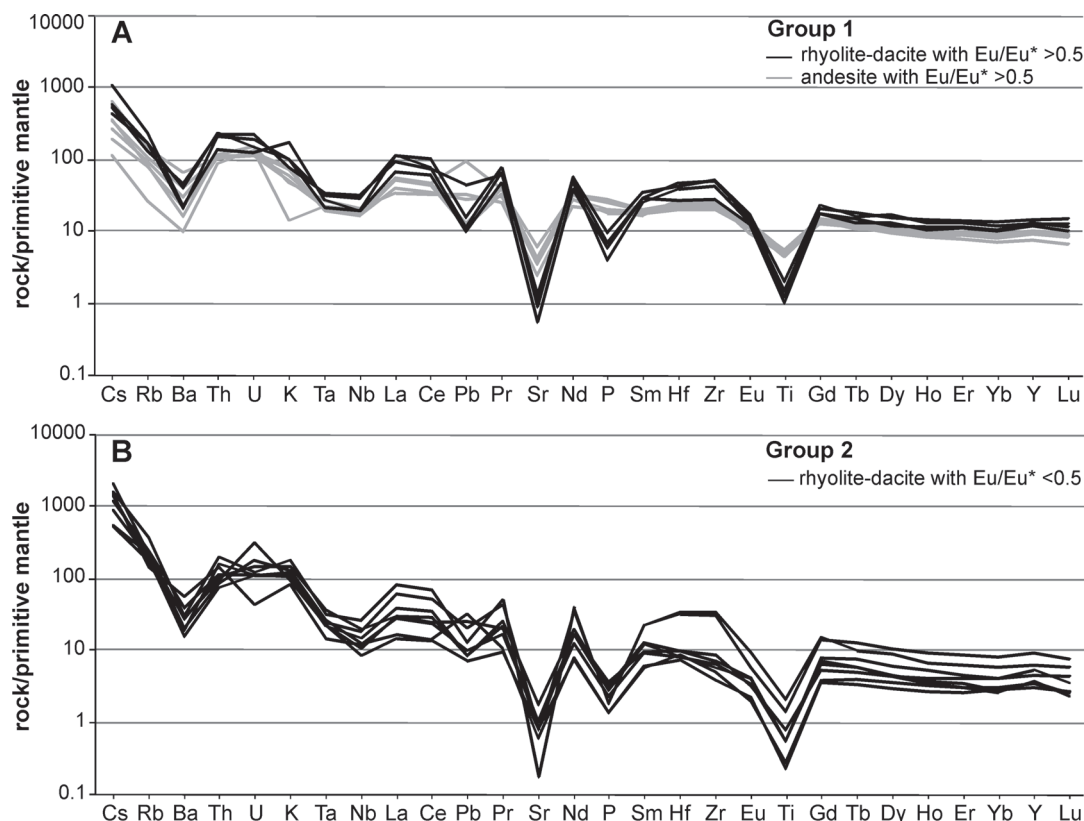


Fig. 5. Multi-element variation diagram of the NGU Permian volcanic rocks. The primitive mantle normalizing values come from Sun & McDonough (1989). **A** — Group I volcanics, **B** — Group II volcanics.

related magma (Pearce 1983). Pearce et al. (1984) described the specific patterns of rock chemical composition for within-plate magmatites. That is exemplified by enrichment of Rb relative to Nb and Ta, as well as Ce and Sm relative to adjacent elements (Fig. 5). According to Harris et al. (1983), such selective enrichment can be attributed to crustal involvement. However, unlike arc-type rocks, the whole studied NGU Permian volcanics display a distinct negative Ba anomaly with respect to the adjacent Rb and Th. Such enrichment of Rb and Th relative to Ba has also been observed in the Permian high-K calc-alkaline magmatism in the Southern Alps (Rottura et al. 1998), in the extension-related Permian calc-alkaline andesites from the Pyrenees (Brouin et al. 1994), in the Permian post-orogenic volcanites in the Apuseni Mts (Nicolae et al. 2014), as well as in the Lower Triassic alkaline rhyolites of the Silicum Unit in the Western Carpathians (Uher et al. 2002). The observed enrichment of Rb and Th relative to Ba cannot be considered in these samples as an effect due to the influence of hydrothermal fluids, since Ba and Rb show a similar mobility and Th is considered immobile. Thus, the trough at Ba represents very likely a primary magmatic feature. The large negative Ba anomaly was also described by Pearce et al. (1984) for within-plate granites situated in areas of attenuated continental lithosphere.

The whole group of the studied NGU Permian acid and intermediate metavolcanics has crustal values for both Nb/La (0.44–0.27) and Nb/U (9.55–4.18) ratios, suggesting that they are predominantly or wholly crustal melts. Magma deri-

vation from continental crust or underplated crust is also indicated by high Y/Nb ratios, ranging from 1.63 to 4.01. According to Eby (1992), these values are characteristic for the A2-type of anorogenic magmatites, derived from partial melting of continental crust or arc-type sources (Fig. 6A,B).

Y-Nb and Yb-Ta are the most effective elements for the tectonic discrimination of granitic rocks as they seem to be independent of alteration (Pearce et al. 1984). Fig. 7A,B show simple projections in Y-Nb and Yb-Ta space. The metarhyolite of Group I, associated with metaandesites, plots in the within-plate granite field. The Group II metarhyodacites overlap the volcanic-arc granite field. This scattered image could indicate the post-collisional tectonic setting that can result from variable mixture of mantle- and crust-derived magma (Colman-Sadd 1982; Pearce et al. 1984). Thus, the metarhyolite of Group I has all the classical characteristics of A-type volcanism, including the high concentrations of alkalis, as well as incompatible elements, such as Nb, Y, Zr and Th. Even associated metaandesites contain higher concentrations of Nb, Y, Zr and Th than the metarhydacite of Group II (Tables 1, 2). The metarhydacites of Group II have significantly lower concentrations of REE, Y, Nb and Zr, and as a result they plot in the volcanic arc field. Similar contrasting types of silicic volcanic rocks were described by Christiansen & McCurry (2008) from Cenozoic volcanism of the western Cordillera. According to their interpretation, they came from different “mantle parents”, i) mantle wedge above subduction zone (linkage to subduction heritage); ii) partial

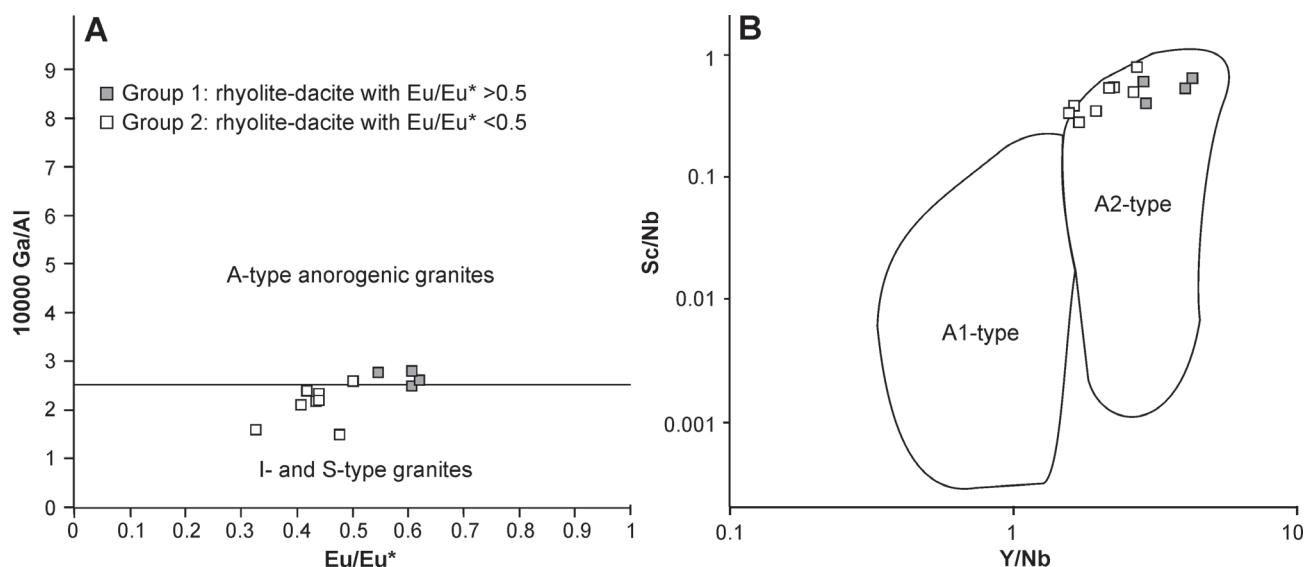


Fig. 6. Chemical characteristics of the NGU Permian volcanites according to Eby's (1992) A-type granitoids subdivision. **A** — 10000Ga/Al vs. Eu/Eu^* discrimination diagram, **B** — Sc/Nb vs. Y/Nb discrimination diagram: A1 — granitoids from rift, plume and hot-spot environments, A2 — granitoids from post-collisional, post-orogenic and anorogenic environments.

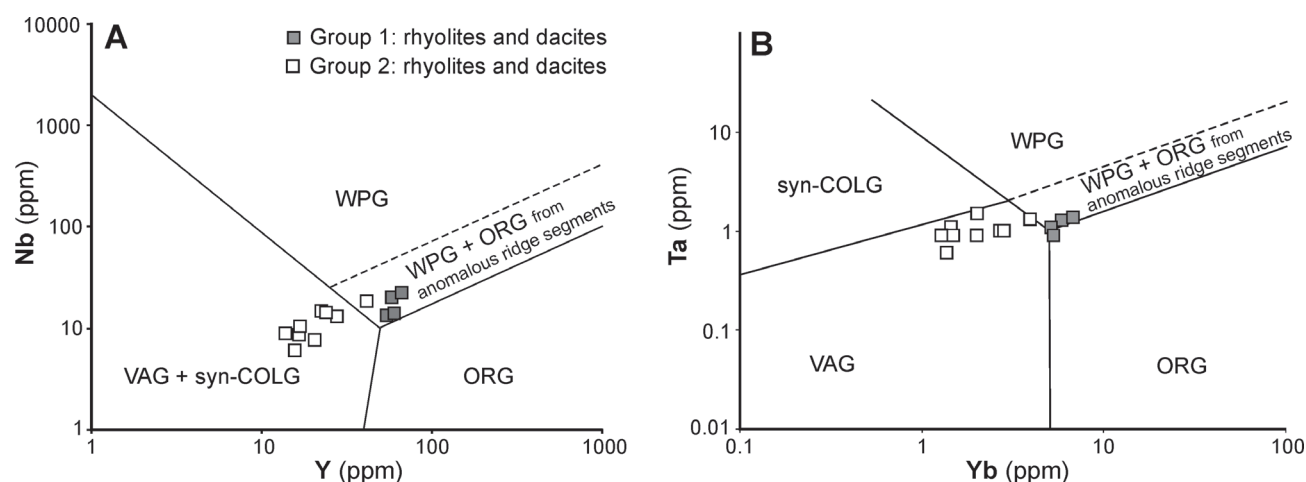


Fig. 7. Nb-Y (A) and Ta-Yb (B) discrimination diagrams for NGU Permian metavolcanics after Pearce et al (1984). **syn-COLG** — syn-collision granites, **VAG** — volcanic arc granites, **WPG** — within-plate granites, **ORG** — ocean ridge granites.

melting in/or above a mantle plume (continental rift and “hot-spots”). The relationship to subduction processes for the NGU Permian volcanics presumed Demko et al. (2007).

Zircon dating

Cathodoluminescence and optic imaging (Fig. 8) reveals that zircons in both studied samples show prismatic and dipyrnidal shapes, obviously with well-developed growth zoning and with less common sector zoning. Perfectly euhedral zircon prisms without evidence of zoning were also observed. Zircon crystals have a rather uniform internal texture, characterized by a narrow fine oscillatory zoning only at their margin. In some zircon crystals, the regular growth zoning is interrupted by textural discontinuities along which

the original zoning is resorbed and succeeded by the new-growth of zoned zircon rims. Textural discontinuities of the magmatic zoning indicate resorption intervals during crystal growths. In some cases, the oscillatory zoning is cut off by areas of re-homogenization, recrystallization and local development of convolute zoning.

Eleven spot analyses in the sample GZ-32 provided Permian ages, in both the oscillatory — zoned rims and the internal parts of crystals. Only one analysis indicates a Mississippian age ($332 \pm 8 \text{ Ma}$). This age represents the maximum age and suggests the involvement of material derived from the Mississippian magmatic rocks. The Permian ages display error ellipses (2σ) overlapping the concordia curve to a greater or lesser extent (Fig. 9). Three results have not been included in the average age calculation (spot analyses 4.1, 4.2, 7.1; Table 4) due to the high U content or higher discordance. All

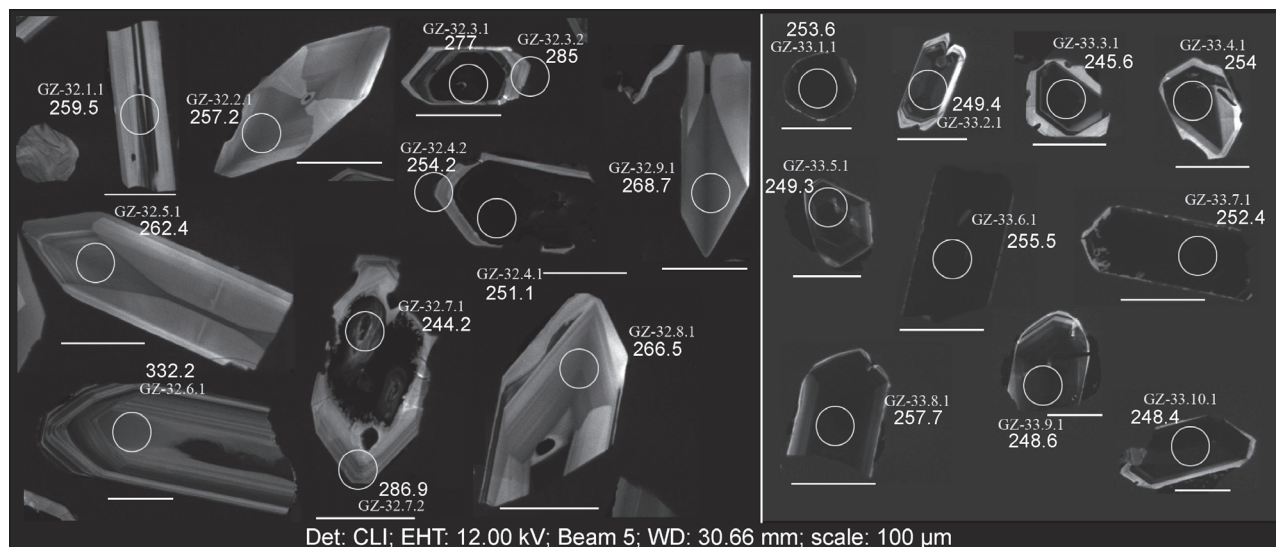


Fig. 8. Selected cathodoluminescence magmatic zircon images from the NGU Permian volcanic rocks with indication of the age data (in Ma) based on $^{206}\text{Pb}/^{238}\text{U}$ ratios.

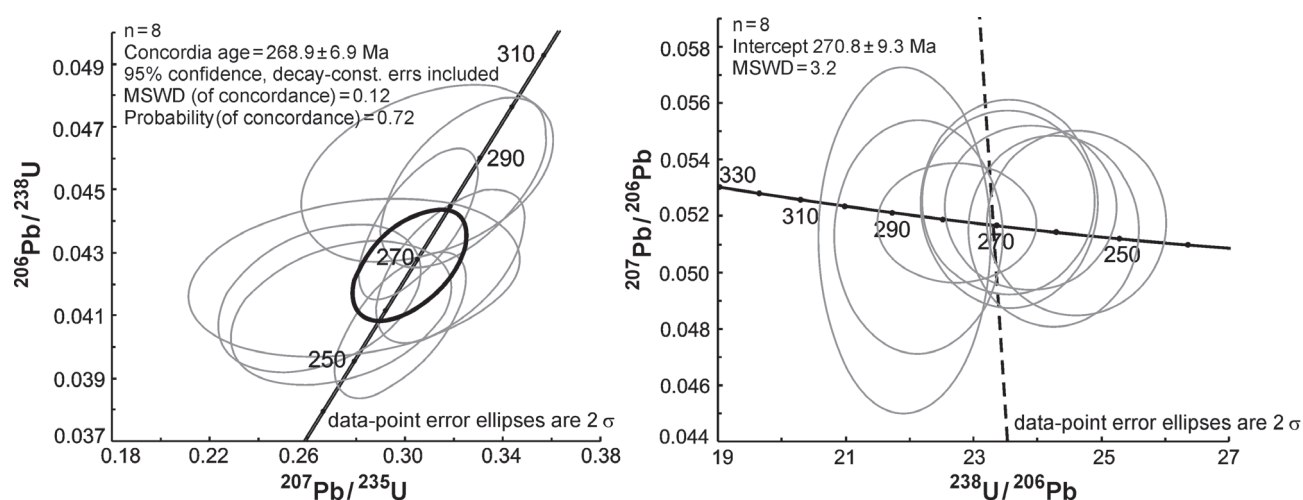


Fig. 9. Concordia plot showing magmatic zircon ages from the sample GZ-32 and corresponding concordia intercept in the Terra-Wasserburg diagram.

the included results indicate U contents of 240–3323 ppm, Th contents of 90–1203 ppm and Th/U ratios between 0.30–0.43. The considered 8 analyses yield $^{206}\text{Pb}/^{238}\text{U}$ concordant ages in the range of 262–276 Ma, with the $^{206}\text{Pb}/^{238}\text{U}$ concordia age of 269 ± 7 Ma (95% confidence, decay-constant errors included; MSWD=0.12; probability=0.72). The total — Pb/U ($^{238}\text{U}/^{206}\text{Pb}$ – $^{207}\text{Pb}/^{206}\text{Pb}$) isochrones indicate the concordia intercept at 271 ± 9 Ma (MSWD=3.2) that coincides approximately with the $^{206}\text{Pb}/^{238}\text{U}$ concordia age (Fig. 9).

Ten zircon grains have been analysed from the sample GZ-33. All the analysed spots were located in the uniform internal parts of the crystals, because the marginal rims of the crystals are either very thin with a faint oscillatory zoning or they are partly recrystallized and resorbed. Compared to the sample GZ-32, zircons from the sample GZ-33 are significantly richer in U and Th (Table 4). All ten measured grains

give $^{206}\text{Pb}/^{238}\text{U}$ apparent ages, ranging between 248 and 255 Ma, which yield the concordia age of 251 ± 4 Ma (2σ decay-constant errors included, with MSWD=0.74 and probability=0.39). The concordia intercept at the Terra-Wasserburg diagram confirms the same age of 252 ± 4 Ma (MSWD=0.49; Fig. 10).

Discussion

The $^{206}\text{Pb}/^{238}\text{U}$ concordia age of 269 ± 7 Ma from the sample GZ-32 corresponds to the uppermost part of the Cisuralian, and/or even straddling the Cisuralian/Guadalupian boundary (Fig. 11). Compared to our previous zircon age data, it fits well into the volcanites of the PHF from the vicinity of Krompachy (272 ± 4 Ma and 275 ± 7 Ma for basaltic andesite

Table 4: U-Pb (SHRIMP) magmatic zircon ages from the NGU Permian volcanic rocks.

Spot	%	ppm	ppm	$\frac{^{232}\text{Th}}{^{238}\text{U}}$	ppm	$\frac{^{206}\text{Pb}}{^{238}\text{U}}$	(1)	Age	%	(1)	%	$\frac{^{207}\text{Pb}^*}{^{206}\text{Pb}^*}$	(1)	%	$\frac{^{207}\text{Pb}^*}{^{235}\text{U}}$	(1)	%	$\frac{^{206}\text{Pb}^*}{^{238}\text{U}}$	(1)	%	err corr
<i>GZ-32</i>	$^{206}\text{Pb}_\text{c}$	U	Th			$^{206}\text{Pb}^*$		$\frac{^{207}\text{Pb}}{^{206}\text{Pb}}$	Disc.			^{238}U	$^{206}\text{Pb}^*$	\pm		\pm		\pm			
<i>GZ-32.1.1</i>	0.39	628	230	0.38	22.2	259.5	± 5.8	116	± 150	-55		24.35	2.3	0.0484	6.4	0.2740	6.8	0.04107	2.3	.337	
<i>GZ-32.2.1</i>	0.00	343	99	0.30	12.0	257.2	± 5.9	335	± 64	30		24.57	2.3	0.0531	2.8	0.2980	3.7	0.04070	2.3	.634	
<i>GZ-32.3.1</i>	0.16	3323	1203	0.37	126.0	277.0	± 6.1	216	± 55	-22		22.78	2.2	0.0505	2.4	0.3054	3.3	0.04390	2.2	.687	
<i>GZ-32.4.1</i>	0.25	3632	1784	0.51	124.0	251.1	± 5.5	146	± 49	-42		25.17	2.2	0.0490	2.1	0.2682	3.0	0.03973	2.2	.731	
<i>GZ-32.4.2</i>	0.30	1104	330	0.31	38.2	254.2	± 5.6	155	± 83	-39		24.87	2.2	0.0492	3.5	0.2730	4.2	0.04022	2.2	.534	
<i>GZ-32.5.1</i>	0.75	399	140	0.36	14.4	262.4	± 6.0	10	± 140	-96		24.07	2.3	0.0462	6.0	0.2650	6.4	0.04154	2.3	.362	
<i>GZ-32.3.2</i>	0.00	240	99	0.43	9.3	285.0	± 6.8	285	± 81	0		22.12	2.4	0.0520	3.5	0.3240	4.3	0.04520	2.4	.568	
<i>GZ-32.6.1</i>	0.18	350	114	0.34	15.9	332.2	± 7.4	311	± 81	-6		18.91	2.3	0.0526	3.5	0.3830	4.2	0.05290	2.3	.543	
<i>GZ-32.7.1</i>	0.00	1915	529	0.29	63.5	244.2	± 5.3	281	± 29	15		25.9	2.2	0.0519	1.3	0.2763	2.6	0.03861	2.2	.865	
<i>GZ-32.7.2</i>	0.23	272	90	0.34	10.7	286.9	± 7.1	161	± 150	-44		21.97	2.5	0.0493	6.3	0.3090	6.8	0.04550	2.5	.369	
<i>GZ-32.8.1</i>	0.55	353	116	0.34	12.9	266.5	± 6.4	98	± 230	-63		23.69	2.4	0.0480	9.6	0.2790	9.9	0.04220	2.4	.245	
<i>GZ-32.9.1</i>	0.00	430	159	0.38	15.7	268.7	± 6.2	383	± 70	42		23.49	2.3	0.0543	3.1	0.3190	3.9	0.04257	2.3	.602	
<i>GZ-33</i>																					
<i>GZ-33.1.1</i>	0.06	9021	10917	1.25	311.0	253.6	± 5.7	267	± 35	5		24.93	2.3	0.0515	1.5	0.2853	2.8	0.04012	2.3	.832	
<i>GZ-33.2.1</i>	0.47	1370	953	0.72	46.7	249.4	± 5.7	293	± 120	17		25.35	2.3	0.0522	5.1	0.2840	5.6	0.03945	2.3	.414	
<i>GZ-33.3.1</i>	0.18	3672	3762	1.06	123.0	245.6	± 5.4	185	± 80	-25		25.75	2.2	0.0498	3.4	0.2670	4.1	0.03884	2.2	.548	
<i>GZ-33.4.1</i>	0.19	2521	1452	0.60	87.2	254.0	± 5.6	244	± 85	-4		24.89	2.3	0.0511	3.7	0.2830	4.3	0.04018	2.3	.525	
<i>GZ-33.5.1</i>	0.22	2194	1709	0.80	74.5	249.3	± 5.7	259	± 130	4		25.36	2.3	0.0514	5.4	0.2790	5.9	0.03943	2.3	.391	
<i>GZ-33.6.1</i>	0.05	6298	4629	0.76	219.0	255.5	± 5.5	303	± 35	18		24.73	2.2	0.0524	1.5	0.2921	2.7	0.04043	2.2	.821	
<i>GZ-33.7.1</i>	0.29	7482	10863	1.50	257.0	252.4	± 5.6	260	± 44	3		25.05	2.2	0.0514	1.9	0.2831	3.0	0.03992	2.2	.760	
<i>GZ-33.8.1</i>	0.47	4461	3564	0.83	157.0	257.7	± 5.7	115	± 130	-55		24.51	2.3	0.0483	5.5	0.2720	5.9	0.04079	2.3	.382	
<i>GZ-33.9.1</i>	0.30	3751	4073	1.12	127.0	248.6	± 5.5	320	± 75	29		25.44	2.2	0.0528	3.3	0.2860	4.0	0.03931	2.2	.562	
<i>GZ-33.10.1</i>	0.23	3077	1467	0.49	104.0	248.4	± 5.5	239	± 78	-4		25.46	2.2	0.0510	3.4	0.2760	4.1	0.03928	2.2	.554	

Errors are 1-sigma; Pb_c and Pb* indicate the common and radiogenic portions, respectively. Error in Standard calibration was 0.73 % (not included in above errors but required when comparing data from different mounts). (1) Common Pb corrected using measured ^{204}Pb . Disc. = diskordia.

and rhyolite, respectively; Vozárová et al. 2012) indicating the Kungurian age. Generally, the new U-Pb zircon dating has a good consistency with that. Nevertheless, zircons from the sample GZ-32 show some recrystallization features and modification in their texture (disruption of oscillatory zoning cutting off by areas of re-homogenization, recrystallization and local development of convolute zoning). Even a slight modification of magmatic zircon crystals during late- and post-magmatic processes could result in resetting of U-Pb ages, (although, hardly distinguishable within error limits). Thus, this effect could be a reason for the slight rejuvenation and then the relatively younger ages in the sample GZ-32 compared to previous results from the Krompachy volcanics. Eventually, all the obtained U-Pb ages are in the same stratigraphic range, corresponding to the Kungurian, and/or just near the boundary of the Kungurian-Roadian. This time range defines a dispersion of the main volcanic events in the Permian of the NGU sedimentary basin. Similar U-Pb zircon ages were received from the Southern Gemic acid volcanites (273.3 ± 2.8 Ma and 275.3 ± 2.9 Ma, respectively; Vozárová et al. 2009b), as well as from the rhyolite-dacites of the Northern Veporic Unit (273 ± 6 Ma and 279 ± 4 Ma; Vozárová et al. 2010) and the Gemic granites (Finger & Broska 1999; Kohút & Stein 2005; Radvanec et al. 2009). Analogous zircon ages, ranging from 279.6 ± 1.1 Ma to 274.1 ± 1.6 Ma, were reported by Bargossi et al. (2004) from the Bolzano Volcanic Complex in the Southern Alps. A corresponding sequence comprising rhyodacites and their ignimbrites is widespread at the top of the Cisuralian succession in the Eastern Alps that also correlates with the Bolzano Volcanic Complex (Krainer in McCann et al. 2008).

However, the detrital zircon age spectra from the two samples of the NGU Permian sandstones (both PHF and NHF) also indicate the presence of older magmatic events in the depositional area, corresponding to the Sakmarian and to the Artinskian (concordia ages 281 ± 7 Ma and 292 ± 6 Ma; Vozárová et al. 2013). No doubt, these zircon grains were redeposited as clastic detritus from the coeval volcanic centers into the sedimentary basin and they mixed with spatially widespread non-volcanic detritus, and even could have been reworked in the younger Permian sediments. Thus, the NGU Permian bulk igneous activity, as in many other areas of the Central and Southern European Variscides (Rottura et al. 1998; Vozárová et al. 2010;

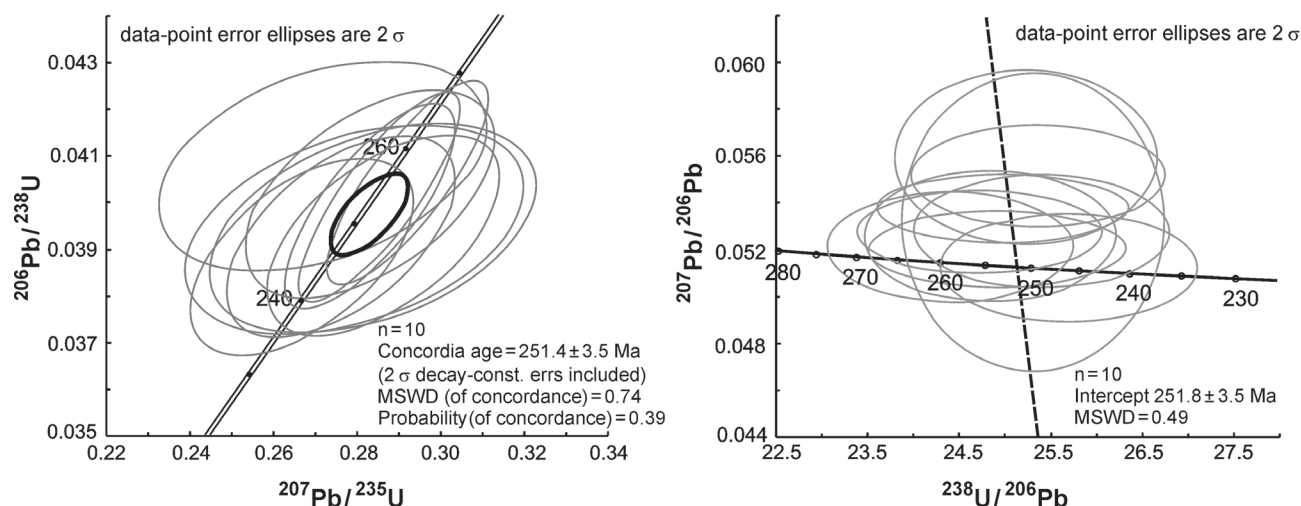


Fig. 10. Concordia plot showing magmatic zircon ages from the sample GZ-33 and corresponding concordia intercept at the Terra-Wasserburg diagram.

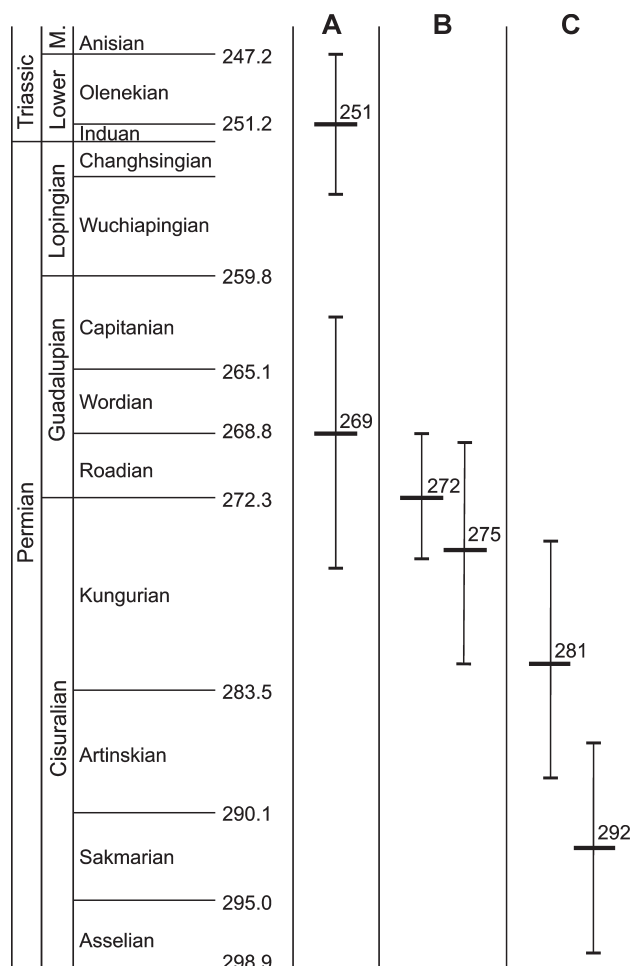


Fig. 11. The SHRIMP zircon age timescale of the NGU Permian volcanic rocks. **Column A** — age results from the present paper, **column B** — magmatic zircon ages published in Vozárová et al. (2012), **column C** — zircon ages derived from detrital zircon assemblages of the Petrova hora and Novoveská Huta Formations (taken from Vozárová et al. 2013).

Nicolae et al. 2014 and references therein), took place mainly throughout the Cisuralian. It seems not to function later than the early Guadalupian (Roadian), that predates the Illawara Reversal geomagnetic event (IR ca. 265 Ma; Menning 2001). The only exceptions in the Western Carpathians are the basaltic volcanic suite of the 2nd eruption phase in the Hronic Unit that is located over the IR (Vozárová & Túnyi 2003) and silicic volcanites in the Bórka Nappe (260 Ma; Vozárová et al. 2012). The question remains, if the NGU Permian volcanism represents one long-lasting episode or two independent volcanic events. The Cisuralian bulk volcanic activity was probably split mostly into two independent events, the first extending throughout the Sakmarian and the second one during the Kungurian. Of course, this assumption should be confirmed by further precise zircon dating.

Sample GZ-33 shows a significantly diverse age (Fig. 10, Table 4). The apparent $^{206}\text{Pb}/^{238}\text{U}$ ages vary between 248 and 255 Ma, which yield the concordia age of 251 ± 4 Ma. Compared to the age results of sample GZ-32, and the samples dated previously from the NGU Permian volcanites (Vozárová et al. 2012), the sample GZ-33 $^{206}\text{Pb}/^{238}\text{U}$ zircon age is significantly younger. The difference between these two data groups is less than ca. 20 Ma. The detected U-Pb zircon ages document, for the first time, the boundary Permian/Triassic volcanism in the Western Carpathians. According to the International Stratigraphic Chart 2014 (International Sub-commission on Stratigraphy, 2014; updated according to Cohen et al. 2013), the boundary between the Permian and Triassic systems is established at 252.17 ± 0.06 Ma.

The NGU Permian-Triassic volcanic event seems to be approximately coeval with the sedimentation of the NHF evaporite member that is correlated with the Zechstein (in the sense of Regional Stratigraphic Scale, Stratigraphic Table of Germany Compact 2012) based on the S and O isotopes (Kantor et al. in Vozárová 1997). The polymict conglomerates (the Strážany Beds according to Mihál in Rojkovič & Mihál 1991) that underlie this evaporitic lithofacies, contain fragments of volcanites, which were redeposited from the Cisuralian volcanic suite.

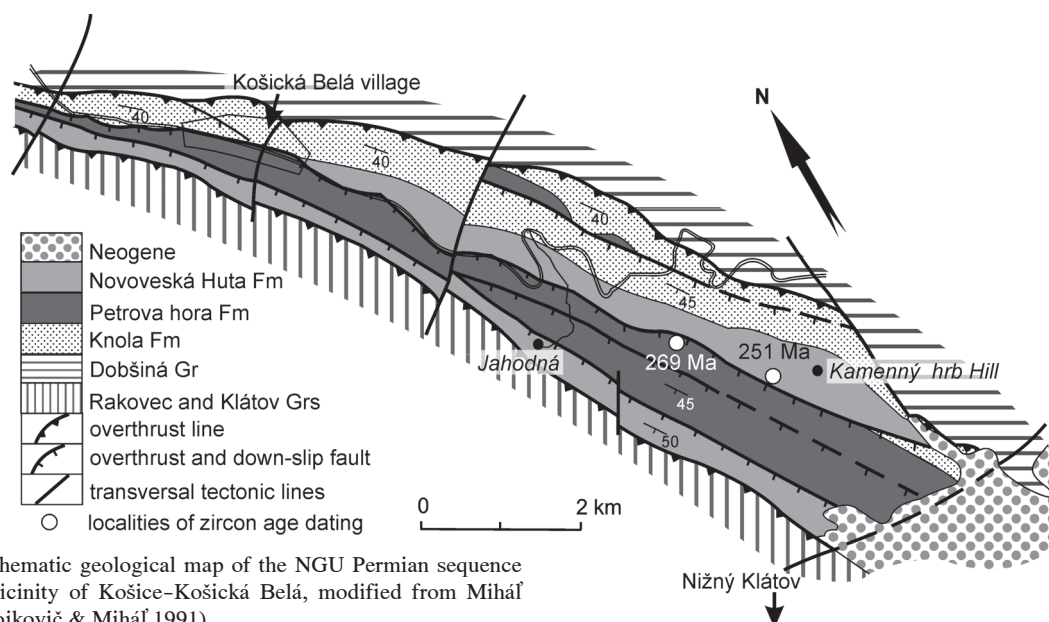


Fig. 12. Schematic geological map of the NGU Permian sequence from the vicinity of Košice-Košická Belá, modified from Mihál' (1990 in Rojkovič & Mihál' 1991).

Occurrences of evaporites, associated with fine-grained sandstones, shales and dolomites have been recognized in the boreholes from the vicinity of the village of Košická Belá, north of the Permian-Triassic boundary volcanic horizon. These sediments fall within the youngest formation of the Permian sequence around Košice and Košická Belá and have been correlated with the evaporite horizon in the area of Novoveská Huta (Václav & Vozárová 1978), and later affiliated to the NHF (Bajaník et al. 1981). As the radiometric age data from the Permian volcanites of the Košice-Košická Belá area are generally missing, all these volcanic rocks were assigned to the PHF. The presented zircon age data enable us to separate a part of these volcanic rocks from the PHF and to synchronize them with the NHF (Fig. 12).

On the account of that, the stratigraphic gap from the end of Cisuralian eventually from the mid-Guadalupian to the Lopingian, is supposed to be trustworthy. The major stratigraphic gap and viable break of sedimentation within the NGU Permian sequence were probably caused by a tectonic pulse that most likely induced extensional faulting and uplift connected with strike-slip movements and erosion at least in some places. This tectonic event could have been related to the so-called "Mid-Permian Episode" of Derooin & Bonin (2003), connected with the transformation of strike-slip to an extensional tectonic regime. A similar stratigraphic gap and geodynamic changes were described in the Eastern and Southern Alps as well as in the wide peri-Mediterranean realm (Krainer 1993; Cassinis et al. 2012 and references therein) that was reflected in the evolution of two major tectono-sedimentary cycles. Cassinis et al. (2012) considered this stratigraphic gap to be synchronous with the geomagnetic IR event (Menning 1995, 2001; Steiner 2006) that has been postulated by Isozaki (2009) as the trigger agent for the Pangea breakup.

However, the $^{206}\text{Pb}/^{238}\text{U}$ zircon ages in the sample GZ-33 undoubtedly document a specific stage of volcanic activity that is different from the Cisuralian one. Its discrepancy is highlighted by differences in time and partly also in geo-

chemistry. As the dacites represented by the sample GZ-32 have prevailing K_2O over Na_2O (5.16 wt. % vs. 0.60 wt. %), they may indicate the high-K calc-alkaline volcanic series. On the contrary, in the samples GZ-33 and GZ-34 (Tables 1, 2), a significant increase of the Na_2O (4.15 and 7.14 wt. %) over K_2O (3.02 vs. 0.42 wt. %) has been determined. However, all the analysed samples show the same trend of enrichment in LREE as well as in incompatible elements such as U, Th, Ta and Nb in comparison with the moderately incompatible Ti and HREE. Similarly, the ratios Nb/La and Nb/U that serve as magma genesis indicators have the same values, for Nb/La in the range of 0.27 to 0.33 and for Nb/U ranging from 5.2 to 4.2. These low ratio values are close to the continental crust data and are characteristic for crustal melting (Nb/La=0.71 and Nb/U=9.7 for continental crust calculated by Rudnick & Fountain 1995).

In the Western Carpathians, Lower to Middle Triassic high-K rhyolites have been described from the Silicic Unit (Uher et al. 2002). They were interpreted by the authors as genetically connected with the early Alpine rifting. Similarly, the U-Pb zircon age of 233 ± 4 Ma (Putiš et al. 2001) from the plagiogranite-aplitic vein bodies cutting the Layered Amphibolite Complex in the Veporic crystalline basement was interpreted. On the contrary, the monazite ages from the geologically equivalent rhyolite body (the Silicic Unit), at Gregová near Telgárt village, confirmed the Middle/Upper Permian age of 263 ± 3.5 Ma (Demko & Hraško 2013). The intermediate to basic Middle Triassic anorogenic volcanism was described from the wide area of the Transdanubia, Bukkia and Adri-Dinaria terranes (Kovács et al. 2010 and references therein).

The acid to intermediate volcanism, as it has been already mentioned, is dominant in the Cisuralian with the exception of the Ligurian Alps, where this volcanism is situated above the IR horizon (Dallagiovanna et al. 2009; Cassinis et al. 2012 and references therein), but not at the Permian/Triassic boundary.

Although the NGU Permian volcanites show some geochemical features similar to arc-related suites (enrichment in

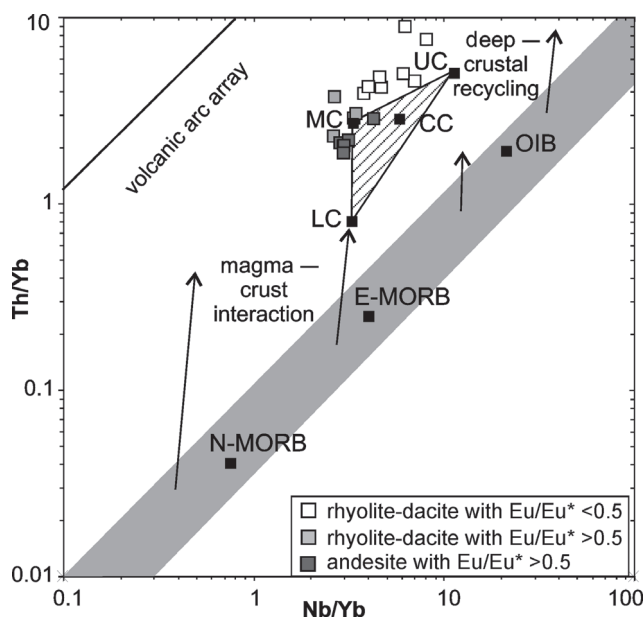


Fig. 13. Th/Yb vs. Nb/Yb diagram of the NGU Permian volcanic rocks (after Pearce 2008). Average N-MORB, E-MORB, OIB are taken from Sun & McDonough (1989); average lower crust (LC), middle crust (MC), upper crust (UC) and total continental crust (CC) are selected from Rudnick & Fountain (1995).

LILE and LREE with troughs at Ta-Nb and Ti; Pearce 1983), the paleogeographic reconstruction and geological and tectonic evidence (Bajanik et al. 1984; Novotný & Mihál 1987; Vozárová & Vozár 1988; Rojkovič & Mihál 1991; Vozárová 1996), do not support any spatial and temporal connection with subduction processes. This volcanism post-dates the 355 peak of the Variscan metamorphism in the NGU realm (Putiš et al. 2009; Vozárová et al. 2013), as well as the late Bashkirian-Moscovian uplift of the metamorphic nappes in the NGU Variscan orogenic belt (Vozárová 1973, 1996; Vozárová et al. 2013 and references therein). It is post-collisional with respect to the Late Devonian-Mississippian collision, that led to the accretion of the NGU orogenic belt to the Prototatricum crust (the term Prototatricum is coined by Broska et al. 2013 for the common Variscan basement of the Tatricum and the Veporicum Units) which was the part of the Galatian Superterrane (von Raumer & Stampfli 2008; von Raumer et al. 2009; Stampfli et al. 2011), with the oceanic crust of the Prototethys. Radvanec et al. (2009) argued that the crustal extension above the Late Variscan subduction zone was the origin of the Gemeric granites, as well as the Permian volcanics.

In the Th/Yb vs. Nb/Yb diagram (Fig. 13), all the NGU Permian samples are plotted outside the diagonal MORB-OIB array, on a vector at a steep angle but closer to E-MORB for Group I, and may be related to the variable fractionation processes and variable crustal contamination (Pearce 2008). Group I, represented by the basaltic andesite-rhyolite suite, shows depletion in Th and Nb compared to rhyolite-dacite suite of Group II. These data suggest that the Group I volcanic rocks were derived by partial melting of enriched lithosphere mantle, modified by subducted slab-derived fluids.

The rhyolite-dacite suite magma of Group II was probably generated by partial melting of newly accreted crust.

Conclusions

1. The new $^{206}\text{U}/^{238}\text{Pb}$ zircon ages confirm the dominant Kungurian volcanic event in the NGU Permian sedimentary basin. Simultaneously, Permian-Triassic boundary volcanism at 251 ± 4 Ma is indicated for the first time;
2. The NGU Permian volcanites have petrological and geochemical characteristics similar to those of a subduction related calc-alkaline suite. However, geological and tectonic evidence points to an intracontinental extensional regime, associated with the Late Paleozoic dextral transtensional tectonics caused by the relative motion of Gondwana and Laurasia (Vai 1991, 2003; Ziegler 1993; Torsvik & Cocks 2004; Muttoni et al. 2009). The NGU volcanic rocks may have been formed by an extensive crustal contamination of basaltic-intermediate magma (Group I) derived from an enriched lithospheric mantle source and by partial melting of newly accreted crust (Group II);
3. The NGU Permian volcanic activity was associated with the polyphase extensional tectonic regime. Based on the U-Pb zircon ages, the bulk of the NGU Permian activity occurred during the Cisuralian, mostly during the Sakmarian and the Kungurian. Both were related to the post-orogenic transpression/transtension and extensional tectonic movements that reflect the consolidation of the Variscan orogenic belt. The last volcanic phase was linked with extension at the Permian-Triassic boundary that was in the NGU realm in connection with the beginning of the Alpine orogenic cycle.

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