GEOLOGICA CARPATHICA, FEBRUARY 2018, 69, 1, 17–29 doi: 10.1515/geoca-2018-0002

Provenance study of detrital garnets and rutiles from basaltic pyroclastic rocks of Southern Slovakia (Western Carpathians)

ONDREJ NEMEC and MONIKA HURAIOVÁ

Department of Mineralogy and Petrology, Faculty of Natural Sciences, Comenius University, Ilkovičova 6, 842 15 Bratislava; ondrej.nemec@uniba.sk, monika.huraiova@uniba.sk

(Manuscript received March 24, 2017; accepted in revised form December 12, 2017)

Abstract: Detrital garnets and rutiles have been recovered from basaltic pyroclastic rocks in the northern part of the Pannonian Basin and characterized using electron probe microanalysis and imaging. All garnets are dominated by the almandine component, except for one sample dominated by spessartine. A total of three garnet groups have been distinguished according to the increased contents of grossular (Group I), pyrope (Group II) and spessartine components (Group III). Compositions of the group I and II garnets with fluctuating Ca- and relatively low Mg contents are consistent with low- to medium-grade metasediments and/or metabasites. Locally increased Mg contents could indicate higher *P–T* metamorphic overprint. The dominantly metamorphic origin of the Group I and II garnets (composed of >99 % of samples) is also corroborated by chlorite, tourmaline, staurolite, ilmenite and andalusite inclusions. Spessartine-rich garnets (Group III composed of <1 % of samples) could be genetically linked with granitoids. Detrital rutiles invariably plot within the field of metasediments metamorphosed under amphibolite-facies conditions. Possible proximal (subjacent basement sampled by ascending lava) or distal sources (catchment sediments from uplifted Central Carpathian basement) of heavy mineral assemblages are discussed.

Keywords: Western Carpathians, Slovakia, maar, diatreme, garnet, rutile, provenance study.

Introduction

A number of studies have been carried out to reveal the provenance of heavy mineral detritus in sedimentary basins (e.g., Mange & Morton 2007). Geochemical characteristics of specific heavy minerals bear information about igneous and metamorphic basement rocks in their source regions and/or distant contemporaneous volcanism. However, only a little attention has been hitherto paid to heavy mineral assemblages from pyroclastic rocks deposited from phreato-magmatic eruptions in intra-plate tectonic settings. Although the vast majority of heavy minerals in the volcanoclastic deposits are unequivocally genetically related to parental magma (e.g., olivine, pyroxene, amphibole, spinel), some minerals (e.g. tourmaline, rutile, staurolite, andalusite) must have been obviously disrupted from the subjacent basement or clastic sedimentary rocks during explosive volcanism, thus possibly providing information about the composition of the continental lithosphere.

Garnet is a key rock-forming mineral of magmatic and metamorphic rocks from various tectonic settings. Its chemical composition is significantly dependent on that of parent rocks, as well as on crystallization conditions. Together with the relative stability under weathering and metamorphic reworking (e.g., Morton & Hallsworth 2007), these factors make garnet the most widely used mineral for the discrimination of sediment provenance (Morton 1985; Méres 2008; Šarinová 2008; Aubrecht et al. 2009; Suggate & Hall 2014).

In contrast to garnet, rutile has received only minor attention as a provenance indicator (e.g., Götze 1996; Preston et al. 1998, 2002), although it is a common accessory mineral in medium- to high-grade metamorphic rocks. In contrast, most igneous and low-grade metamorphic rocks are practically devoid of rutile (Force 1980, 1991) with some exceptions for authigenic rutile and sagenitic rutile crystals (Mange & Maurer 1992) that are only rarely preserved in heavy mineral fraction during the separation process.

Rutile's structure allows for Al, V, Cr, Fe, Nb, Ta, Zr, Hf and U to substitute for Ti (Graham & Morris 1973; Brenan et al. 1994; Hassan 1994; Murad et al. 1995; Smith & Perseil 1997; Rice et al. 1998; Zack et al. 2002; Bromiley & Hilairet 2005; Scott 2005; Carruzzo et al. 2006). Cr and Nb contents are particularly useful for the discrimination between metapelitic and metamafic source lithologies (Zack et al. 2004a). In addition, the incorporation of Zr into the rutile crystal lattice has a strong temperature and pressure dependence, thus allowing for the calculation of crystallization *P–T* conditions (Zack et al. 2004b; Watson et al. 2006; Tomkins et al. 2007). Given the above reasons, variations in chemical compositions of rutile combined with the Zr-in-rutile thermometry yield an important tool for deciphering source rock lithology and/or metamorphic facies necessary for reliable provenance study.

This paper is focused on the garnet and rutile recovered from pyroclastic infillings of maars and diatremes of the south Slovakian Volcanic Field located in the northern part of the

Pannonian Basin (Fig. 1). The study area comprises two maars in Fiľakovo town (Hradný vrch, 48°16'17" N, 19°49'33" E and Červený vrch, 48°16'43" N, 19°49'24" E), maars near Hodejov (48°17'52" N, 19°59'3" E), Hajnáčka (Kostná dolina, 48°12'35" N, 19°57'59" E) and Gemerské Dechtáre (48°14'7" N, 20°1'35" E) villages, as well as two diatremes within the municipalities of Šurice (48°13'34" N, 19°54'47" E) and Tachty (48°9'22" N, 19°56'47" E) villages. The main research objective was to elucidate the source rocks and origin of detrital garnets and rutiles from pyroclastic deposits using geochemical characteristics. The obtained data provide information about the nature of pre-Tertiary basement supplemental to that obtained by the direct investigation of xenoliths (e.g., Hovorka & Lukáčik 1972; Elečko et al. 2008).

Geological setting

The South Slovakian Volcanic Field (SSVF) covers an area of about 150 km², which extends over the Lučenská kotlina Depression and the Cerová Vrchovina Upland continuing into northern Hungary. Both regions represent a part of the Juhoslovenská kotlina Depression in the northernmost promontory of the Pannonian basin within the Carpathian arc (Fig. 1a). The Panonnian basin is a back-arc basin formed on thinned crust during the extension established after a Miocene subduction (Konečný et al. 2002). Alkali basalt volcanism in this area represents typical intraplate association developed as a response to a decompression melting associated with the back-arc extension coincidental with a diapiric

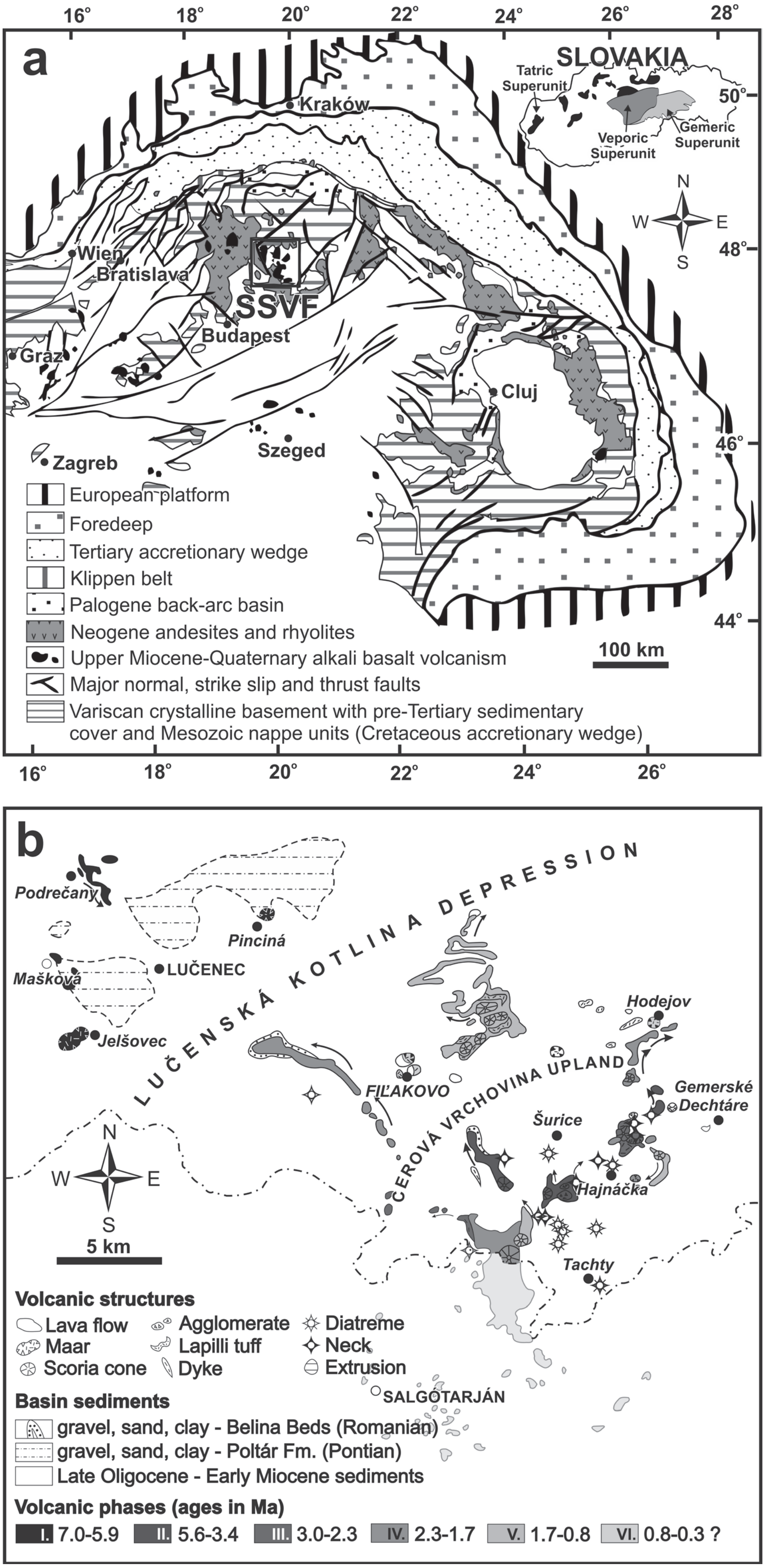

Fig. 1. a — Schematic map of the Carpathian arc and the intra-Carpathian back-arc (Pannonian) basin (modified after Pécskay et al. 2006). Rectangle marks the south-Slovakian Volcanic Field (SSVF). **b** — Sketch map of SSVF with marked volcanic phases (modified after Vass et al. 2007).

updoming of asthenospheric mantle (Dobosi et al. 1995; Downes et al. 1995; Konečný et al. 1995).

Mafic alkali magma of the SSVF erupted within the time interval from ~7 to 0.2 Ma (Vass et al. 2007) during a total of six consecutive volcanic phases (Fig. 1b). The initial Late Miocene phase (1st phase) in north-western part of the Juhoslovenská kotlina Depression includes lava flows along the western margin of the Lučenská kotlina Depression (Podrečany and Mašková) and two maars near Jelšovec and Pinciná villages. Whole-rock K–Ar radiometric ages (6.44±0.47 Ma and 6.6±0.4 Ma) of the lava flow near Podrečany (Balogh et al. 1981) corresponded to biostratigraphic data from the Poltár Formation (Planderová 1986) deposited in fluvial/limnic environment contemporaneously with the volcanic activity of this area (Vass et al. 2007). Products of the Late Miocene volcanic activity are affiliated with the Podrečany Basalt Formation (Balogh et al. 1981; Vass & Kraus 1985). Recent U–Pb and U–Th(He) data on zircon and apatite from Jelšovec and Pinciná maars, however, indicate their Late Pliocene ages (Hurai et al. 2010, 2013).

The following volcanic activity (2nd to 6th phase) taking place in the terrestrial environment of the south-eastern part of the SSVF during the Pliocene to Quaternary was triggered by a local overheating caused by the updomed mantle plume (Konečný et al. 1995). Alkali basalts of the Cerová Vrchovina Upland are affiliated with the Cerová Basalt Formation (Vass & Kraus 1985). Volcanism in this area gave rise to a number of effusive forms, such as lava flows, necks and dykes, as well as products of phreatic and phreato-magmatic eruptions involving maars, tuff rings, scoria- and spatter cones. Diatremes representing feeder conduits of overlying maars removed by erosion due to vertical movements along NW–SE and NE–SW faults can also be discerned in this area (Konečný et al. 1995).

Volcanic activity of 2nd stage (5.5–3.7 Ma) occurred dominantly inside and occasionally along margins of the updomed area. It included several lava necks, cinder cones and lava flows located in the southern part of the Cerová Vrchovina Upland. Two diatremes near Tachty and Stará Bašta villages were probably also created during this stage. The 3rd stage took place within the time interval from 2.9 to 2.6 Ma close to margins of the updomed area. The stage comprises the Šurice and Hajnáčka diatremes that are subjects of this study. After short-lasting break (about 0.3 Ma), volcanic activity expanded over the margins of the updomed area during the 4th volcanic stage (2.3–1.6 Ma), creating several lava flows and a complex maar near Bulhary village. The 5th volcanic stage (1.6–1.1 Ma) occurred dominantly in the Lučenská kotlina Depression accompanied by sporadic activity within the updomed area. Two maars near Fiľakovo (Hradný vrch and Červený vrch) and Hodejov municipality were affiliated with the youngest 6th volcanic stage according to their relationship to river terraces and their position on presumably Quaternary erosion palaeosurfaces (Konečný et al. 2004; Vass et al. 2007). However, combined U/Pb and (U-Th)/He zircon and apatite geochronometry showed considerably older ages, corresponding to 2.8±0.2 Ma at Hodejov and 5.5±0.6 Ma at Fiľakovo-Hradný vrch (Hurai et al. 2013).

Volcanic products of the SSVF penetrate Upper Oligocene to Lower Miocene sedimentary formations deposited onto pre-Tertiary low-to-medium grade basement units. The pre-Tertiary basement in the northern part of the Lučenská kotlina Depression consists of early Variscan high-grade metamorphic and granitoid rocks of the Veporicum Unit covered by Late Carboniferous (Revúca Group) and Late Triassic (Foederata Group) sedimentary formations. The upper part of the basement is represented by the Gemericum superunit located to the south from the Lubeník-Margecany Line. The Gemericum superunit consists of low grade metamorphic rocks of the Early Palaeozoic Gelnica Group (porphyroids, silicic metatuffs, metasandstones and phyllites) overlain by remnants of the Carboniferous Ochtiná Formation of the Dobšiná Group (sericite-chlorite and graphite-sericite phyllites, metabasalts and carbonates with local occurrences of serpentinites). The Mesozoic Meliata group composed mainly of limestones, shales and volcanic rocks is exposed in the southern part of the Gemericum Superunit (Vass & Elečko 1992).

All afore-mentioned tectonic units are demarcated by the Tertiary, SW–NE-striking Rapovce–Plešivec transform fault. Tectonic assignment of rock complexes occurring south from this fault is ambiguous. Knowledge of the pre-Tertiary basement in this area is only based on a single, relatively shallow (~2 km) borehole near Blhovce (FV-1) and rare xenoliths found in maars, diatremes and basalt lava flows. Low-grade metamorphic rocks (green-schist, phyllite) intercepted by the FV-1 borehole are alternatively correlated either with Palaeozoic rocks of the Gemericum superunit (Snopková & Bajaník 1979; Vass et al. 2007) or those of the Agtelek-Rudabánya unit (Dank & Fülop 1990). High-grade metamorphic rocks (gneiss, amphibolite) described as xenoliths in andesite laccoliths near Šiatorská Bukovinka are tentatively correlated either with the Variscan basement of the Veporicum superunit (Hovorka & Lukáčik 1972) or with the Meliata unit (Plašienka et al. 1997). The Late Oligocene (Kiscellian) Číž Formation and the Eggerian Lučenec Formation subjacent to Early Eggenburgian coastal sediments of the Fiľakovo Formation (Vass & Elečko 1992) cover older unknown tectonic units beneath the Lučenská kotlina Depression and Cerová Vrchovina Upland.

Methods

Samples of volcanoclastic material, 10–15 kg in weight were taken from non-coherent tuff and lapilli tuff horizons of maar structures and diatremes. The heavy mineral fraction was obtained by panning of the clastic material <2 mm in diameter. The follow-up separation process included sieving to the 0.5–0.63 mm fraction, gravitational separation in heavy liquid (bromoform with D=2.8 g/cm^3 or sodium polytungstate with D=2.9 g/cm^3) and electromagnetic separation. Garnet and rutile grains were handpicked from the paramagnetic fraction under the binocular microscope, then mounted in epoxy resin, sectioned and polished.

Mineral identification was carried out using a HORIBA Jobin–Yvon Xplora Raman spectrometer at the Geological division of the Earth Science Institute of the Slovak Academy of Sciences (Banská Bystrica). Spectra were recorded using 532 or 638 nm excitations of a 25 mW Nd-YAG laser. A long-working-distance LMPLanFI 100×0.8 objective lens of an Olympus BX-51 optical microscope focused the laser beam and collected the scattered light with a Peltier-cooled (−70 °C), multi-channel CCD detector (1024×256 pixels) with spectral resolutions of 1.8 and 1.0 cm^{-1}, respectively, for the two mentioned excitations and the holographic grating with 1800 grooves/mm.

Chemical compositions of separated mineral grains were determined using a CAMECA SX-100 electron microprobe at the Department of Electron Microanalysis of the State Geological Institute of Dionýz Štúr in Bratislava. Accelerating voltage of 15 kV, beam current of 20 nA and beam focused to 5 µm were applied during measurements of garnet grains. The following standards and measured lines were used: Si (TAP, Kα, wollastonite), F (LPCO, Kα, LiF), Cl (LPET, Kα, NaCl), Al (TAP, Kα, Al_2O_3), Ca (LPET, Kα, apatite), Fe (LLIF, Kα, fayalite), Ti (LLIF, Kα, TiO2), K (LPET, Kα, orthoclase), Na (TAP, Kα, albite), Mg (TAP, Kα, forsterite), Mn (LLIF, Kα, rhodonite), Cr (LLIF, Kα, Cr). Detection limits were within 0.01–0.05 wt. % of oxide.

Analytical conditions for rutile followed those proposed by Zack et al. (2004a) specially tailored for the Zr-in-rutile thermometry. Each grain was analysed for Ti, Cr, Al, Fe, Nb, Zr, Si, Ta and Mg. The following standards and excitation lines were used: Si (TAP, Kα, $ZrSiO_4$), Al (TAP, Kα, Al_2O_3), Ti (LLIF, Kα, TiO_2), Mg (TAP, Kα, forsterite), Cr (LLIF, Kα, Cr), Fe (LLIF, Kα, fayalite), Zr (LPET, Lα, ZrO_2), Nb (TAP, Lα, $LiNbO_3$) and Ta (LLIF, Lα, $LiTaO_3$). Chemical homogeneity was checked in back-scattered electron images and by multiple analyses of single grains.

Garnet and rutile crystallochemical formulae were calculated on the basis of 8 and 1 cations, respectively. Formation temperatures of rutiles were calculated using an empirical Zr-in-rutile thermometer proposed by Zack et al. (2004b) and Watson et al. (2006).

Results

Heavy mineral assemblages and their abundances

The following minerals have been recovered from the samples studied: pyroxene, amphibole, garnet, tourmaline, epidote, titanite, olivine, apatite, zircon, rutile, spinel, ilmenite, corundum, staurolite and andalusite (Fig. 2). Abundances of individual minerals are rather different in the localities studied (Table 1). Garnet, amphibole and pyroxenes are dominant in Hodejov, Hajnáčka and both maars in Fiľakovo. Samples from maar localities as well as diatremes are also similar in terms of the volume fraction of heavy minerals separated from sediments. Abundance of individual minerals in the Hajnáčka-Kostná dolina maar was probably influenced by the redeposition of maar lake sediments (Sabol et al. 2004; Hurai et al. 2012). The Tachty and Šurice diatremes are substantially enriched by a heavy mineral fraction composed mainly of pyroxene and olivine. In contrast to other localities, spinel and andalusite are missing in the heavy mineral assemblages from these diatremes.

Chemical composition of garnets

Garnet forms pink-to-orange, subhedral to anhedral grains with rounded edges, up to 900 µm in size. BSE images do not show any inherited cores or overgrowth marginal zones (Fig. 3a–d). Numerous mineral inclusions have been identified

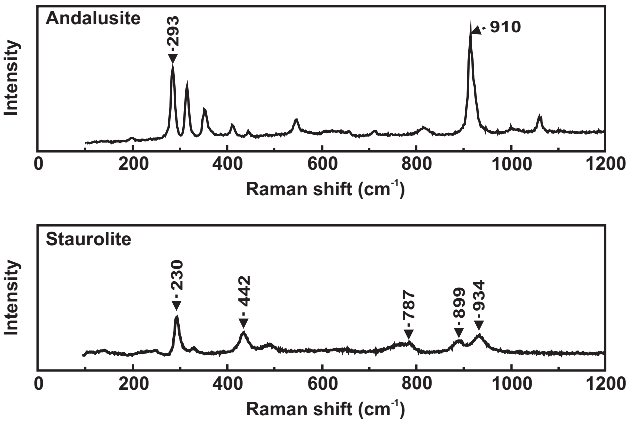

Fig. 2. a — Representative Raman spectrum of andalusite from Hodejov, with distinctive bands at 293 and 910 cm^{-1}. **b** — Representative Raman spectrum of staurolite from Fiľakovo-Červený vrch, with distinctive bands at 230, 442, 787, 899, 934 cm^{-1}.

Table 1: Modal composition (vol. %) of heavy mineral assemblages in volcanoclastic deposits.

Locality	HO	F-CV	F-C	TA	SE	H-KD
HM (vol. %)	0.8	1.5	2.3	18.3	15.7	3.2
amphibole	25	21	25	7	10	14
garnet	28	30	31	2	3	19
epidote	2	1	4	2		
titanite	4	7	3	+	+	3
ilmenite						+
olivine	2	2	4	23	31	9
zircon	1	3		+		4
pyroxene	29	32	28	64	53	42
tourmaline	3					5
apatite	2	2			+	+
rutile	3	2	2	+	+	2
spinel			+			1
staurolite	+	+	+	+	+	
andalusite	+	+	+			
corundum						+

+ indicates less than 1 % of mineral content

Abbrevation of localities: HO: Hodejov, F-CV: Fiľakovo-Červený vrch, F-C: Fiľakovo-Hradný vrch, TA: Tachty, SE: Šurice, H-KD: Hajnáčka-Kostná dolina in the investigated garnet grains: quartz, epidote, zircon, apatite, xenotime, chlorite, muscovite, biotite, tourmaline, staurolite, Al_2SiO_5 polymorphs and Fe-Ti oxides, such as rutile, ilmenite and spinel. Garnets from Fiľakovo-Červený vrch and Hodejov also contained silicate melt inclusions.

The compositional variability of the investigated garnets is surprisingly wide, although the majority of garnets are dominated by almandine with variable contents of grossular, pyrope and spessartine. Spessartine-dominated garnet was found in the Hodejov maar (Table 2).

A total of two major and one minor compositional group can be recognized in all investigated localities (Fig. 4). The major group I consists of almandines with a lower pyrope content (up to 14 mol. % prp) whereas group II comprises almandine garnets with increased content of the pyrope component (15–30 mol. % prp). The third minor group corresponds to spessartine-rich almandine or spessartine. Both major groups can be further subdivided into two subgroups based on the contrasting grossular content.

The largest **group (Ia)** comprises almandine garnets (56–78 mol. % alm) with an increased grossular component (10–30 mol. % grs). Pyrope and spessartine end-member contents reach up to 13 mol. % within this subgroup. Inclusions of staurolite, chlorite, tourmaline and Al_2SiO_5 polymorphs are basically similar to those found in the group II garnets. Some garnets from this group also exhibit higher spessartine content (up to 32 mol. %) in the core with decreasing of Mn towards the rim of the garnet (Table 2). The grs-rich almandine occurs in all localities studied.

The almandine-rich **group Ib** garnets contain 71–86 mol. % of almandine component accompanied by 4–14 mol. % prp, up to 10 mol. % sps, and up to 10 mol. % grs. The group Ib garnets occur mainly in the Tachty diatreme, and in small amounts also in all other localities, except for the Hodejov maar and Šurice diatreme. The group Ib garnets usually

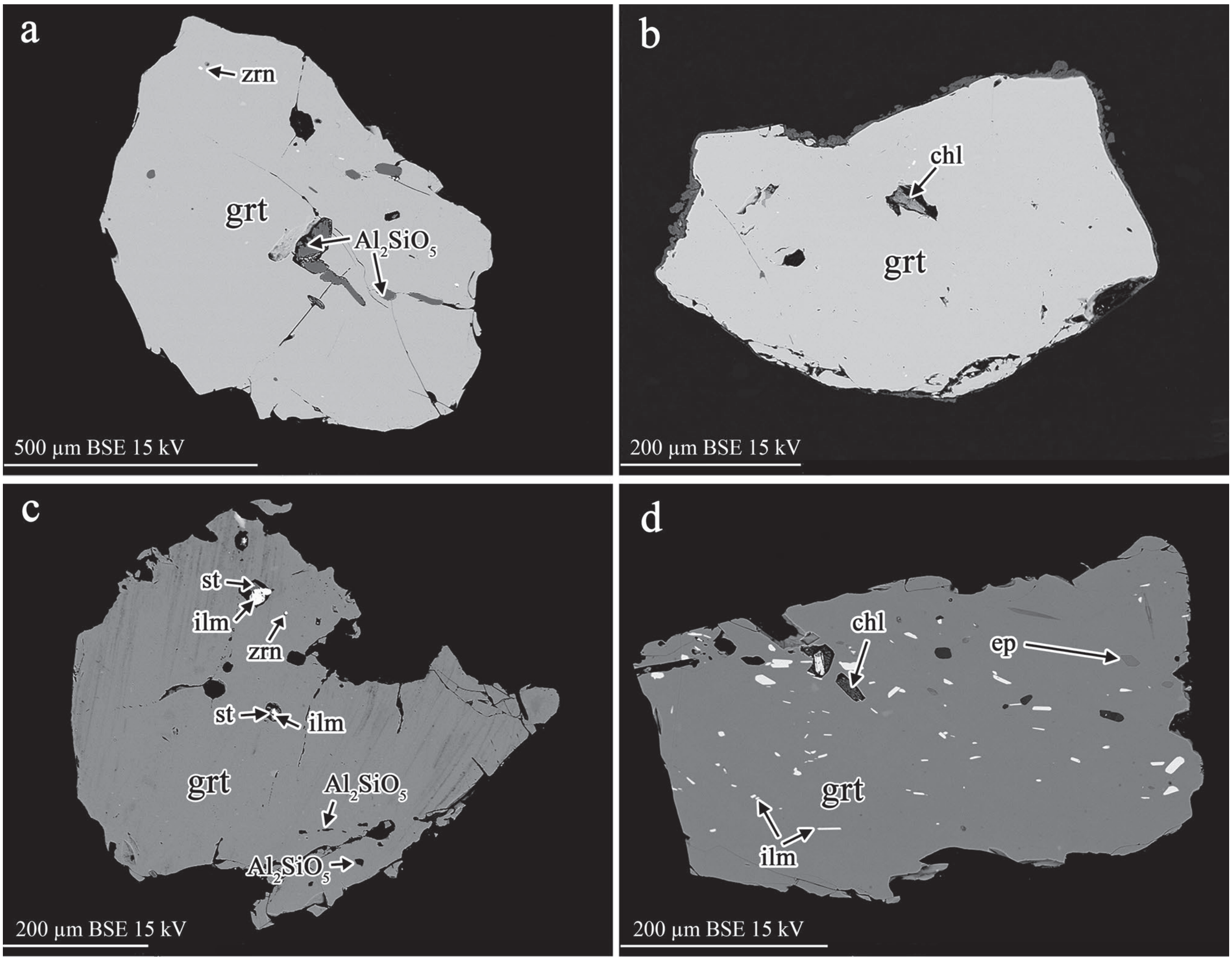

Fig. 3. Back-scattered electron (BSE) images of garnets (grt) from pyroclastic tuffs. **a** — Garnet with inclusions of zircon (zrn) and Al_2SiO_5 minerals from Hodejov maar (sample HO-2G, an3 — group IIb). **b** — Garnet with inclusions of chlorite (chl) from Gemerské Dechtáre maar (sample GD-1G, an5 — group Ia). **c** — Garnet with inclusions of staurolite, kyanite, ilmenite and zircon from Hodejov maar (sample HO-5-3, an03 — group IIb). **d** — Garnet with mineral inclusions of chlorite (chl), ilmenite (ilm) and epidote (ep) from Fiľakovo-Červený vrch maar (sample CV-1, an5 — group Ia).

Table 2: Representative electron probe microanalyses, crystallochemical formulae and endmember contents of detrital garnets from pyroclastic sediments of the SSVF.

Sample:	HO-5-3	HO-2G	HA-KD-7	CVV-3-1	HV-1G	HV-1-G	SE-2-3	TA-IH-1	TA-2-8	HA-KD-7	HA-KD-7	HO-2G
Anal.No	3	3	13	5	11-c	12-r	1	15	4	20	1	10
Locality	HO	HO	H-KD	F-CV	F-C	F-C	SE	TA	TA	H-KD	H-KD	HO
Group	IIb.	IIb.	IIb.	IIa.	Ia.	Ia.	IIa.	Ib.	Ib.	Ia.	III.	III.
SiO_2	38.35	38.52	38.32	38.33	37.66	37.44	38.01	37.19	37.22	37.62	37.21	36.76
TiO_2	0.00	0.04	0.01	0.04	0.08	0.16	0.02	0.07	0.03	0.12	0.17	0.27
Al_2O_3	21.57	22.08	21.35	21.16	21.34	20.85	21.53	20.87	21.23	20.96	20.82	20.68
Cr_2O_3	0.00	0.01	0.02	0.02	0.01	0.00	0.04	0.00	0.03	0.00	0.00	0.05
FeO	30.59	30.76	33.27	28.89	25.96	30.05	30.48	38.50	38.17	29.90	16.75	6.97
MnO	0.65	0.85	1.19	0.62	9.36	3.00	0.62	0.18	0.65	2.61	19.20	31.75
MgO	6.94	6.72	5.59	5.78	0.79	1.00	5.07	1.81	3.00	1.51	0.40	0.40
CaO	1.59	1.67	1.38	5.40	6.27	8.26	5.47	2.04	0.61	8.20	7.15	4.22
Total	99.71	100.67	101.12	100.23	101.50	100.77	101.25	100.68	101.01	100.92	101.70	101.10
Si^{4+}	3.009	2.996	3.002	2.995	2.999	2.991	2.956	3.003	2.978	2.990	2.965	2.964
Ti^{4+}	0.000	0.002	0.000	0.002	0.005	0.010	0.001	0.004	0.002	0.007	0.010	0.016
Al^{3+}	1.995	2.024	1.971	1.949	2.003	1.963	1.974	1.987	2.001	1.963	1.956	1.966
Cr^{3+}	0.000	0.000	0.001	0.001	0.000	0.000	0.002	0.000	0.002	0.000	0.000	0.003
Fe^{2}	2.006	1.999	2.178	1.887	1.728	2.007	1.915	2.598	2.552	1.986	1.115	0.470
Mg^{2+}	0.812	0.779	0.653	0.673	0.094	0.119	0.588	0.218	0.358	0.179	0.047	0.048
Mn^{2+}	0.043	0.056	0.079	0.041	0.631	0.203	0.041	0.012	0.044	0.175	1.296	2.169
Ca^{2+}	0.134	0.139	0.115	0.452	0.535	0.382	0.456	0.176	0.053	0.699	0.611	0.364
Total	8.000	8.000	8.000	8.000	8.000	8.000	8.000	8.000	8.000	8.000	8.000	8.000
Prp	27.10	26.21	21.58	22.05	3.14	3.92	19.18	7.26	11.90	5.88	1.53	1.59
Alm	66.98	67.22	72.00	61.80	57.82	66.10	64.61	86.47	84.89	65.36	36.34	15.40
Grs	4.47	4.68	3.81	14.81	17.91	23.28	14.87	5.86	1.75	22.99	19.90	11.94
Sps	1.45	1.89	2.61	1.34	21.13	6.69	1.34	0.41	1.46	5.77	42.23	71.07

-c: core analyses, -r: rim analyses

Abbreviations of localities: HO: Hodejov, F-CV: Fiľakovo-Červený vrch, F-C: Fiľakovo-Hradný vrch, TA: Tachty, SE: Šurice, H-KD: Hajnáčka-Kostná Dolina, GD: Gemerské Dechtáre

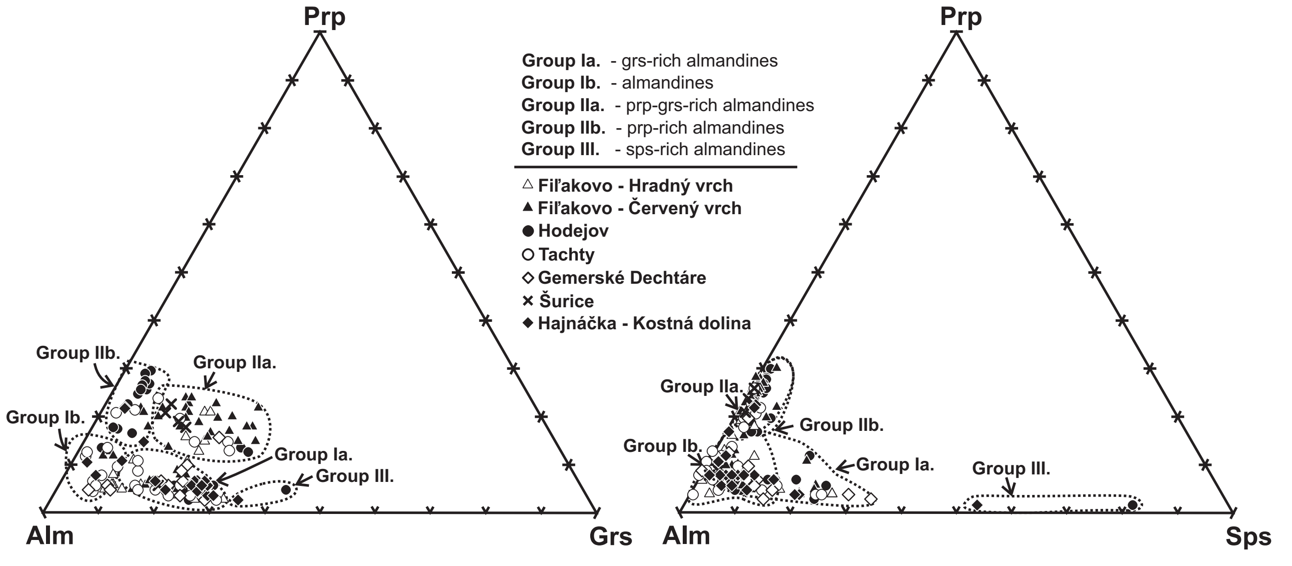

Fig. 4. Chemical compositions of SSVF garnets (n=140) projected onto the classification diagram based on endmember abundance (mol. %). Abbreviations: Alm — almandine, Prp — pyrope, Grs — grossular, Sps — spessartine.

enclose quartz, ilmenite and zircon, but some of them also contained chlorite and tourmaline inclusions (e.g., Fiľakovo-Hradný vrch, Gemerské Dechtáre).

Group IIa garnets are almandine garnets proportionally enriched with pyrope (14–24 mol. %) and grossular (11–30 mol. %) end-members. The spessartine component is also relatively abundant, reaching up to 10 mol. %. Quartz and Fe–Ti oxides are typical inclusions. Some garnets of this group contain silicate melt inclusions (Fiľakovo-Červený vrch). Group IIa garnets are typical for the Fiľakovo maars, but they also occur in other localities studied.

Group IIb garnets are almandine garnets (65–75 mol. %) with an increased pyrope content ranging from 17 to 29 mol. %. Grossular (up to 10 mol. %) and spessartine (up to

7 mol. %) contents are relatively low. Mineral inclusions correspond to staurolite, chlorite and Al_2SiO_5 polymorphs. A majority of the pyrope-rich group IIb garnets occur in Hodejov maar. However, they have been encountered in all localities studied, except for the Fiľakovo-Hradný vrch maar.

The minor **group III** comprises one spessartine-rich almandine garnet (42 mol. % sps) from Hajnáčka-Kostná dolina maar and one spessartine grain from the Hodejov maar with as much as 71 mol. % sps. Other components are generally low: up to 20 mol. % grs and up to 2 mol. % prp.

Chemical composition and crystallization temperatures of rutiles

Rutile grains separated from pyroclastic sediments are reddish-brown in colour and they form anhedral to subhedral prismatic crystals up to 400 µm in size. Rutiles are chemically homogenous, usually without mineral inclusions, except for one rutile from the Hodejov maar, which contained numerous minute zircon inclusions. Rutile grains are also very frequently intergrown with quartz. Rare quartz rods (Fig. 5) indicate an over-saturation with silica which is an essential prerequisite for the application of the Zr-in-rutile thermometer (Ferry & Watson 2007).

Raman spectra of rutile (Fig. 6) showed distinctive bands at 143, 247, 447, 612 cm^{-1} distinguishing the tetragonal rutile from other major structural TiO_2 polymorphs, such as anatas (144, 197, 400, 516 and 640 cm^{-1}) and brookite (153, 247, 322 and 633 cm^{-1}) (Porto et al. 1967; Ohsaka et al. 1978; Tompsett et al. 1995).

All the investigated rutiles are essentially pure compounds with ~99 wt. % averaged normalized content of TiO_2. The remaining 1 wt. % was distributed among Cr_2O_3, FeO,

Fig. 5. Back-scattered electron (BSE) image of rutile (sample HO-3R, Hodejov). Small grey needles represent quartz inclusions. Circles mark spots analysed by electron probe. Numbers refer to Zr concentrations (in ppm), T_Z and T_W values correspond to temperatures (°C) calculated after Zack et al. (2004b) and Watson et al. (2006). The inferred temperatures indicate a homogenous distribution of Zr in the investigated rutile grain.

ZrO_2, Nb_2O_5 and Ta_2O_5. Concentrations of the substituent elements displayed large variations. Iron content varied between 1038 and 4397 ppm. Nb contents attained 3968 ppm, with the majority of values ranging between 2500 and 3500 ppm. Chromium contents were most variable, ranging from 44 to 1820 ppm.

Crystallization temperatures calculated after the empirical calibration of Zack et al. (2004b) fluctuated between 592 and 782 °C in Hodejov, from 548 to 753 °C in Fiľakovo-Červený vrch, from 570 to 766 °C in Šurice and from 662 to 710 °C in Tachty. The same thermometer calibrated by Watson et al. (2006) yielded slightly lower temperatures clustered in narrower intervals: 568–685 °C in Hodejov, 545–665 °C in Fiľakovo-Červený vrch, 556 to 673 °C in Šurice, and 607 to 637 °C in Tachty. Electron probe microanalyses of rutile and calculated temperatures are summarized in Table 3. The discrepancy between the two selected thermometer calibrations was discussed by several authors (Watson et al. 2006; Chen & Li 2008, Meinhold et al. 2008, Meinhold 2010). The two thermometers intersect at a temperature of about 540 °C but diverge significantly both at lower and higher temperatures, implying possible pressure-driven Zr incorporation into the rutile crystal lattice (Watson et al. 2006).

Discussion

Provenance of garnets

Deciphering the provenance of almandine garnets may be ambiguous, because they can crystallize under different conditions in various rock types, comprising plutonic and volcanic rocks (e.g., granite, andesite), and metamorphic rocks of amphibolite to granulite facies (Deer et al. 1997). Indeed, detrital garnets from pyroclastic rocks of the SSVF fall into at least three different fields in the discrimination diagram proposed by Morton et al. (2004), thus overlapping possible metamorphic and magmatic origins (Fig. 7).

Increased pyrope content is diagnostic of garnets formed under high-pressure to ultra-high-pressure metamorphic conditions (e.g., Nandi 1967; Miyashiro & Shido 1973; Oszczypko & Salata 2005), whereas Mg-rich, Ca-depleted garnets are generally affiliated with granulites or charnockites (Sabeen et al. 2002; Morton et al. 2004; Mange & Morton 2007). In contrast, sediments metamorphosed in amphibolite facies conditions usually contain Mg-depleted garnets with variable Ca contents (Morton et al. 2004; Mange & Morton 2007). Therefore, we attribute the group I of Mg-depleted garnets with variable Ca contents from the SSVF to amphibolite-facies metasediments despite the fact that they also overlap the field of acid to intermediate magmatic rocks. According to Mange & Morton (2007), this field was mainly defined to better distinguish garnets with an increased spessartine content genetically related to granites and/or pegmatites. The subgroup Ia of grs-rich almandine also correlates with garnets from phyllites and garnet mica-schists of the Gemericum and

Veporicum Superunits (Méres & Hovorka 1989; Hovorka & Méres 1990; Janák et al. 2001; Vozárová in Šarinová 2008). Part of group Ia garnets also exhibit sps and grs contents decreasing towards the rim, thus resembling the similar trend observed in garnet mica-schists by Hovorka et al. (1987), Méres & Hovorka (1991) and Korikovsky et al. (1990). The subgroup Ib of alm-rich garnets is similar to those found in amphibolite facies metasediments (paragneisses) of the pre-Alpine basement rocks of the Western Carpathians (Hovorka et al. 1987; Méres & Hovorka 1989; Faryad 1990, 1995, 1996; Vozárová 1993; Vozárová & Faryad 1997; Plašienka et al. 1999).

The increased prp content observed in the group II garnets, particularly in the subgroup Ib, would indicate higher grade metamorphic *P-T* conditions. The medium- to high-grade metamorphic conditions are also indicated in both the subgroup Ia and IIb garnets by staurolite and Al_2SiO_5 inclusions, as well as by the ubiquitous presence of these minerals in the associated heavy mineral assemblage. The subgroup IIa garnets with increased pyrope and grossular components are similar to those described from high-grade metabasites and metasediments (Méres 2008; Aubrecht et al. 2009; Šarinová 2008; Morton et al. 2004; Mange & Morton 2007). However, similar garnets may also occur in garnet mica-schists, amphibolites or granulites. On the other hand, peridotite or eclogite can be excluded as possible source rocks of the investigated garnets because of their low pyrope (<50 mol. %) content (Coleman et al. 1965; Deer et al. 1992; von Eynatten & Gaupp 1999). Based on different grs content, we infer that the group IIa garnets with proportional abundance of grs and prp components could be genetically related to amphibolite-to-granulite facies metabasites. The composition of this garnet group is also similar to that of garnets described from amphibolites of the pre-Alpine basement of Western Carpathians (Spišiak & Hovorka 1985; Faryad 1996; Hovorka et al. 1992; Hovorka & Méres 1990; Janák et al. 1996; Janák & Lupták 1997; Vozárová & Faryad 1997; Méres et al. 2000; Faryad et al. 2005). Garnets with increased pyrope content have also been rarely found in basalts as xenocrysts or products of secondary metasomatic processes (e.g. Skewes & Stern 1979; Rollinson 1999; Aydar & Gourgaud 2002; Rankenburg et al. 2004); but there is no evidence of garnet-bearing basalts in the SSVF area (e.g., Miháliková & Šímová 1989). However, part of the group IIa almandines overlaps the field of magmatic garnets genetically related to andesites (Bouloton & Paquette 2014; Harangi et al. 2001; Bónová 2005). Hence, the existence of magmatic garnets in pyroclastic sediments of the SSVF cannot be entirely ruled out.

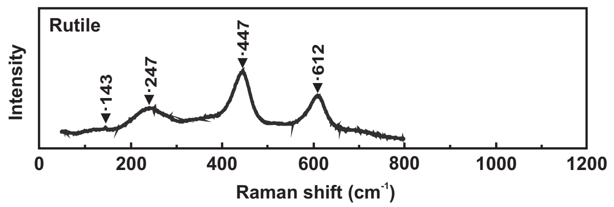

Fig. 6. Representative Raman spectrum of rutile from Fiľakovo-Červený vrch with distinctive bands at 143, 247, 447, 612 cm^{-1}.

Spessartine-rich garnets in pyroclastic sediments of the Hajnáčka-Kostná dolina and Hodejov maars deserve special attention. Significant sps content may occur in almandine garnets derived from felsic igneous rocks or low-grade metasediments (Deer et al. 1997). Sps-rich garnets commonly occur in granites, granitic pegmatites and skarn deposits (e.g. Suggate & Hall 2014). We assume that the small group III of sps-rich almandine and spessartine from Hajnáčka-Kostná dolina and Hodejov may have been derived either from underlying basement granitoids envisaged in this area by Kantor (1960) and Vozárová & Vozár (1988), or from granitoid pebbles found in sediments of the Bukovinka Formation (Vass et al. 1981) penetrated by the EHJ-1 borehole drilled west of Čamovce and Nová Bašta (Vass et al. 2007) in the proximity of the Hajnáčka and Hodejov maars. Faryad & Dianiška (1989) also described high-spessartine garnets (up to 58 %) in granitoid rocks from the Gemericum Superunit.

Provenance of rutiles

Rutile is a common mineral phase in a wide range of lithologies, including high-grade metamorphic rocks, magmatic rocks, sediments or hydrothermal ore deposits (Force 1980; Deer et al. 1992). However, rutile mainly crystallizes in

Table 3: Representative electron probe microanalyses of detrital rutiles from pyroclastic sediments of the SSVF.

Sample	HO-10	HO-10	HO-3R	CVV-3-1	F-CV-R3	F-CVR2	SE-SP-R1	SE-V-R3	SE-V-R3	TA-R1	TA-R1
Anal. No	7	5	10	8	1	3	7	3	6	2	4
Locality	HO	HO	HO	F-CV	F-CV	F-CV	SE	SE	SE	TA	TA
Fe	2976	1538	1970	2141	2164	2075	2707	2669	2540	2428	1649
Cr	210	585	1396	293	826	753	917	1479	1093	444	337
Nb	3015	1426	2292	1014	3159	2418	942	1958	3593	2063	2883
Zr	212	139	492	159	276	304	432	227	172	192	218
Ta	347	143	191	82	376	108	249	127	107	137	230
Mg	139	68	185	98	205	83	b.d.	122	b.d.	b.d.	b.d.
log(Cr/Nb)	−1.16	−0.39	−0.22	−0.54	−0.58	−0.51	−0.01	−0.12	−0.42	−0.67	−0.93
T_Z (°C)	675	621	782	638	708	720	766	683	648	662	678
T_w (°C)	615	584	685	594	636	643	673	620	599	607	617

Concentrations are given as parts per million (ppm), bdl = below detection limit

Abbreviations of localities: HO: Hodejov, F-CV: Fiľakovo-Červený vrch, TA: Tachty, SE: Šurice

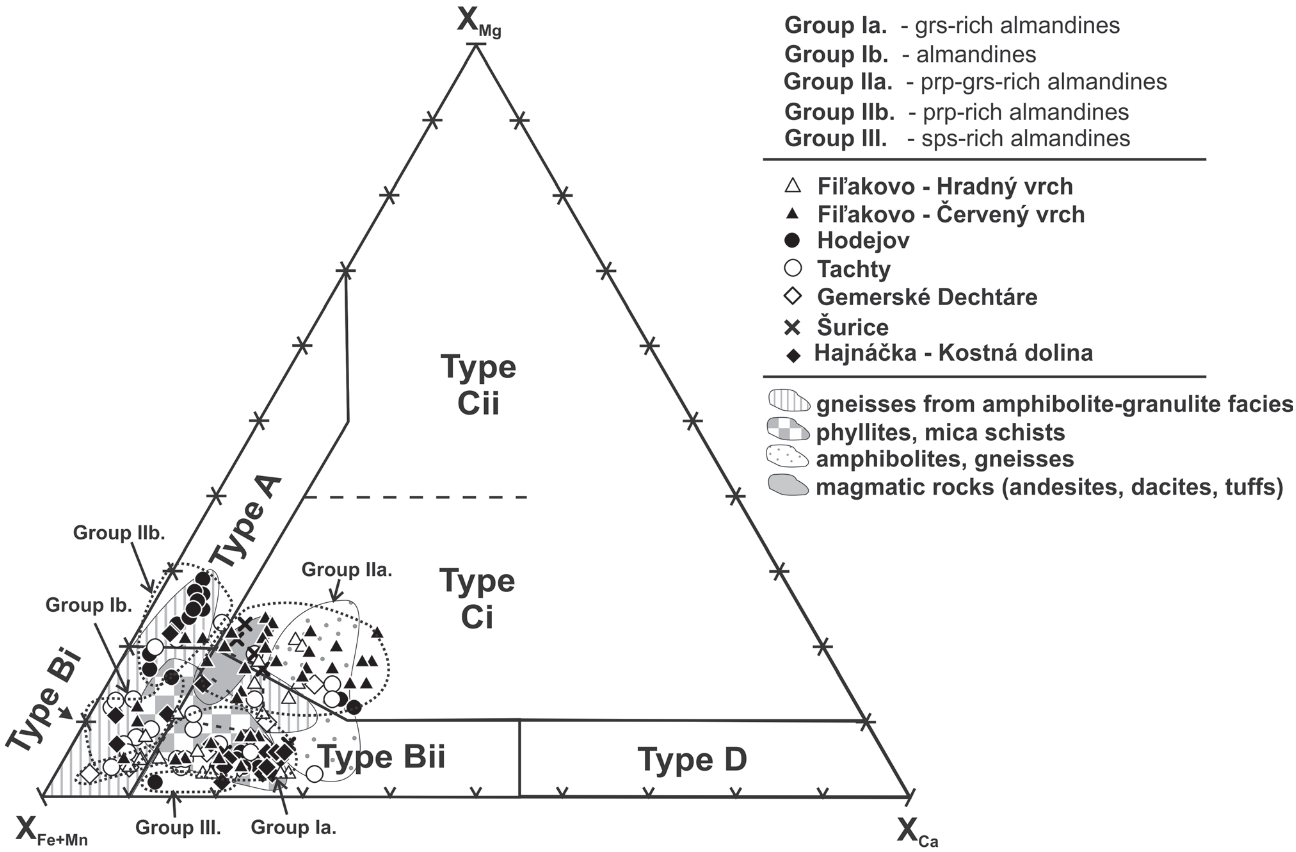

Fig. 7. Detritic garnets from volcanoclastic deposits of the SSVF plotted on the ternary diagram with almandine+spessartine (X_{Fe+Mn}), grossular (X_{Ca}) and pyrope (X_{Mg}) endmembers and subdivision lines dividing garnets from different source rocks (modified after Mange & Morton 2007). The type-A field denotes garnets from high-grade granulites or charnokites and intermediate-to-acidic rocks sourced from deep crust, the type-Bi field corresponds to intermediate-acidic igneous rocks, the type-Bii field denotes amphibolite-facies metasediments, the type-Ci field is affiliated with high-grade metabasic rocks. Other garnet types include ultramafic source rocks, such as pyroxenite and peridotite (type-Cii), metasomatic rocks (skarns), low-grade metabasic rocks, and ultra-high temperature calc-silicate granulites (type-D). Fields for garnets from phyllites, mica-schists, gneisses, amphibolites and amphibolized eclogites from pre-Alpine basement rocks of the Western Carpathians were compiled from Hovorka et al. (1987, 1992), Hovorka & Méres (1990), Korikovsky et al. (1990), Spišiak & Hovorka (1985), Méres & Hovorka (1989), Vozárová (1993), Faryad (1990, 1995, 1996), Faryad et al. (2005), Janák et al. (1996, 2001), Janák & Lupták (1997), Vozárová & Faryad (1997), Plašienka et al. (1999), Méres et al. (2000) and Šarinová (2008). The field for magmatic garnets (andesites dacites & tuffs) was compiled from data in Bouloton & Paquette (2014), Harangi et al. (2001), Bónová (2005) and Vozárová in Šarinová (2008).

medium- to high-grade metamorphic conditions (e.g., Goldsmith & Force 1978; Force 1980). Zack et al. (2002, 2004a) proposed that Cr and Nb abundances in rutile can be employed to distinguish between metamafic and metapelitic source lithologies. These authors inferred that metapelite rutiles contain 900–2700 ppm Nb that predominates over Cr. Meinhold et al. (2008) proposed that the lowermost limit should be equal to 800 ppm Nb in rutile from metapelitic lithologies. Rutiles with Cr>Nb or those with Cr<Nb and Nb<800 ppm should be derived from metamafic rocks. To simplify this concept, Triebold et al. (2007) introduced the log(Cr/Nb) value to discriminate between metamafic and metapelitic source lithologies (Fig. 8). Similar to the Cr/Nb ratio, Zack et al. (2004b) suggested the iron content is an additional indicator of metamorphic origin, since metamorphic rutiles mostly contain >1000 ppm Fe.

Using the approach of Zack et al. (2002) combined with temperatures calculated after Watson et al. (2006) we infer that rutiles from the Hodejov and Fiľakovo-Červený Vrch maars and those from Tachty and Šurice diatremes may have been derived from amphibolite-facies metasedimentary rocks (mica-schist or paragneiss), as is documented in Fig. 8. Hence, the provenance of rutiles is basically the same as that of the associated metamorphic garnet from amphibolite facies metasediments.

Proximal versus distal origin of heavy minerals?

In summary, the group I and group II garnets of the SSVF are be most likely to be affiliated to metamorphic source rocks, whereas group III is likely magmatic in origin, being genetically associated with granitic rocks. Possible source areas of these rock types include subjacent deep-seated crystalline basement units or shallow basin catchment sediments transported from the Central Carpathians. The first possibility is indicated by the borehole FV-1 near Blhovce that penetrated

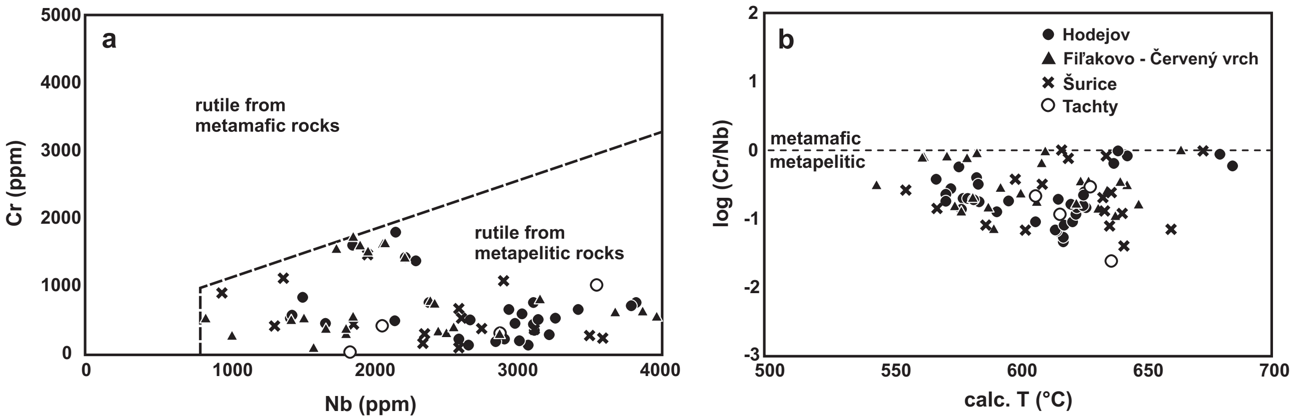

Fig. 8. a — Nb *versus* Cr discrimination diagrams for rutile from different metamorphic lithologies (modified after Zack et al. 2002). **b** — Plot of temperatures calculated from Zr contents after Watson et al. (2006) *versus* mafic and pelitic compositions discriminated according to log(Cr/Nb) value (modified after Triebold et al. 2007). Positive and negative log(Cr/Nb) values indicate rutile from metamafic and metapelitic rocks, respectively. Note that the terms "metamafic" and "metapelitic" were introduced by Zack et al. (2002, 2004a) to distinguish between the rutile sources, although simplified terms "mafic" and "felsic" would be more appropriate.

mid- to upper Devonian green-schists and phyllites (Vass & Bajaník 1988). These metasedimentary sequences, however, did not contain any garnet. Mica schist and amphibolite known as xenoliths in Miocene andesite intrusions near Šiator and Karanč (Hovorka & Lukáčik 1972; Elečko et al. 2008) may be an alternative proximal garnet source derived from underlying basement rocks.

Pebbles and heavy minerals in Tertiary sediments redeposited from distal sources may also have contributed to the heavy mineral assemblage of pyroclastic deposits in the SSVF. A certain amount of garnets accompanied by staurolite and kyanite was mentioned in the heavy mineral fraction of clastic sediments of the Juhoslovenská kotlina Basin (Marková et al. 1980, 1982); however, garnet composition has not been studied. These minerals diagnostic of high-grade metamorphic rocks may have been transported by rivers from the uplifted Central Carpathian basement involving the Gemeric (Gelnica Group) and/or the Veporic Superunits (Vass & Elečko 1992; Vass et al. 2007), deposited in catchment sediments of the Juhoslovenská kotlina Basin, and finally redistributed in the volcanoclastic deposits by phreato-magmatic eruptions. Obviously, we are unable to discriminate with our present state of knowledge between the various proximal and distal sources of heavy minerals in the pyroclastic deposits of the SSVF, mainly due to missing compositional data on heavy minerals from Tertiary clastic sediments.

Interestingly, systematic study of zircons in primary pyroclastic deposits of the Pinciná, Fiľakovo-Hradný vrch, Hodejov, and Gemerské Dechtáre maars (Hurai et al. 2010, 2013) and in redeposited sediments of the Hajnáčka-Kostná dolina maar (Hurai et al. 2012) did not provide any evidence for zircons inherited from proximal or distal pre-Tertiary sources. In turn, all investigated volcanic structures only contained populations of very young (2–5 Ma) magmatic zircons derived from A-type granite/syenite melts produced by advanced fractional crystallization of underplated alkali basalt (e.g., Huraiová et al. 1996, 2017) and entrained in younger basalt portions as zircon-bearing xenoliths or isolated zircon xenocrysts. Fragmentation coincidental with shallow phreatomagmatic explosions triggered by the contact of the ascending basaltic magma with aquifers is indicated by morphological features of the investigated zircons: fragments of larger rounded zircons reflect non-equilibrium melting and transport of xenocrysts in contact with basaltic magma prior to the final eruption, whereas small euhedral zircons of the same age and composition must have been armoured in xenoliths disrupted during the final eruption, being thus isolated from the surrounding basalt during ascent to the surface.

Conclusions

1. We provide the first study focused on garnet and rutile in pyroclastic sediments of the South Slovakian Volcanic Field with the aim of deciphering their origin and provenance.
2. Almandine garnets have been derived from two contrasting magmatic and metamorphic lithologies. Metamorphic garnets (>99 % of samples) with increased grossular and pyrope contents were likely derived from garnet-mica schists, gneisses, amphibolites or granulites, whereas spessartite-rich magmatic garnets (<1 % of samples) are probably derived from underlying basement granitoids or granitoid pebbles in Tertiary basin deposits.
3. Based on Nb and Cr contents, rutiles can be affiliated with metasedimentary source rocks. Formation temperatures between 545 and 673 °C indicate amphibolite facies conditions.
4. We assume that the assemblage of metamorphic minerals in the pyroclastic sediments comes from the fragmented pre-Tertiary gneiss-amphibolite basement. Some garnets may also be correlated with granitoid host rocks that occur as pebbles in Tertiary clastic sediments.

Acknowledgements: The authors wish to express their thanks to the reviewers for their thorough reviews, which considerably improved the quality of this paper. This work was supported by the Comenius University project under the contract No. UK/184/2017 and the VEGA grant 1/0143/18. We would like to offer our special thanks to Prof. Pavel Uher for providing samples of sediments from Hajnáčka-Kostná dolina maar, and to Dr. Patrik Konečný for electron probe analytical work.

References

Aubrecht R., Méres Š., Sýkora M. & Mikuš T. 2009: Provenance of the detrital garnets and spinels from the Albian sediments of the Czorstyn Unit (Pieniny Klippen Belt, Western Carpathians, Slovakia). *Geol. Carpath.* 60, 463–483.

Aydar E. & Gourgaud A. 2002: Garnet-Bearing Basalts: An Example from Mt. Hasan Central Anatolia Turkey. *Mineral. Petrol.* 75, 185–201.

Balogh K., Miháliková A. & Vass D. 1981: Radiometric dating of basalt in Southern and Central Slovakia. *Záp. Karpaty Ser. Geol.* 7, 113–126.

Bónová K. 2005: Mineralogy, petrology and P-T conditions of magma crystallization of the andesite bodies Maliniak and Lysá Stráž from Lysá Stráž – Oblík formation, Eastern Slovakia. *Miner. Slov.* 37, 503–512.

Bouloton J. & Paquette J.-L. 2014: In situ U–Pb zircon geochronology of Neogene garnet-bearing lavas from Slovakia (Carpatho–Pannonian region, Central Europe). *Lithos* 184–187, 17–26.

Brenan J.M., Shaw H.F., Phinney D.L. & Ryerson F.J. 1994: Rutile–aqueous fluid partitioning of Nb, Ta, Hf, Zr, U and Th: implications for high field strength element depletions in island-arc basalts. *Earth. Planet. Sci. Lett*. 128, 327–339.

Bromiley G.D. & Hilairet N. 2005: Hydrogen and minor element incorporation in synthetic rutile. *Mineral. Mag*. 69, 345–358.

Carruzzo S., Clarke D.B., Pelrine K.M. & MacDonald M.A. 2006: Texture, composition and origin of rutile in the South Mountain Batholith, Nova Scotia. *Can. Mineral.* 44, 715–729.

Chen Z.Y. & Li Q.L. 2008: Zr-in-rutile thermometry in eclogite at Jinheqiao in the Dabie orogen and its geochemical implications. *Chinese Sci. Bull.* 53, 768–776.

Coleman R.G., Lee D.E., Beatty L.B. & Brannock W.W. 1965: Eclogites and eclogites: their differences and similarities. *Geol. Soc. Am. Bull.* 76, 483–508.

Dank V. & Fülöp J. (Eds.) 1990: Geological Structural map of Hungary. *MAFI*, Budapest (in Hungarian).

Deer W.A., Howie R.A. & Zussman J. 1992: An introduction to the rock-forming minerals. 2nd Ed. *Longmans*, Essex, 1–696.

Deer W.A., Howie R.A. & Zussman J. 1997: Rock-forming minerals. Volume 1A. Orthosilicates. 2nd Ed. *Longmans*, London, 1– 919.

Dobosi G., Fodor R.V. & Goldberg S.A. 1995: Late-Cenozoic alkali basalt magmatism in Northern Hungary and Slovakia: petrology, source compositions and relationship to tectonics. *Acta Vulcanol*. 7, 199–207.

Downes H., Pantó Gy., Póka T., Mattey D.P. & Greenwood P.B. 1995: Calc-alkaline volcanics of the Inner Carpathian arc, Northern Hungary: new geochemical and oxygen isotopic results. *Acta Vulcanol*. 7, 29–41.

Elečko M., Hraško L. & Konečný P. 2008: Refinement of continuation of crystalline complexes in the basement of neovolcanites (Southern Slovakia). Open-file report, *D. Štúr Inst. Geol.*, Bratislava, 1–123.

Faryad S.W. 1990: Gneiss-amphibolite complex of Gemericum. *Miner. Slov*. 22, 303–318 (in Slovak).

Faryad S.W. 1995: Determination of P–T conditions of metamorphism in the Spiš-Gemer Ore Mts. (Western Carpathians). *Miner. Slov*. 27, 9–19 (in Slovak).

Faryad S.W. 1996: Petrology of amphibolites and gneisses from Branisko massif. *Miner. Slov.* 28, 265–272 (in Slovak).

Faryad S.W. & Dianiška I. 1989: Garnets from granitoids. *Geol. Zbor. Geol. Carpath.* 40, 715–734.

Faryad S.W., Ivan P. & Jacko S. 2005: Metamorphic petrology of metabasites from the Branisko and Čierna Hora Mountains (Western Carpathians Slovakia). *Geol. Carpath.* 56, 3–16.

Ferry J.M. & Watson E.B. 2007: New thermodynamic models and revised calibration for the Ti-in-zircon and Zr-in-rutile thermometers. *Contrib. Mineral. Petrol*. 154, 429–437.

Force E.R. 1980: The provenance of rutile. *J. Sediment. Petrol.* 50, 485–488.

Force E.R. 1991: Geology of titanium-mineral deposits. *Geol. Soc. Amer. Spec. Paper* 259, 1–112.

Goldsmith R. & Force E.R. 1978: Distribution of rutile in metamorphic rocks and implications for placer deposits. *Miner. Deposita* 13, 329–343.

Götze J. 1996: Genetic information of accessory minerals in clastic sediments. *Zbl. Geol. Paläont*. 1, 101–118.

Graham J. & Morris R.C. 1973: Tungsten- and antimony-substituted rutile. *Mineral. Mag.* 39, 470–473.

Harangi Sz., Downes H., Kósa L., Szabó Cs., Thirlwall M. F., Mason P.R.D. & Mattey D. 2001: Almandine garnet in calc-alkaline volcanic rocks of the Northern Pannonian Basin (Eastern-Central Europe): Geochemistry, petrogenesis and geodynamic implications. *J. Petrol.* 42, 1813–1843.

Hassan W.F. 1994: Geochemistry and mineralogy of Ta-Nb rutile from Peninsular Malaysia. *J. Soc. Am. Earth Sci.* 10, 11–23.

Hovorka D. & Lukáčik E. 1972: Xenoliths in andesites of the Massifs Karanč, Šiator (Southern Slovakia) and their geologic interpretation. *Geol. Zborn. Geol. Carp.* 23, 297–303.

Hovorka D. & Méres Š. 1990: Clinopyroxene-garnet metabasites from the Tribeč Mts. (Central Slovakia). *Miner. Slov.* 22, 533–538 (in Slovak).

Hovorka D., Méres Š. & Krištín J. 1987: Garnets from paragneisses of the central zone of the West Carpathians. *Miner. Slov.* 19, 289–309.

Hovorka D., Méres Š. & Caňo F. 1992: Petrology of the garnet clinopyroxene metabasites from the Malá Fatra Mts. *Miner. Slov.* 24, 45–52 (in Slovak).

Hurai V., Paquette J.-L., Huraiová M. & Konečný P. 2010: U–Th–Pb geochronology of zircon and monazite from syenite and pincinite xenoliths in Pliocene alkali basalts of the intra-Carpathian back-arc basin. *J. Volcanol. Geotherm. Res.* 198, 275–287.

Hurai V., Paquette J.-L., Huraiová M. & Sabol M. 2012: U–Pb geochronology of zircons from fossiliferous sediments of the Hajnáčka I maar (Slovakia) — type locality of the MN16a biostratigraphic subzone**.** *Geol. Mag*. 149, 989–1000.

Hurai V., Danišík M., Huraiová M., Paquette J.-L. & Ádám A. 2013: Combined U/Pb and (U–Th)/He geochronometry of basalt maars in Western Carpathians: implications for age of intraplate volcanism and origin of zircon metasomatism. *Contrib. Mineral. Petrol*. 166, 1235–1251.

Huraiová M., Konečný P., Konečný V., Simon K. & Hurai V. (1996) Mafic and salic xenoliths in Late Tertiary alkaline basalts: fluid inclusion and mineralogical evidence for a deep-crustal magmatic reservoir in the Western Carpathians. *Eur. J. Mineral.* 8, 901–916.

Huraiová M., Paquette J.-L., Konečný P., Gannoun A.-M. & Hurai V. 2017: Geochemistry, mineralogy, and zircon U-Pb-Hf isotopes in peraluminous A-type granite xenoliths in Pliocene–Pleistocene basalts of northern Pannonian Basin (Slovakia). *Contrib. Mineral. Petrol*. 172, 8, Article number 59.

Janák M. & Lupták B. 1997: Pressure-temperature conditions of high grade metamorphism and migmatitization in the Malá Fatra crystalline complex, the Western Carpathians. *Geol. Carpath.* 48, 5, 287–302.

Janák M., O'Brien P.J., Hurai V. & Reutel Ch. 1996: Metamorphic evolution and fluid composition of garnet-clinopyroxene amphibolites from the Tatra Mts., Western Carpathians. *Lithos* 39, 57–79.

Janák M., Plašienka D., Frey M., Cosca M., Schmidt S.T., Lupták B. & Méres Š. 2001: Cretaceous evolution of a metamorphic core complex, the Veporic unit, Western Carpathians (Slovakia): P–T conditions and in situ $^{40}Ar/^{39}Ar$ UV laser probe dating of metapelites. *J. Metamorph. Geol.* 19, 197–216.

Kantor J. 1960: Cretaceous orogenic processes in the light of geochronology of Veporic crystalline complex (Kohút zone). *Geol. Práce Správy* 20, 5–27 (in Slovak).

Konečný V., Lexa J., Balogh K. & Konečný P. 1995: Alkali basalt volcanism in Southern Slovakia — Volcanic forms and time evolution. *Acta Vulcanol.* 7, 167–171.

Konečný V., Kováč M., Lexa J. & Šefara J. 2002: Neogene evolution of the Carpatho-Pannonian region: an interplay of subduction and back-arc diapiric uprise in the mantle. *EGU Stephan Mueller Spec. Publ. Ser.* 1, 105–123.

Konečný V., Lexa J., Konečný P., Balogh K., Elečko M., Hurai V., Huraiová M., Pristaš J., Sabol M. & Vass D. 2004: Guidebook to the Southern Slovakia Alkali Basalt Volcanic Field. *D. Štúr Inst. Geol.,* Bratislava, 1–143.

Korikovsky S.P., Dupej J., Boronikhin V.A. & Zinovieva N.G. 1990: Zoned garnets and their equilibria in mica schists and gneisses of Kohút crystalline complex, Hnúšťa region, Western Carpathians. *Geol. Zborn. Geol. Carpath.* 41, 99–124.

Mange M.A. & Maurer H. 1992: Heavy minerals in the study of sediments: their application and limitations. In: Mange M.A. & Maurer H. (Eds.): Heavy Minerals in Colour. *Springer*, 4–10.

Mange M.A. & Morton A.C. 2007: Geochemistry of Heavy Minerals. In: Mange M.A. & Wright D.T., (Eds.): Heavy Minerals in Use. *Developments in Sedimentology* 58, *Elsevier*, Amsterdam, 345–391.

Marková M. 1980: Mineralogical, petrographic and geochemical investigation of Tertiary sediments of Lučenská kotlina Depression. *D. Štúr Inst. Geol.,* Bratislava (in Slovak).

Marková M. 1982: Report from mineralogical and petrographic investigation of samples from borehole JH-1 Nižný Skálnik, *D. Štúr Inst. Geol.,* Bratislava (in Slovak).

Meinhold G. 2010: Rutile and its applications in earth sciences. *Earth Sci. Rev.* 102, 1–28.

Meinhold G., Anders B., Kostopoulos D. & Reischmann T. 2008: Rutile chemistry and thermometry as provenance indicator: an example from Chios Island, Greece. *Sediment. Geol.* 203, 98–111.

Méres Š. 2008: Garnets — important informations resource about source area and parental rocks of the siliciclastic sedimentary rocks. In: Jurkovič L. (Ed.): Conference "Cambelove dni 2008", Abstract Book, *Comenius Univ.*, Bratislava, 37–43 (in Slovak).

Méres Š. & Hovorka D. 1989: Metamorphic development of gneisses in the Suchý, Malá Magura and Malá Fatra Mts. (Central Slovakia). *Miner. Slov.* 21, 203–216 (in Slovak).

Méres Š. & Hovorka D. 1991: Geochemistry and metamorphic evolution of the Kohút crystalline complex mica schists (the Western Carpathians). *Acta Geol. Geogr. Univ. Com. Geol.* 47, 15–66.

Méres Š., Ivan P. & Hovorka D. 2000: Garnet-pyroxene metabasites and antigorite serpentinites — evidence of the leptyno-amphibolite complex in the Branisko Mts. (Tatric Unit, central Western Carpathians). *Miner. Slov*. 32, 479–486.

Miháliková A. & Šímová M. 1989: Geochemistry and petrology of Miocene-Pleistocene alkali basalts of Middle and South Slovakia. *Záp. Karpaty Ser. Geol.* 12, 7–142 (in Slovak).

Miyashiro A. & Shido F. 1973: Progressive compositional change of garnet in metapelite. *Lithos* 6, 13–20.

Morton A.C. 1985: Heavy minerals in provenance studies. In: Zuffa G.G. (Ed.): Provenance of Arenites. *Reidel*, Dordrecht, 249–277.

Morton A.C. & Hallsworth C.R. 2007: Stability of detrital heavy minerals during burial diagenesis. In: Mange M.A., Wright D.T. (Eds.): Heavy minerals in Use. *Developments in Sedimentology* 58, *Elsevier*, Amsterdam, 215–245.

Morton A.C., Hallsworth C. & Chalton B. 2004: Garnet compositions in Scottish and Norwegian basement terrains: a framework for interpretation of North Sea sandstone provenance. *Mar. Petrol. Geol.* 21, 393–410.

Murad E., Cashion J.D., Noble C.J. & Pilbrow J.R. 1995: The chemical state of Fe in rutile from an albitite in Norway. *Mineral. Mag*. 59, 557–560.

Nandi K. 1967: Garnets as indices of progressive regional metamorphism. *Mineral. Mag*. 36, 89–93.

Ohsaka, T., Izumi, F. & Fujiki, Y., 1978. Raman spectrum of anatase, TiO_2. *J. Raman Spectrosc*. 7, 321–324.

Oszczypko N. & Salata D. 2005: Provenance analyses of the Late Cretaceous–Palaeocene deposits of the Magura Basin (Polish Western Carpathians) – evidence from a study of heavy minerals. *Acta Geol. Pol*. 55, 237–267.

Pécskay Z., Lexa J., Szakács A., Seghedi I., Balogh K., Konečný V., Zelenka T., Kovacs M., Póka T., Fülöp A., Márton E., Panaiotu C. & Cvetković V. 2006: Geochronology of Neogene magmatism in the Carpathian arc and intra-Carpathian area. *Geol. Carpath.* 57, 511–530.

Planderová E. 1986: Biostratigraphic evaluation of sediments of the Poltár Formation. *Geol. Práce Správy* 84, 113–118 (in Slovak).

Plašienka D., Grecula P., Putiš M., Kováč M. & Hovorka D. 1997: Evolution and structure of the Western Carpathians: An overview. In: Grecula P., Hovorka D. & Putiš M. (Eds.): Geological Evolution of the Western Carpathians. *Miner. Slov. Monogr.*, *Geocomplex*, Bratislava, 1–24.

Plašienka D., Janák M., Lupták B., Milovský R., Frey M. 1999: Kinematics and Metamorphism of Cretaceous Core Complex: the Veporic Unit of the Western Carpathians. *Phys. Chem. Earth (A)* 24, 8, 651–685.

Porto, S.P.S., Fleury, P.A. & Damen, T.C. 1967: Raman spectra of TiO_2, MgF_2, ZnF_2, FeF_2, and MnF_2. *Phys. Rev.* 154, 522–526.

Preston R.J., Hartley A., Hole M.J., Buck S., Bond J., Mange-Rajetzky M. & Still J. 1998: Integrated whole-rock trace element geochemistry and heavy-mineral chemistry studies: aids to the correlation of continental red-bed reservoirs in the Beryl Field, U.K. North Sea. *Petrol. Geosci.* 4, 7–16.

Preston J., Hartley A., Mange-Rajetzky M., Hole M.J., May G. & Buck S. 2002: The provenance of Triassic continental sandstones from the Beryl Field, northern North Sea: mineralogical, geochemical, and sedimentological constraints. *J. Sedim. Res.* 72, 18–29.

Rankenburg K., Lassiter J.C. & Brey G.P. 2004: Origin of megacrysts in volcanic rocks of the Cameroon Volcanic Chain — Constraints on magma genesis and crustal contamination. *Contrib. Mineral. Petrol.* 147, 129–144.

Rice C., Darke K. & Still J. 1998: Tungsten-bearing rutile from the Kori Kollo gold mine, Bolívia. *Mineral. Mag*. 62, 421–429.

Rollinson H. R. 1999: Petrology and geochemistry of metamorphosed komatiites and basalts from the Sula Mountains Greenstone Belt, Sierra Leone. *Contrib. Mineral. Petrol*. 134, 86–101.

Sabeen H. M., Ramanujam N. & Morton A.C. 2002: The provenance of garnet: constraints provided by studies of coastal sediments from southern India. *Sediment. Geol.* 152, 279–287.

Sabol M., Balogh K., Ďurišová A., Elečko M., Hensel K., Holec P., Hudáčková N., Janštová M., Kernátsová J., Klembara J., Konečný P., Konečný V., Pipík R., Slamková M., Sitár V., Túnyi I. & Vass D. 2004: Early Villanyian site of Hajnáčka I (southern Slovakia). *Gemer-Malohont Musem*, Rimavská Sobota, *Comenius Univ.*, Bratislava, 143 p.

Šarinová K. 2008: Identification of the source rocks of detrital garnets by their chemical composition (Western Carpathians, Slovakia). *Miner. Slov.* 40, 33-44.

Scott K.M. 2005: Rutile geochemistry as a guide to porphyry Cu–Au mineralization, Northparkes, New South Wales, Australia. *Geochem. Explor. Env. A* 5, 247–253.

Skewes M.A. & Stern C.R. 1979: Petrology and geochemistry of alkali basalts and ultramafic inclusions from the Pali-Aike Volcanic Field in Southern Chile and the origin of Patagonian Plateau lavas, *J. Volcanol. Geotherm. Res.* 6, 3–25.

Smith D. & Perseil E.A. 1997: Sb-rich rutile in the manganese concentrations at St. Marcel-Praborna, Aosta Valley, Italy, petrology and crystal-chemistry. *Mineral. Mag*. 61, 655–669.

Snopková, P. & Bajaník, Š. 1979: Evidence of Devonian (givetian–frasnian) in borehole FV-1 Blhovce. *Geol. Práce Správy* 72, 7–17 (in Slovak).

Spišiak J. & Hovorka D. 1985: Two types of garnet-bearing amphibolites from Klátov Group. *Miner. Slov.* 17, 167–174.

Suggate S.M. & Hall R. 2014: Using detrital garnet compositions to determine provenance: a new compositional database and procedure. In: Scott R.A., Smyth H.R., Morton A.C. & Richardson N. (Eds.): Sediment Provenance Studies in Hydrocarbon Exploration and Production. *Geol. Soc. London Spec. Publ.* 386, 373–393.

Tomkins H.S., Powell R. & Ellis D.J. 2007: The pressure dependence of the zirconium-in-rutile thermometer. *J. Metamorph. Geol*. 25, 703–713.

Tompsett, G.A., Bowmaker, G.A., Cooney, R.P., Metson, J.B., Rodgers, K.A. & Seakins, J.M. 1995: The Raman spectrum of brookite, TiO_2 (Pbca, Z=8). *J. Raman Spectrosc*. 26, 57–62.

Triebold S., von Eynatten H., Luvizotto G.L. & Zack T. 2007: Deducing source rock lithology from detrital rutile geochemistry: an example from the Erzgebirge, Germany. *Chem. Geol.* 244, 421–436.

Vass D. & Bajaník Š. 1988: Structural Borehole FV-1 (Blhovce). *Reg. Geol. Záp. Karpát* 23, 1–86.

Vass D. & Elečko M. 1992: Explanation to the gological map of Lučenská kotlina Depression and Cerová vrchovina Upland. *D. Štúr Inst. Geol.*, Bratislava, 1–196 (in Slovak).

Vass D. & Kraus I. 1985: Two basalts of different age in southern Slovakia and their relation to the Poltár Formation. *Miner. Slov.* 17, 435–440 (in Slovak).

Vass D., Elečko M. & Bodnár J. 1981: Tectonics of Rimavská kotlina Depression. *Geol. Práce Spr*. 75, 77–90.

Vass D., Elečko M. & Konečný V. 2007: Geology of Lučenská kotlina Depression and Cerová vrchovina Upland. *D. Štúr Inst. Geol.*, Bratislava, 1–117 (in Slovak).

von Eynatten H. & Gaupp R. 1999: Provenance of Cretaceous synorogenic sandstones in the Eastern Alps: constraints from framework petrography, heavy mineral analysis and mineral chemistry. *Sediment. Geol.* 124, 81–111.

Vozárová A. 1993: Pressure-temperature conditions of metamorphism in the northern part of the Branisko Crystalline Complex. *Geol. Carpath.* 44, 219–232.

Vozárová A. & Faryad S.W. 1997: Petrology of Branisko crystalline rock complex. In: Grecula P., Hovorka D. & Putiš M. (Eds.): Geological Evolution of the Western Carpathians. *Miner. Slov. Monogr.*, Bratislava, 343–350.

Vozárová A. & Vozár J. 1988: Late Paleozoic in West Carpathians. *D. Štúr Inst. Geol.*, Bratislava, 1–314.

Watson E.B., Wark D.A. & Thomas J.B. 2006: Crystallization thermometers for zircon and rutile. *Contrib. Mineral. Petrol*. 151, 413–433.

Zack T., Kronz A., Foley S.F. & Rivers T. 2002: Trace element abundances in rutiles from eclogites and associated garnet mica schists. *Chem. Geol.* 184, 97–122.

Zack T., von Eynatten H.V. & Kronz A. 2004a: Rutile geochemistry and its potential use in quantitative provenance studies. *Sediment. Geol.* 171, 37–58.

Zack T., Moraes R. & Kronz A. 2004b: Temperature dependence of Zr in rutile: empirical calibration of a rutile thermometer. *Contrib. Mineral. Petrol*. 148, 471–488.