

Geochemical and Sr–Nd–Pb isotopic compositions of Mts Pieniny dykes and sills (West Carpathians): Evidence for melting in the lithospheric mantle

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Abstract

Mineralogical, geochemical and Sr–Nd–Pb isotopic data are presented for the Middle Miocene (13.5–10.8 Ma) Mts Pieniny magmatic rocks which occur in a portion of the outermost post-collisional volcanic arc in the Carpathian orogen. The analysed rocks cover a compositional range from basaltic andesites to andesites of the medium-K calc-alkaline series. Despite their arc-like trace element signature, Pieniny rocks show unusual isotopic compositions different from the Neogene–Quaternary calc-alkaline volcanic rocks erupted in the nearby Carpathian–Pannonian region. Their $^{87}\text{Sr}/^{86}\text{Sr}$ (0.7053–0.7070) and $^{143}\text{Nd}/^{144}\text{Nd}$ (0.5121–0.5124) ratios suggest that these magmatic rocks have originated from lithospheric sources enriched in Rb with low Sm/Nd ratios. Pb isotopic compositions ($^{206}\text{Pb}/^{204}\text{Pb}=18.62\text{--}18.86$; $^{207}\text{Pb}/^{204}\text{Pb}=15.66\text{--}15.75$; $^{208}\text{Pb}/^{204}\text{Pb}=38.74\text{--}39.84$) are also consistent with a lithospheric origin of Pieniny rocks. Sr and Nd depleted mantle model ages suggest that parental magmas of Pieniny rocks derived from a metasomatized subcontinental lithospheric mantle recording ancient (>1.1 Ga) subduction-related enrichments. Geochemical features of Pieniny basic rocks allow an estimate of the mineralogy of their lithospheric mantle source region. The small range (from 11 up to 15) of La/Yb and the lack of significant Eu anomalies preclude the presence of residual garnet and plagioclase, respectively; the low Rb/Sr and Rb/Ba ratios as well as the range observed in Ba/Th, K/Ba and La/Yb ratios require involvement of an heterogeneous source in terms of amphibole abundance. The delamination process of the European plate that occurred in this sector of the Carpathian orogen during Middle Miocene should have favoured partial melting of metasomatized amphibole-bearing veins within the lithospheric mantle of the overriding Alcapa micro-plate, giving rise to magma genesis in the Mts Pieniny post-collisional arc segment.

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1. Introduction

The relationship between Miocene–Quaternary calc-alkaline (CA) volcanism and tectonic events in the

Carpathian–Pannonian Region (CPR) has long been the subject of debate (Nemčok et al., 1998a,b; Seghedi et al., 1998; Wortel and Sparkman, 2000; Seghedi et al., 2004) due to the complex spatial and temporal variations displayed by the CA magmatic activity.

In the Western CPR (WCPR), the vast majority of the Neogene CA volcanism (20–10 Ma; Seghedi et al., 2001

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and references therein) occurs in the internal part of the orogenic system and is randomly distributed over a wide area, roughly perpendicular to the curvature of the Carpathian Arc (Fig. 1). In the Eastern CPR (ECPR), CA volcanism shows two distinct distributions (Fig. 1): a linear “arc-type” distribution in the Miocene–Quaternary (10–0.2 Ma; Seghedi et al., 2004) Eastern Carpathian Arc (ECA), and a random distribution in the Apuseni Mt area, where CA magmatic activity is restricted to Miocene (15–8 Ma; Seghedi et al., 2004).

Recently, Seghedi et al. (2004) showed that genesis and evolution of CA magmas in the CPR can be explained in terms of W-directed subduction, roll-back followed by slab break-off and extensional processes. Although the outermost CA magmatic area of the WCPR (e.g., Moravia and Pieniny Mts, Fig. 1) represents a particular case of post-orogenic magmatism intimately linked to the Tertiary geodynamic evolution of the WCPR, a detailed petrological study of this area is still lacking.

In this paper, we present the first detailed trace element and isotopic (Sr, Nd, Pb) investigation of the

Mts Pieniny rocks. These CA rocks are represented by hypabyssal dykes and sills, which are intruded along a junction of the Pieniny Klippen Belt and the Magura Nappe tectonic units (Fig. 1). Our data reveal that Mts Pieniny CA rocks are distinct from CA rocks of the CPR. Because of that and of their peculiar tectonic and structural position, the Mts Pieniny rocks can provide important information for understanding the genesis of the WCPR post-orogenic magmatism. By using the geochemical and isotopic characteristics of Mts Pieniny rocks we will try to: 1) document the geochemical characteristics of these rocks; 2) address their magma source and petrogenesis; 3) explore implications for post-collisional tectonic history in the region.

2. Geological setting

The Miocene Mts Pieniny magmatic rocks are represented by numerous small- to moderate-size andesitic hypabyssal dykes and sills which form a belt about 20 km long (Fig. 1: P). They represent the

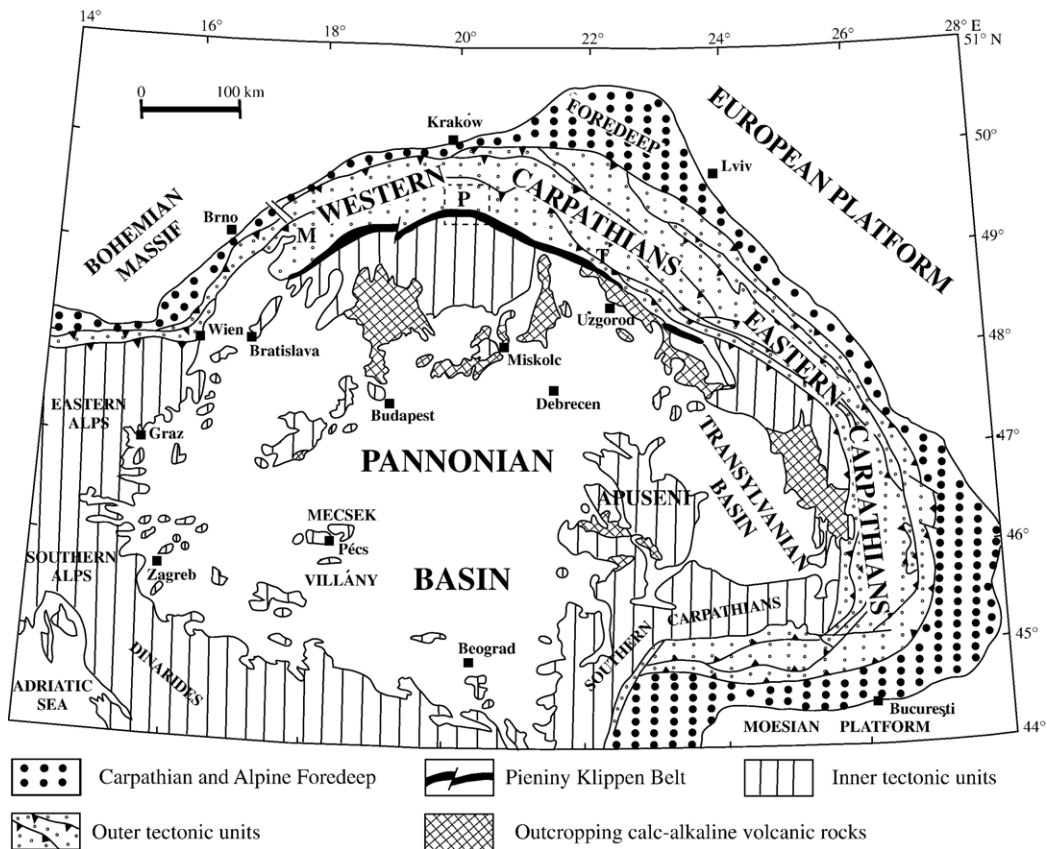


Fig. 1. Location of the post-collisional Sarmatian volcanic arc of the Pieniny Mts (P), and its possible equivalents in the Moravian Carpathians (M) and Transcarpathian Ukraine (T). Dotted square on P shows location of studied area (Fig. 2).

outermost post-collisional magmatic area in the WCPR (Birkenmajer and Pécskay, 1999, 2000). Andesitic volcanics cutting the Magura Nappe flysch in the Moravian Carpathians (Fig. 1: M) may represent the western terminus of the Pieniny magmatic area, whereas coeval andesite intrusions emplaced in the Magura Nappe flysch of Transcarpathian Ukraine may form the eastern termination (Fig. 1: T).

Mts Pieniny hypabyssal rocks intruded along a junction of the Pieniny Klippen Belt (Inner Carpathians) and the Magura Nappe (Outer Carpathians) tectonic units, and cut the Lower Jurassic through Upper Cretaceous marine sedimentary rocks of the Grajcarek Unit (northernmost tectonic unit of the Pieniny Klippen Belt) and its Paleogene sedimentary cover, and the Upper Cretaceous through Eocene flysch rocks of the Magura Nappe (Fig. 2).

Mts Pieniny intrusions post-date the Savian (Early Miocene) orogenic compression and folding phase which was followed by longitudinal strike-slip fault displacement (Birkenmajer, 1983, 1984, 1986). Two phases of intrusive activity have been recognized (Fig. 2). The 1st phase dyke swarm runs parallel/subparallel with the Pieniny Klippen Belt, and occurs in the Mt Wzar, Krościenko, Szczawnica, Mt Jarmuta and

Mt Krupianka areas. Transversal faults, some syn-intrusive but mainly post-intrusive (Sarmatian age), often displace the 1st phase dykes and sills. The post-intrusive faults were used by the 2nd phase intrusions, restricted to the Mt Wzar area and are not tectonized (Birkenmajer and Pécskay, 1999).

Mts Pieniny rocks range from basic to acidic varieties. In previous petrographic studies, they have been classified into two main groups: the amphibole andesites and the amphibole–augite andesites (Mal-kowski, 1921, 1958). Local varieties (magnetite andesite, plagioclase andesite, etc.), were sometimes recognized, based on phenocryst-type domination (see Youssef, 1978, and references therein).

3. Samples and analytical techniques

This paper is based on analyses of the same samples on which K–Ar dating was carried out by Birkenmajer and Pécskay (1999, 2000). According to the K–Ar age data, the Pieniny magmatic activity occurred between 13.5 and 10.8 Ma. In spite of the obvious geological relationships between the 1st and the 2nd phase Pieniny intrusions, the relative time of their emplacement was difficult to establish on K–Ar dating since the analytical

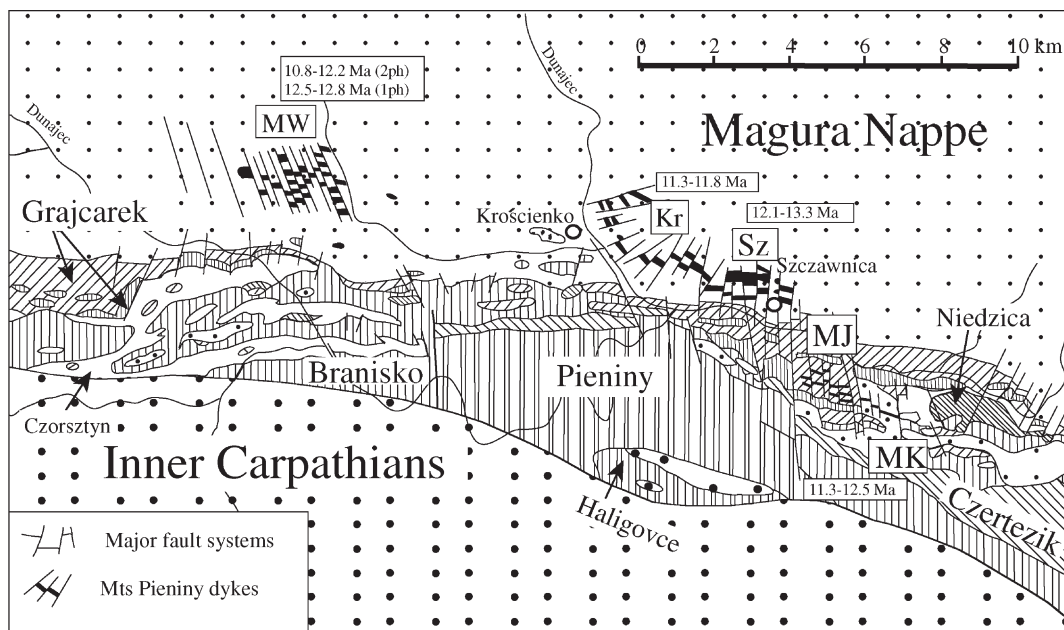


Fig. 2. Occurrence of the K–Ar-dated Sarmatian hypabyssal volcanic rocks in the Pieniny Mts (modified from Birkenmajer and Pécskay, 2000). Tectonic units of Pieniny Klippen Belt: Inner Carpathians (Podhale Paleogene flysch and Podhale-type Paleogene in the Pieniny Klippen Belt); Magura Nappe (Cretaceous–Paleogene flysch deposits, folded during early Miocene Savian phase, and autochthonous uppermost Cretaceous–Paleogene in the Pieniny Klippen Belt); Grajcarek Unit (Jurassic–Upper Cretaceous deposits); Czorsztyn, Czertezik, Niedzica, Branisko, Pieniny, and Haligovce units (Subhercynian through Laramin tectonic units of the Pieniny Klippen Belt consisting of Cretaceous, Jurassic, and partly Triassic deposits). MW = Mt Wzar (1ph, first phase; 2ph, second phase); MJ = Mt Jarmuta; MK = Mt Krupianka; Sz = Szczawnica; Kr = Krościenko.

K–Ar errors of both intrusive phases usually overlap (Birkenmajer and Pécskay, 2000).

The location of analysed Pieniny samples is reported in Fig. 2 and details on their field location can be found in Birkenmajer and Pécskay (1999, 2000). Analysed samples derive from five areas of the Pieniny Mts (Fig. 2): Mt Wzar, Mt Jarmuta, Mt Krupianka, Szczawnica and Kroszcienko.

Microprobe analyses were carried out on selected samples, covering the compositional range observed in the Pieniny volcanics (see Appendix A. Supplementary data). Mineral analyses were carried out at the Dipartimento Scienze della Terra, University of Parma, on a Jeol 6400 scanning electron microscope equipped with Oxford (Link) EDS microanalysis. Operating conditions were 15 kV, 0.28 nA, electron beam $\sim 1\mu\text{m}$ in diameter, 60s counting time.

The samples were broken into small chips, hand-picked to eliminate altered fragments, rinsed in distilled water, and then crushed to powder using an agate mill. Geochemical and Sr, Nd, Pb isotopic analyses were performed at Activation Laboratories LTD (Ancaster, Canada).

The analytical procedures for the major and trace element analyses are the following. Samples are mixed with a flux of lithium metaborate and lithium tetraborate and fused in an induction furnace. The molten melt is immediately poured into a solution of 5% nitric acid containing an internal standard, and mixed continuously until completely dissolved ($\sim 30\text{min}$). The samples are run for major oxides and selected trace elements on a combination simultaneous/sequential Thermo Jarrell-Ash ENVIRO II ICP or a Spectro Cirros ICP. Calibration is performed using USGS and CANMET certified reference materials. Trace elements are determined by further diluting the fused sample adding internal standards and analyzing by ICP/MS on a Perkin Elmer-Sciex Elan 6000.

The analytical procedures for isotopic analyses are the following. Rock powders for Sm–Nd and Rb–Sr studies were dissolved in a mixture of HF, HNO₃ and HClO₄. Rb and Sr were separated using conventional cation-exchange techniques. Sm and Nd were separated by extraction chromatography on teflon powder (PFTE) coated with HDEHP (bis-2 ethyl-hexyl-phosphoric acid). The analysis was performed on Finnigan MAT 261 8-collector mass-spectrometer in static mode. During the period of work the weighted average of 15 SRM–987 Sr and of 10 La Jolla Nd standard runs yielded 0.710261 ± 12 (2σ) and 0.511850 ± 5 (2σ) for $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{143}\text{Nd}/^{144}\text{Nd}$, respectively. Nd isotopic analysis is corrected for $^{143}\text{Nd}/^{144}\text{Nd} = 0.511860$. U and

Pb were separated using the ion-exchange technique with Bio-Rad 1x8. Pb isotope compositions were analysed on Finnigan MAT — 261 multicollector mass spectrometer. The measured Pb isotope ratios were corrected for mass fractionation of 0.13% per amu calculated from replicate measurements of Pb isotope composition in NBS SRM — 982 standards. External reproducibility of lead isotope ratios are 0.1% for $^{206}\text{Pb}/^{204}\text{Pb}$, 0.15% for $^{207}\text{Pb}/^{204}\text{Pb}$, 0.2% for $^{208}\text{Pb}/^{204}\text{Pb}$ based on repeated measurements of standard BCR-1.

Further details of these methods can be found on Activation Laboratories website (www.actlabs.com).

4. Petrography and mineral chemistry

Previous studies reveal that Pieniny rocks show petrographic evidence of having suffered variable degrees of secondary transformation (Youssef, 1978 and references therein). At Mt Wzar, hydrothermal/thermal alteration of the 1st phase dykes and their country rocks was associated with the 2nd phase magma intrusion. Chabasite, often succeeding calcite, is a frequent secondary mineral there.

In this study we have analysed samples as fresh as possible, based on petrographic observations. Texture and modal mineralogy of analysed Pieniny rocks are shown in Table 1. The relative freshness of most of these samples is supported by their low LOI ($< 3\text{ wt.}\%$). Pieniny samples have been classified using combined chemical (Total Alkalis and K₂O vs Silica diagrams; Peccerillo and Taylor, 1976; Le Maitre, 1989; see Fig. 3) and mineralogical criteria. With one exception, the studied rocks can be classified as medium-K calc-alkaline ranging from basaltic andesites to andesites. Only one basaltic andesite sample (i.e., 20S) falls in the field of high-K calc-alkaline rocks.

All the investigated rocks show porphyritic texture with the groundmass ranging from micro- to cryptocrystalline. Plagioclase (pl) and amphibole (amph) are the most abundant, ubiquitous phenocryst phase, and opaques (opq) and apatite (ap) are the main accessory minerals (Table 1). In all the analysed Pieniny rocks, pl is often sieve-textured, locally showing evidence of resorption, with a younger plagioclase generation surrounding the older one. Pl composition ranges from bytownite to labradorite (An_{76–50}) in the basaltic andesite (BA) rocks, and from labradorite to andesine (An_{70–30}) in the medium-K andesite (MKA) ones (see data in Appendix A). Amph, which is commonly zoned, has been optically identified as hornblende, since no microprobe analyses of this phase are available. Clinopyroxene (cpx) occurs only in the BA rocks and

Table 1
Synthetic petrographic description of the analysed Mts. Pieniny samples

Locality	Phenocrysts and microphenocrysts ⁽¹⁾	Secondary minerals ⁽¹⁾	Comment ⁽²⁾	Rock type ⁽³⁾
<i>Mt. Wzar</i>				
1st phase				
6S, 7S	pl, amph ^a , cpx, opq, ap	Fe-hy	fr.	MK-BA
9S, 10S	pl, amph ^a , cpx, opq, ap		fr.	MK-BA
99/26	pl ^b , amph, cpx, opq, ap	Fe-hy, cl.m.	sl. a.	MK-BA
2nd phase				
1S	pl ^b , amph, cpx, opq, ap	zeol, carb, qz	sl. a.	MK-BA
2S	pl, amph, cpx, opq, ap	cl.m., Fe-hy, qz	st. a.	MK-BA
5S	pl ^b , amph, cpx, opq, ap	carb	st. a.	MK-BA
8S	pl, amph, cpx, opq, ap		fr.	MK-BA
99/25	pl ^b , amph, cpx, opq, ap	cl.m., Fe-hy	sl. a.	MK-BA
99/27	pl ^b , amph ^a , cpx, opq, ap	carb, cl.m., w-m, Fe-hy	st. a.	MK-BA
<i>Mt. Jarmuta</i>				
11S: rock	pl ^b , amph ^c , ap, opq, Kfd	carb, cl.m., chl	st. a.	MKA
11S: cumulate	amph, pl, ap, opq, Fe-hy		fr.	
12S	pl, amph ^c , opq, ap, sph, Kfd	carb, cl.m., chl, w-m	st. a.	MKA
99/21	pl ^b , amph, ap, opq, sph, Kfd		fr.	MKA
99/20	pl, cpx, bt, amph, opq, ap		fr.	HK-BA
<i>Mt. Krupianka</i>				
13S	pl ^b , amph ^c , opq, ap, Kfd, sph	cl.m., carb, Fe-hy	sl. a.	MKA
14S	pl ^b , amph, opq, ap, sph, Kfd		fr.	MKA
99/19	pl, amph ^c , opq, ap, Kfd	cl.m., carb, chl	sl. a.	MKA
<i>Szczawnica</i>				
Grajcarek Stream				
15S	pl ^b , amph ^c , opq, ap	carb, w-m	st. a.	MKA
Mt. Bryjarka				
16S, 17S	pl ^b , amph ^c opq, ap	carb, w-m, cl.m., chl	sl. a.	MKA
Mt. Cizowa				
99/22	pl, amph, opq, ap, Kfd		fr.	MKA
<i>Kroscienko</i>				
Kozlecki Stream				
99/23	pl, amph ^c , opq, ap, sph, Kfd		fr.	MKA
Zakijowski Stream				
99/24	pl, amph, cpx, opq, ap	carb, cl.m.	sl. a.	MK-BA

(1) Phases are reported in order of estimated abundance; pl, plagioclase; cpx, clinopyroxene; amph, greenish-brown amphibole; opq, opaques; bt, biotite; qz, quartz; ap, apatite; sph, sphene; Kfd, K-feldspar; carb, carbonates; cl.m., clay minerals; w-m, white mica; Fe-hy, Fe-hydroxides; zeol, zeolites. a: crystals are often corroded and surrounded by opq, cpx and pl; b: some crystal are totally or largely pseudomorphically replaced by sericite and carbonates; c: some crystals are totally or largely pseudomorphically replaced by opq, carb, w-m, cl.m. (2): sl. a., slightly altered; fr., fresh; st. a., strongly altered. (3): nomenclature is given according to chemical (Total Alkalies and K₂O versus SiO₂ diagrams) criteria: MK-BA, Medium-K Basaltic Andesite; HK-BA, High-K Basaltic Andesite; MKA, Medium-K Andesite.

ranges between magnesium-rich augite (Wo₄₂–En₄₂) and ferroan diopside (Wo₅₀–En₃₅), according to the nomenclature of Morimoto (1988) (see data in Appendix A). Sporadic microphenocrysts of biotite (bt) are encountered in a few MKA rocks, whereas phenocrysts of this mineral are present in the high-K BA. K-feldspar (Or₆₀) and sphene (sph) occur in the MKA (see data in Appendix A). Microphenocrysts of apatite are present in one HKBA sample (10S). Cumulates of amph, pl, op, sph, ap are present in the Mt Jarmuta MKA rocks.

Most of the investigated rocks show clear petrographic evidence of having suffered variable degrees of secondary transformation. The most evident one is that affecting the amph crystals of almost all the studied samples, except those of the 2nd phase Mt Wzar dykes. Some amph crystals may display reaction rims consisting of opq, cpx and pl (i.e., Mt Wzar 1st BA rocks). Similar rims may occur in amph phenocrysts of CA volcanic rocks and represent the decompression breakdown products of amph crystallized at depth

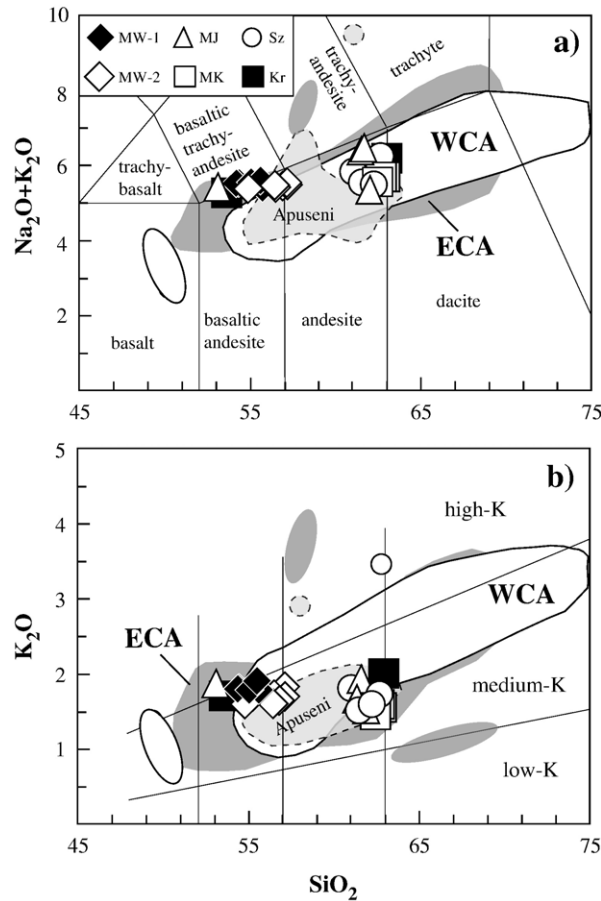


Fig. 3. Mts. Pieniny samples plotted on (a) Total Alkalis–Silica diagram (TAS; Le Maitre, 1989), and (b) K_2O vs SiO_2 diagram (Peccerillo and Taylor, 1976). Symbols: MW-1, first phase Mt Wzar intrusions; MW-2, second phase Mt Wzar intrusions; MJ, Mt Jarmuta intrusions; MK, Mt Krupianka intrusions; Sz, Szczawnica intrusions; Kr, Kroszcienko intrusions. Reference data: WCA, Western Carpathian Arc calc-alkaline volcanic rocks (Downes et al., 1995; Seghedi et al., 2001); ECA, Eastern Carpathian Arc calc-alkaline volcanic rocks (Mason et al., 1996); Apuseni (Seghedi et al., 2004).

(Deer et al., 1997 and references therein). Other amphibole crystals are pseudomorphically replaced by opq, carbonates (carb), white mica (w-m), clay minerals (cl.m.) and chlorite (chl) (i.e., MKA rocks), suggesting extensive water loss occurring for a long time in the magma chamber before eruption (Deer et al., 1997 and references therein). Moreover, Fe-hydroxides (Fe-hy), cl, carb, chl and w-m may occur as secondary minerals in the groundmass of the investigated rocks; SiO_2 polymorph and zeolite (zeol), identified as tridimite and chabasite, respectively (Youssef, 1978, and references therein), are only present in the MKBA of the Mt Wzar 2nd phase dykes.

Although various types of xenoliths (i.e., moderately to strongly thermally altered and/or metasomatised sedimentary rocks; igneous and metamorphic rocks; Malkowski, 1921; Kardymowicz, 1957) occur in Mts Pieniny intrusive rocks, they have not been found in our samples.

5. Geochemistry

5.1. Major and trace elements

The chemical compositions of the Pieniny volcanic rock samples analysed in this study are shown in Table 2.

In the variation diagrams of major and minor elements relative to SiO_2 (Figs. 4 and 5) the BA and the MKA are clearly distinguished by a small gap in silica content (from 58 to 60 wt.% SiO_2). MgO , $\text{Fe}_2\text{O}_{3\text{tot}}$, CaO and TiO_2 show negative trends against SiO_2 . Na_2O increases from HKBA to MKA rocks, but is very variable among the BA ones. Pieniny BA and MKA rocks display the same restricted range in the K_2O and Al_2O_3 contents (1.4–2.0 wt.% and 18–19 wt.%, respectively). P_2O_5 (not shown) displays a scattered distribution with respect to silica among the most basic

Table 2
Major and trace element data for Mts. Pieniny samples

	Mt Wzar-1st					Mt Wzar-2nd				
	6S	7S	9S	10S	99/26	99/27	1S	2S	5S	
SiO ₂	54.74	54.06	54.97	53.79	53.73	52.91	55.89	55.06	56.3	
TiO ₂	0.72	0.79	0.78	0.79	0.76	0.77	0.67	0.67	0.71	
Al ₂ O ₃	18.92	18.91	18.57	18.52	18.10	17.63	18.64	18.39	18.89	
Fe ₂ O ₃	7.35	7.75	6.97	7.76	7.43	6.92	6.75	6.54	6.83	
MnO	0.14	0.16	0.14	0.15	0.14	0.13	0.15	0.10	0.15	
MgO	2.90	3.48	3.47	3.41	3.64	4.07	2.88	2.72	2.90	
CaO	8.07	8.79	8.18	8.77	8.11	8.66	8.32	7.77	8.15	
Na ₂ O	3.60	3.81	3.64	3.50	3.73	3.64	3.83	3.67	3.67	
K ₂ O	1.89	1.70	1.71	1.74	1.67	1.54	1.58	1.59	1.71	
P ₂ O ₅	0.28	0.28	0.25	0.36	0.34	0.26	0.32	0.32	0.33	
LOI	1.24	0.62	1.56	1.65	2.25	4.31	1.41	2.53	1.24	
Total	99.87	100.34	100.25	100.44	99.90	100.83	100.43	99.35	100.87	
Mg#	0.45	0.48	0.50	0.47	0.50	0.55	0.47	0.49	0.46	
Cr	15	25	26	25	33	41	22	24	25	
Co	14	14	17	17	17	17	13	13	12	
Ni	7	9	11	8	nd	nd	9	9	9	
Rb	53	52	48	50	48	42	52	54	51	
Sr	672	620	680	695	619	597	821	657	638	
Y	21.0	20.2	19.6	21.6	20.8	17.7	19.8	20.2	19.8	
Zr	120	109	116	117	117	110	124	124	121	
Nb	9.6	10.9	10.1	15.2	13.2	9.9	11.0	11.0	10.7	
Cs	2.7	3.4	2.4	0.8	1.0	1.4	1.5	1.3	1.3	
Ba	621	607	599	710	683	581	633	598	635	
La	28.9	23.9	29.1	34.5	33.0	26.1	31.4	31.8	31.6	
Ce	45.6	43.0	45.3	54.2	50.5	42.4	51.7	51.4	51.4	
Pr	6.27	5.17	6.53	7.45	7.03	5.80	6.95	6.92	6.92	
Nd	24.1	20.5	25.0	28.2	26.5	22.3	26.0	26.2	26.2	
Sm	4.70	4.25	4.87	5.48	5.06	4.36	4.82	4.90	4.98	
Eu	1.56	1.36	1.59	1.79	1.66	1.45	1.60	1.61	1.62	
Gd	4.25	3.72	4.30	4.78	4.62	3.88	4.39	4.35	4.39	
Tb	0.71	0.64	0.72	0.79	0.75	0.65	0.71	0.72	0.73	
Dy	4.02	3.66	3.96	4.38	4.23	3.58	3.93	3.97	4.04	
Ho	0.76	0.73	0.76	0.84	0.80	0.68	0.76	0.75	0.77	
Er	2.22	2.11	2.18	2.42	2.27	1.93	2.19	2.17	2.20	
Tm	0.329	0.305	0.315	0.356	0.336	0.278	0.327	0.328	0.326	
Yb	2.11	1.96	2.02	2.24	2.16	1.86	2.10	2.14	2.15	
Lu	0.314	0.304	0.306	0.341	0.317	0.272	0.324	0.324	0.322	
Hf	3.6	3.25	3.6	3.6	3.5	3.4	3.7	3.6	3.6	
Ta	0.74	0.68	1.45	1.01	0.92	0.76	0.86	0.87	0.85	
Tl	0.27	0.18	0.06	0.10	0.19	0.09	0.27	0.26	0.21	
Pb	19	15	12	9	10	9	10	10	7	
Th	3.89	5.49	3.72	4.58	4.33	3.54	4.40	4.39	4.43	
U	2.53	1.57	1.25	1.21	1.17	1.10	1.15	1.21	1.15	
Eu/Eu2*	1.07	1.04	1.06	1.07	1.05	1.08	1.07	1.07	1.06	
(La/Yb) _N	9.8	8.8	10.3	11.0	11.0	10.1	10.7	10.6	10.5	

	Mt Wzar-2nd		Mt Jarmuta				Mt Krupianka	
	8S	99/25	11SXeno	11Sroc	12Sroc	99/20	99/21	13S
SiO ₂	56.64	55.76	34.33	60.58	60.57	52.77	61.17	62.31
TiO ₂	0.69	0.68	1.90	0.53	0.49	0.78	0.51	0.51
Al ₂ O ₃	18.72	18.36	14.56	18.16	18.44	18.87	19.18	18.66
Fe ₂ O ₃	6.77	6.72	19.41	4.96	4.67	8.18	4.96	4.76
MnO	0.15	0.15	0.25	0.14	0.13	0.19	0.14	0.12
MgO	2.68	2.88	8.36	1.09	1.12	3.57	1.17	0.99
CaO	7.61	7.38	13.31	6.64	6.27	9.18	5.71	5.99

(continued on next page)

Table 2 (continued)

	Mt Wzar-2nd		Mt Jarmuta					Mt Krupianka
	8S	99/25	11SXeno	11Sroc	12Sroc	99/20	99/21	13S
Na ₂ O	3.65	3.68	1.78	3.75	4.46	3.52	4.7	4.09
K ₂ O	1.80	1.64	1.09	1.49	1.88	1.85	1.66	1.54
P ₂ O ₅	0.33	0.32	1.80	0.25	0.24	0.38	0.24	0.24
LOI	1.78	3.17	2.80	2.90	2.19	1.04	1.06	1.26
Total	100.81	100.74	99.59	100.50	100.46	100.33	100.50	100.45
Mg#	0.45	0.47		0.32	0.34	0.47	0.33	0.31
Cr	22	nd	42	6	5	nd	nd	4
Co	13	13	39	4	4	17	5	4
Ni	6	nd	13	4	4	nd	nd	4
Rb	56	52	12	53	58	69	61	54
Sr	678	596	423	899	910	927	879	976
Y	22.0	19.6	26.5	16.8	17.3	22.3	17.8	18.0
Zr	129	121	36	172	170	134	173	169
Nb	11.3	10.9	4.3	13.0	13.8	10.1	14.4	13.3
Cs	1.8	1.1	0.6	2.2	1.3	5.2	2.0	1.0
Ba	621	630	201	836	892	597	891	880
La	36.0	31.6	22.4	37.8	36.2	30.4	33.5	38.6
Ce	56.9	50.4	41.9	61.7	61.9	50.2	58.0	61.6
Pr	8.00	6.88	6.60	8.28	7.35	6.89	6.84	8.41
Nd	29.6	25.8	29.9	30.7	27.8	26.9	26.3	31.6
Sm	5.62	4.89	7.47	5.51	4.91	5.46	4.93	5.60
Eu	1.82	1.59	2.65	1.86	1.69	1.78	1.64	1.93
Gd	4.90	4.30	7.19	4.38	3.95	4.95	3.99	4.52
Tb	0.79	0.72	1.19	0.67	0.65	0.82	0.65	0.70
Dy	4.41	3.94	6.43	3.57	3.37	4.39	3.47	3.61
Ho	0.84	0.75	1.14	0.65	0.62	0.82	0.64	0.65
Er	2.44	2.16	3.00	1.85	1.78	2.39	1.82	1.89
Tm	0.357	0.325	0.384	0.267	0.264	0.346	0.272	0.269
Yb	2.36	2.09	2.32	1.87	1.78	2.25	1.87	1.81
Lu	0.361	0.320	0.320	0.284	0.264	0.340	0.270	0.277
Hf	3.8	3.6	1.8	5.1	4.6	3.8	4.7	4.8
Ta	0.90	0.85	0.31	0.96	0.92	0.78	0.96	0.96
Tl	0.27	0.21	0.08	0.30	0.21	0.44	0.27	0.18
Pb	12	9	bdl	7	8	13	16	6
Th	4.61	4.38	2.07	4.54	5.01	4.98	4.97	4.46
U	1.21	1.20	0.57	1.74	1.86	1.58	2.00	1.59
Eu/Eu*	1.06	1.06		1.15	1.18	1.05	1.13	1.17
(La/Yb) _N	10.5	10.9		14.5	14.6	9.7	12.9	15.3
	Mt Krupianka		Szczawnica			Kroscienko		
			Grajcarek S.	Mt Bryjarka		Mt. Cizowa	Kozlecki S.	Zakijowski S.
	14S	99/19	15S	16S	17S	99/22	99/23	99/24
SiO ₂	62.10	61.80	59.40	60.70	60.34	62.05	60.56	52.30
TiO ₂	0.50	0.49	0.52	0.51	0.51	0.47	0.53	0.74
Al ₂ O ₃	18.65	18.46	17.30	18.35	18.04	18.75	18.25	18.69
Fe ₂ O ₃	4.77	4.81	4.94	5.05	5.02	4.58	4.71	8.05
MnO	0.13	0.15	0.14	0.13	0.13	0.12	0.12	0.16
MgO	1.04	1.11	1.79	1.71	1.44	1.30	0.64	3.26
CaO	6.03	6.41	7.33	6.49	5.95	5.37	5.21	8.89
Na ₂ O	4.06	4.07	3.89	4.00	3.76	4.43	4.01	3.48
K ₂ O	1.58	1.44	1.77	1.50	1.56	1.72	1.93	1.67
P ₂ O ₅	0.25	0.24	0.25	0.27	0.26	0.24	0.26	0.37
LOI	1.31	1.50	3.06	1.69	3.45	1.45	3.03	2.70
Total	100.42	100.48	100.40	100.40	100.46	100.47	99.25	100.28
Mg#	0.32	0.33	0.42	0.42	0.38	0.37	0.22	0.45
Cr	4	nd	11	10	10	nd	nd	nd

Table 2 (continued)

	Mt Krupianka		Szczawnica			Kroszcienko		
	14S	99/19	Grajcarek S.	Mt Bryjarka		Mt. Cizowa	Kozlecki S.	Zakijowski S.
			15S	16S	17S	99/22	99/23	99/24
Co	4	4	5	7	8	6	7	17
Ni	4	nd	6	6	6	nd	nd	nd
Rb	54	61	56	50	52	62	73	47
Sr	964	921	888	985	937	981	877	792
Y	16.8	17.4	19.5	17.5	20.4	14.9	18.2	20.1
Zr	163	169	166	161	165	177	156	108
Nb	13.1	13.8	13.7	10.6	10.7	12.3	13.0	6.3
Cs	2.0	2.3	1.8	1.8	6.1	2.3	4.2	1.3
Ba	858	928	904	743	674	892	871	515
La	36.2	32.9	41.0	34.8	36.8	31.9	36.6	23.5
Ce	59.2	56.8	66.2	58.3	59.8	56.7	57.7	40.8
Pr	8.05	6.70	8.82	7.89	8.39	6.49	7.78	5.73
Nd	30.1	25.3	32.5	29.3	31.4	23.9	28.4	23.1
Sm	5.38	4.59	5.65	5.20	5.72	4.13	5.02	4.91
Eu	1.86	1.62	1.99	1.78	1.86	1.45	1.63	1.58
Gd	4.24	3.90	4.54	4.18	4.59	3.30	4.26	4.49
Tb	0.66	0.61	0.71	0.66	0.73	0.53	0.67	0.75
Dy	3.45	3.27	3.86	3.65	3.95	2.81	3.59	4.18
Ho	0.63	0.61	0.72	0.69	0.74	0.54	0.68	0.79
Er	1.86	1.75	2.08	1.99	2.15	1.60	1.95	2.24
Tm	0.262	0.258	0.300	0.294	0.315	0.242	0.297	0.328
Yb	1.78	1.76	2.03	2.00	2.10	1.70	2.01	2.05
Lu	0.280	0.260	0.313	0.303	0.321	0.248	0.300	0.308
Hf	4.7	4.4	4.9	4.6	4.8	4.5	4.5	3.3
Ta	0.95	0.92	0.97	0.81	0.82	0.80	1.03	0.53
Tl	0.23	0.29	0.32	0.28	0.27	0.33	0.42	0.19
Pb	9	14	11	10	10	12	15	6
Th	4.30	4.95	4.91	4.07	4.09	4.73	6.12	3.88
U	1.58	1.92	2.35	1.73	1.79	2.03	2.12	1.41
Eu/Eu*	1.19	1.17	1.20	1.17	1.11	1.20	1.08	1.03
(La/Yb) _N	14.6	13.4	14.5	12.5	12.6	13.4	13.0	8.2

LOI=total volatile lost on ignition. Mg#=(Mg/(Mg+Fe²⁺))*100, with Fe³⁺/Fe²⁺ as suggested by Middlemost (1989). Normalizing values used in Eu/Eu* and (La/Yb)_N are from Sun and McDonough (1989). nd = not determined; bdl = below detection limit.

BA (0.2–0.4), with the MKA rocks partially overlapping this range.

The compatible elements (i.e., Cr, Ni, Co) display low concentrations in even the most basic magmas (Table 2) supporting the assertion that fractionation of ol, chromium spinel and cpx occurred at an early stage. Some of the incompatible trace elements (i.e., Zr, Nb, Sr, Rb, Ba, LREE, P), although displaying an average increase with silica, reveal large intersample variations especially among the most basic BA samples. We do not observe any negative correlation of LOI vs these elements, which would be expected during alteration. Furthermore, the same intersample variations persist once these trace elements are plotted against Zr, generally regarded as a poorly immobile element during secondary transformations. Therefore, we can argue that the geochemical variations observed

among the most basic BA rocks are pristine characters.

MKA rocks exhibit higher Zr, Sr, and Ba, and similar Nb, Y, and Rb contents compared to the BA rocks. These geochemical features partially reflect the fractionation of pl–amph–sph, that occurred as phenocrysts and microphenocrysts in the MKA rocks and that represent the major phases in the cumulate rocks from Mt Jarmuta (Table 2). This hypothesis is supported by the observation that these cumulate rocks represent one of the ends of the trends, which pass through the BA and the MKA rocks, once plotted on Harker diagrams of Figs. 4 and 5.

In general, Pieniny rocks are enriched in highly incompatible trace elements such as the light-rare earth elements (LREE) and large-ion lithophile elements (LILE) and depleted in high field strength elements

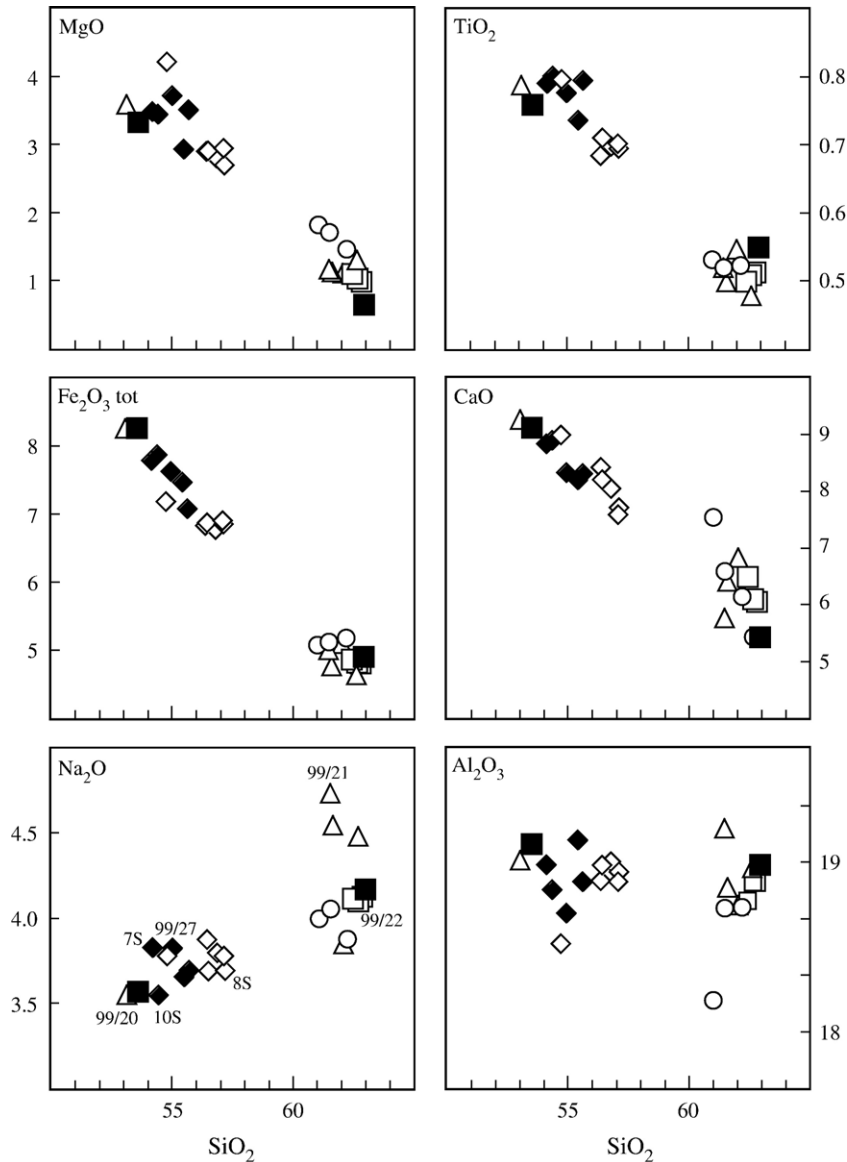


Fig. 4. Variation diagrams of major elements vs SiO_2 (wt.%) for Mts. Pieniny samples. Symbols as in Fig. 2. The signed samples are those on which the Sr–Nd–Pb isotopic determinations were made (see Table 3).

(HFSE) compared to primitive mantle (Fig. 6), similar to most CA arc lavas.

Differences in slopes of REE patterns between the Pieniny lavas are subtle ($(\text{La}/\text{Yb})_N$ ratio range from 8 to 11 for BA and from 12 to 15 for MKA; N =normalizing value of chondrites from Sun and McDonough, 1989; see Fig. 7). Positive Eu anomalies are ubiquitous and are of similar size in BA ($\text{Eu}/\text{Eu}^*=1.03\text{--}1.08$) and slightly larger for MKA ($\text{Eu}/\text{Eu}^*=1.07\text{--}1.20$) rocks (Table 2) suggesting plagioclase cumulation. The analysed Mts Pieniny cumulate rock shows degree of enrichment or

depletion opposite to that observed in evolved MKA rocks, which is consistent with its cumulate origin (Figs. 6 and 7).

5.2. Isotope geochemistry

The Sr, Nd, and Pb isotopic determinations were made on five BA and two MKA samples. The isotopic ratios are presented in Table 3 and plotted on Figs. 8 and 9. No age corrections have been applied to the measured isotopic compositions because they

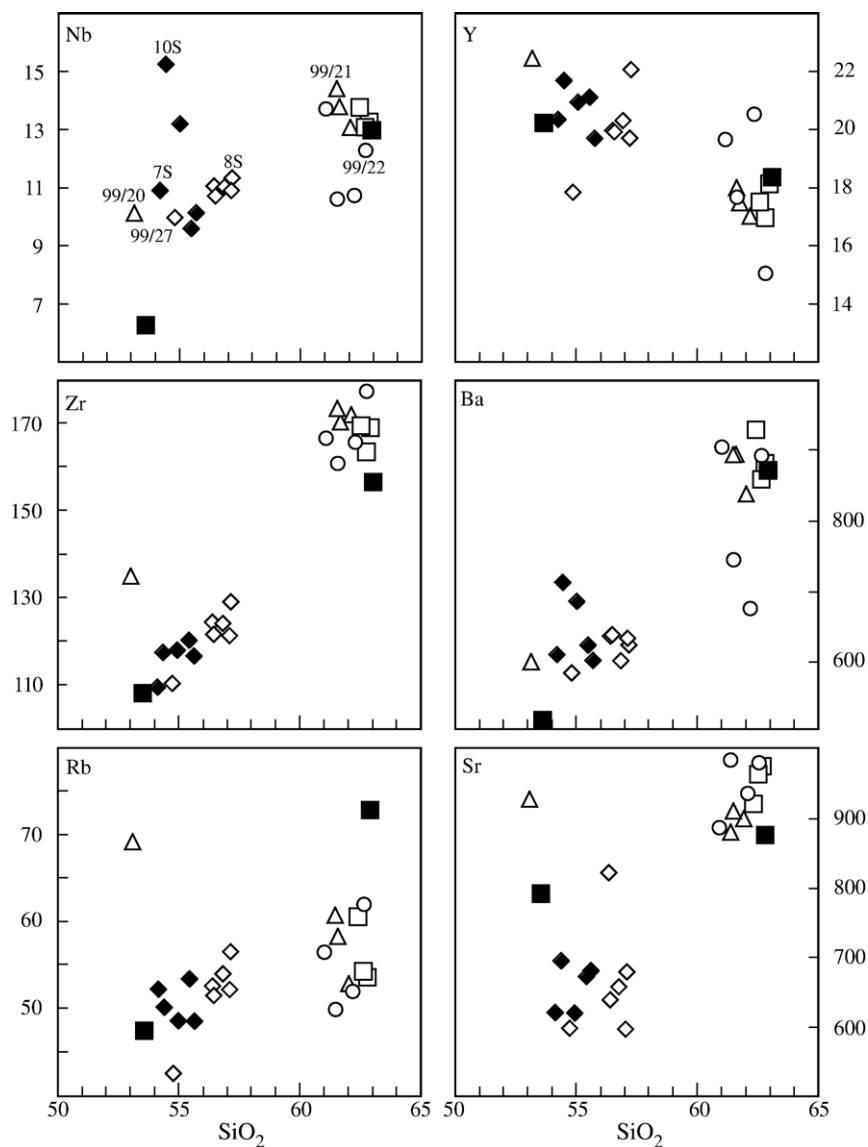


Fig. 5. Variation diagrams of trace elements (ppm) vs SiO_2 (wt.%) for Mts. Pieniny samples. Symbols as in Fig. 2. Signed samples as in Fig. 4.

are less than the analytical error. Also shown on Figs. 8 and 9 are fields of CA rocks from the CPR (Salters et al., 1988; Mason et al., 1996; Seghedi et al., 2001, 2004).

Pieniny volcanic rocks have distinct $^{87}\text{Sr}/^{86}\text{Sr}$ (0.7053–0.7070) and $^{143}\text{Nd}/^{144}\text{Nd}$ (0.5121–0.5124) isotopic compositions compared with the CA volcanic rocks from the CPR, plotting at the extension of Southern Harghita CA lavas on the Sr–Nd isotope diagram (Fig. 8). In particular, the BA rocks show an increase of $^{87}\text{Sr}/^{86}\text{Sr}$ and a decrease of $^{143}\text{Nd}/^{144}\text{Nd}$ whereas the evolved MKA has similar $^{87}\text{Sr}/^{86}\text{Sr}$ to the most depleted Pieniny BA but lower $^{143}\text{Nd}/^{144}\text{Nd}$.

Pieniny BA rocks exhibit a limited range of $^{206}\text{Pb}/^{204}\text{Pb}$ isotopic ratio (18.6–18.8) resulting similar to the CA rocks of the CPR (Fig. 9). Nevertheless, these rocks have scattered $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{208}\text{Pb}/^{204}\text{Pb}$ isotopic ratios showing a general shift to high $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{208}\text{Pb}/^{204}\text{Pb}$ at a particular $^{206}\text{Pb}/^{204}\text{Pb}$ isotopic ratio. A similar trend has been also observed for the Southern Harghita CA rocks (Mason et al., 1996). Pieniny MKA has lower Pb-isotopic ratios, than those of BA plotting in the field of Southern Harghita magmas.

According to Mason et al. (1996) the trends defined by the Southern Harghita CA rocks in Sr–Nd–Pb isotopic diagrams may have resulted from the

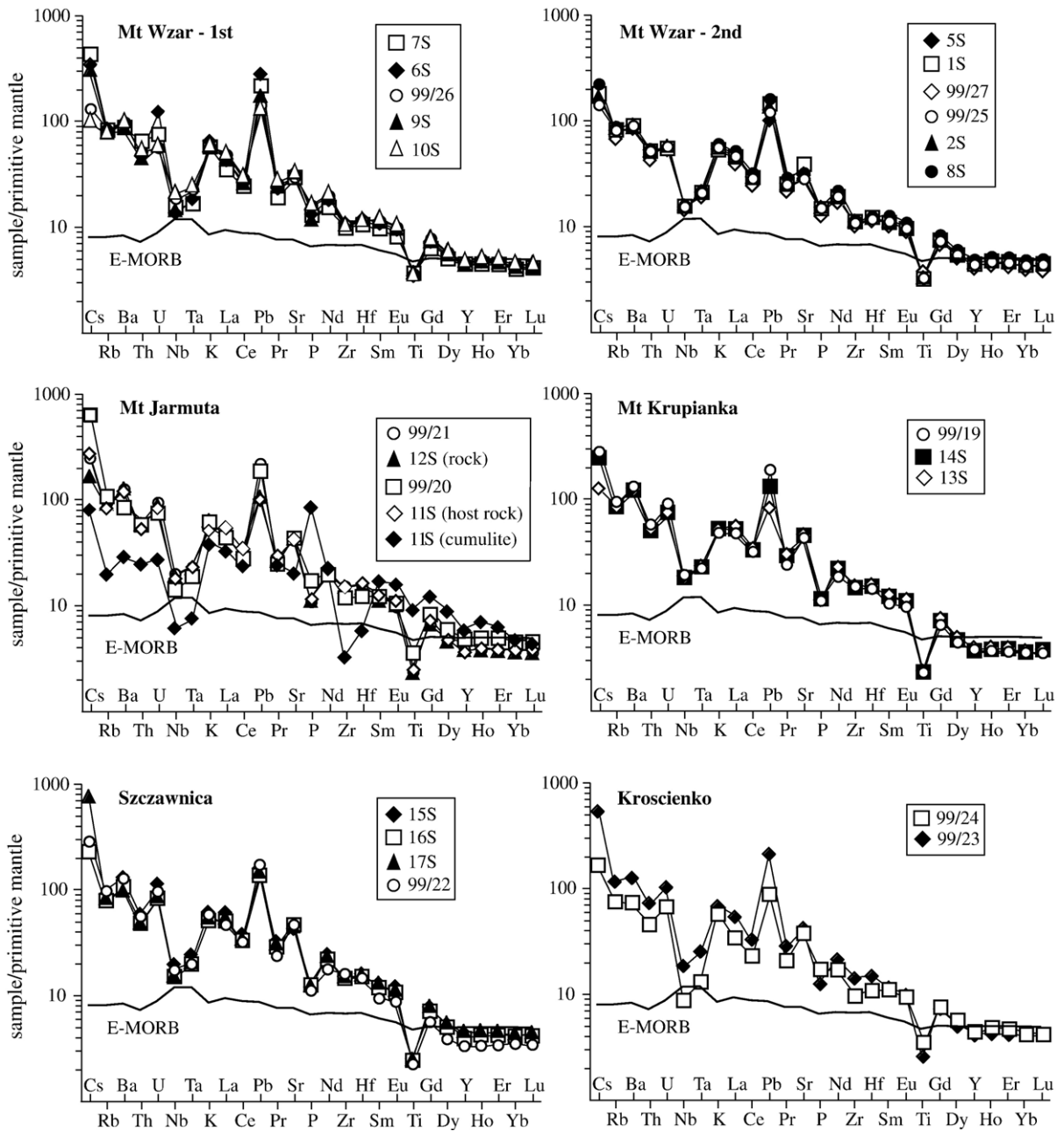


Fig. 6. Primitive mantle normalized incompatible element variation diagrams for Mts. Pieniny samples. Normalizing values and E-MORB data from Sun and McDonough (1989).

involvement of a crustal component, not yet identified in the sampled pale-accretionary wedge or upper crust of this region. We discuss below that the finding of distinct Sr–Nd isotopic ratios as well as the higher $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{208}\text{Pb}/^{204}\text{Pb}$ values in the less differentiated Pieniny BA rocks suggest the addition of a component with variable isotopic compositions to the mantle source rather than a crustal contamination

process as a more likely mechanism for the genesis of Pieniny lavas.

6. Discussion

All the studied Pieniny samples are crystalline, variable phyric volcanic rocks. Petrographically, they are characterized by the ubiquitous presence of

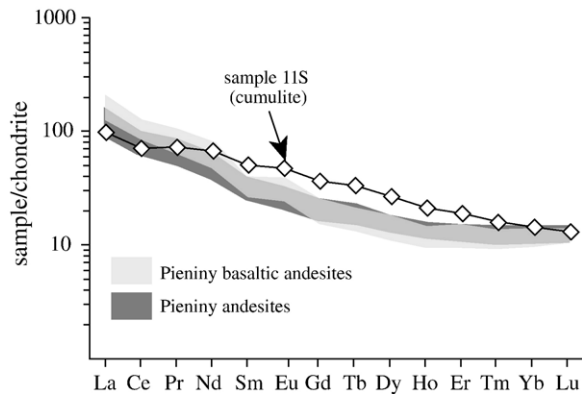


Fig. 7. Chondrite normalized rare earth patterns for Mts. Pieniny samples. Normalizing values from Sun and McDonough (1989).

amphibole in both BA and MKA rocks, resulting differently from the other CA volcanic rocks from the CPR where amphibole generally occurs in rock with $\text{SiO}_2 > 56$ wt.% (Mason et al., 1996; Downes et al., 1995). They also have distinct Sr and Nd isotopic compositions compared with the CA volcanic rocks from the CPR. The full geochemical and Sr–Nd–Pb isotopic data set from the least to the most evolved Pieniny rocks is extremely useful to deduce the mantle–crust processes able to explain the formation of these rocks.

We discuss below the constraints that these data impose on the characteristics of the mantle source of Pieniny rocks, which appear to be different from those recognised in most of the CPR arc magmas. We also briefly discuss the important constraints that the origin of Mt Pieniny rocks places on geodynamic models for the evolution of the CPR.

6.1. Fractional crystallization and contamination processes

Before we can assess the processes operating in the subarc mantle, we must consider the likelihood of high-level contamination. It has been already recognized that fractional crystallization (FC), crustal assimilation and fractional crystallization (AFC), and mixing processes play an important role in controlling the compositional variation within the CA rocks from the CPR (Mason et al., 1996; Seghedi et al., 2001, 2004).

The range of Pieniny rocks, their quite evolved geochemical characters (Figs. 4 and 5) and occurrence of phenocrysts showing discontinuous zoning in all the samples suggest that FC was an important process in controlling the evolution of these rocks. Nevertheless, Pieniny CA rocks are characterized by unusual geochemical trends in respect to those observed in the CA rocks from the CPR. Relative to these latter, Pieniny volcanic rocks have higher Sr/Y ratio (30–65) and lower Yb concentration (1.7–2.4 ppm) at a given SiO_2 contents and define a distinct trend both in La/Yb vs Yb and Y vs Sr/Y diagrams (Fig. 10).

The high Sr/Y and the low Yb contents of Pieniny CA rocks are very similar to those of the Apuseni CA rocks that have been identified as adakite-like lavas by Seghedi et al. (2004). We discuss later that in spite of these geochemical similarities with Apuseni rocks, other geochemical and the isotopic features of the Pieniny BA rocks suggest that their parental magmas are not adakites-like. However, whatever is the origin of parental Pieniny magmas, it is evident that the Pieniny MKA plot at the extension of Pieniny BA in these diagrams (Fig. 10) suggesting that evolved Pieniny

Table 3
Isotopic data for Mts. Pieniny samples

Sample	$^{87}\text{Sr}/^{86}\text{Sr}$	$^{143}\text{Nd}/^{144}\text{Nd}$	$^{206}\text{Pb}/^{204}\text{Pb}$	$^{207}\text{Pb}/^{204}\text{Pb}$	$^{208}\text{Pb}/^{204}\text{Pb}$
<i>Mt. Wzar</i>					
1st phase					
7S	0.706793±22	0.512300±7	18.821	15.750	39.775
10S	0.705791±17	0.512357±5	18.749	15.688	39.226
2nd phase					
8S	0.705875±17	0.512255±6	18.691	15.701	39.171
99/27	0.706991±19	0.512265±7	18.815	15.742	39.837
<i>Mt. Jarmuta</i>					
99/20	0.705353±19	0.512389±5	18.860	15.663	38.881
99/21	0.705460±19	0.512124±5	18.626	15.669	38.746
<i>Szczawnica</i>					
<i>Mt. Cizowa</i>					
99/22	0.705406±21	0.512114±5	18.624	15.662	38.767

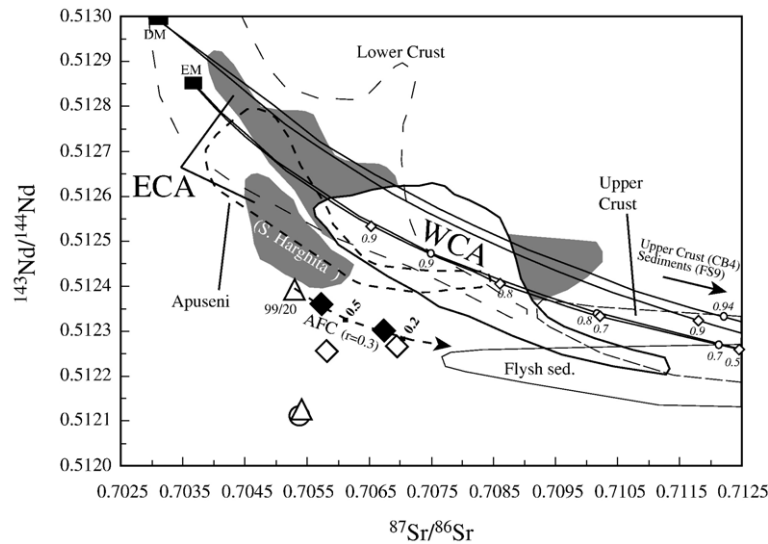


Fig. 8. $^{87}\text{Sr}/^{86}\text{Sr}$ vs $^{143}\text{Nd}/^{144}\text{Nd}$ isotopic composition of Mts. Pieniny samples compared with Carpathian–Pannonian Region calc-alkaline rocks: ECA field (that also include S. Harghita lavas), as Fig. 3; WCA from Salters et al. (1988); Apuseni from Seghedi et al. (2004). Fields for flysh sediments and upper crust from Mason et al. (1996). Field for lower crust from Kempton et al. (1997). End-member compositions used in source bulk mixing calculations are the same of Seghedi et al. (2001). For AFC modelling we assume 30% plagioclase, 40% amphibole, 20% clinopyroxene, 10% titanomagnetite as fractionating mineral assemblage. Partition coefficients used are from Castillo et al. (1999). Symbols as in Fig. 2.

rocks are related to BA through shallow level fractionation processes. Interestingly, the different trends observed in CA rocks from Pieniny and CPR can be attributed to a variable fractionation of different low-pressure phases: amphibole fractionation was important in the evolution of the Pieniny rocks, whereas plagioclase fractionation plays a more important role in the petrogenesis of CPR lavas.

However, FC alone is unable to explain the Sr–Nd–Pb isotope variation observed for the Pieniny rocks. The fact that these rocks passed through continental crust raises the possibility that crustal contamination or mixing produced some of their isotopic and incompatible trace element signatures. To test this possibility we carried out AFC and mixing modelling using the mantle end-members and the East Carpathian upper crustal composition already used by Mason et al. (1996) and Seghedi et al. (2001, 2004) to constrain the petrogenesis of CA rocks from CPR. The AFC curve was calculated using the composition of the least isotopically enriched basaltic andesite (99/20) as hypothetical parental magma, assuming r (ratio of mass assimilation/mass crystallization) = 0.3, and using mineral phases observed in the Pieniny basaltic andesites (amphibole, plagioclase, clinopyroxene and Ti-magnetite) as fractionating phases. The isotope modelling scheme is shown in Fig. 8 where Sr–Nd AFC and bulk mixing lines are plotted. Mixing modelling indicates that it is virtually impossible to model the Pieniny samples with a mixing curve between

upper crust and mid-ocean ridge basalt (MORB)- or ocean–island basalt (OIB)-like mantle source. Yet, AFC modelling failed to produce the isotope compositions of Pieniny MKA and reveals an unrealistic amount of fractional crystallization (90%) to generate the most enriched isotope signature of Pieniny BA.

We conclude that the enriched isotope signature of Pieniny volcanic rocks cannot be primarily due to crustal contamination processes. Obviously, some fractional crystallization must have occurred in the petrogenesis of the Pieniny rocks, but partial melting and source composition were more important than FC and AFC processes in controlling the geochemical and isotopic variation observed within the Pieniny CA rocks.

6.2. Constraining the source of parental lavas in Pieniny Mts

Asthenospheric mantle wedge (MORB and OIB) is an important component in CPR magma petrogenesis (Mason et al., 1996; Seghedi et al., 2004 and references therein), but Pieniny volcanic rocks have isotopic values that preclude a model involving partial melting from a typical MORB or OIB mantle source. Also an asthenospheric mantle source, previously enriched in slab-derived components (melts, fluids), seems unlikely since bulk mixing curves between mantle (MORB and OIB) sources and local sediments do not deviate

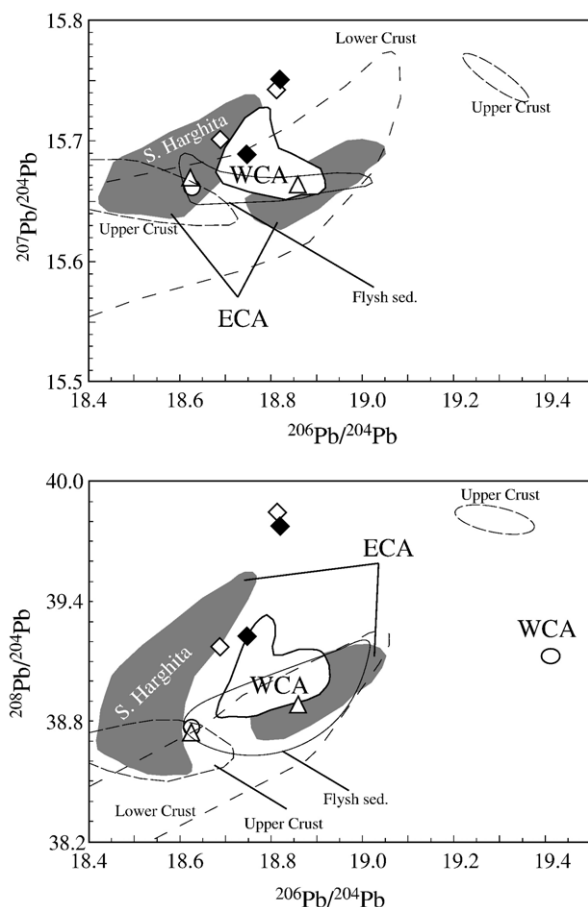


Fig. 9. $^{206}\text{Pb}/^{204}\text{Pb}$ – $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{206}\text{Pb}/^{204}\text{Pb}$ – $^{208}\text{Pb}/^{204}\text{Pb}$ systematics for Mts. Pieniny samples compared with Carpathian–Pannonian Region calc-alkaline rocks. Data sources as in Fig. 8. Symbols as in Fig. 2.

markedly from mantle–upper crust mixing curves (Fig. 8). High LILE/REE and LILE/HFSE ratios similar to those observed in Pieniny BA rocks (i.e., $\text{Pb}/\text{Nd}=0.33\text{--}0.73$; $\text{Ba}/\text{Nb}=46\text{--}82$; $\text{Ba}/\text{Zr}=4\text{--}6$) are usually attributed to mass transfer of fluids from the subducted slab into the overlain mantle wedge (Ishizuka et al., 2003; Vroon et al., 1993; Chesley et al., 2002). Nevertheless, the variation of Ba/Th ratio, extensively used to quantify the “fluid signature” in arc volcanoes (Turner et al., 1996), versus Nd isotopic ratios clearly indicates the presence of a high Ba/Th component distinct from fluid component in the source of Pieniny rocks (Fig. 11).

Models for the source regions of parental magmas of Pieniny BA must account for the distinctive enriched Sr, Nd, Pb isotopic character of these basic rocks. The low $^{143}\text{Nd}/^{144}\text{Nd}$ and high $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{208}\text{Pb}/^{204}\text{Pb}$ ratios observed in the most basic Pieniny BA are not consistent with a derivation exclusively from an asthenospheric source.

Convincing evidence of that comes from the $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{143}\text{Nd}/^{144}\text{Nd}$ vs $^{208}\text{Pb}^*/^{206}\text{Pb}^*$ diagrams (Fig. 12), where the most mafic ($\text{MgO}>3$ wt.%; $\text{SiO}_2<53$ wt.%) CA rocks from Pieniny and CPR have been plotted. Asthenospheric derived magmas (e.g., MORB and many OIB) define an array on these diagrams (e.g., Rogers, 1992). Most of CPR rocks define steeper trends with a shift toward the composition of the upper crust or sediments, in agreement with the observation that source contamination and AFC are important petrogenetic processes for these volcanic rocks (Mason et al., 1996; Seghedi et al., 2001, 2004). By contrast, Pieniny rocks define distinct trends in both these diagrams showing a restricted range in $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{143}\text{Nd}/^{144}\text{Nd}$ ratios and a shift in $^{208}\text{Pb}^*/^{206}\text{Pb}^*$. These trends result very similar to those expected for lavas derived from a lithospheric mantle source region (Rogers, 1992) and suggest that the fractionation of parent/daughter trace element ratios (e.g., Th/U , Rb/Sr , Sm/Nd) in the Pieniny basic rocks can be inherited from their enriched lithospheric mantle source. The age of this lithospheric mantle source can be partially constrained by the isotope data. Indeed, Sr and Nd isotope variations in the Pieniny basic rocks reflect similar model ages (T_{DM} range from 1.1 to 1.2 Ga for Nd and from 0.9 to 1.2 Ga for Sr), based on a depleted mantle source and measured Rb/Sr and Sm/Nd ratios in these lavas. Furthermore, if an age of 1.1 Ga is applied to Th/U fractionation, assuming evolution from a second-stage depleted precursor (following Stacey and Kramers, 1975), the elevated $^{208}\text{Pb}/^{204}\text{Pb}$ ratios of the less differentiated Pieniny BA rocks (i.e., 7S and 99/27) require a source $^{232}\text{Th}/^{238}\text{U}$ ratio of 3.7, that is close to the value of 3.78 required by the Stacey and Kramers model for the depleted precursor.

Thus, radiogenic isotope ratios of Pieniny BA rocks are consistent with a derivation of their parental magmas from a metasomatized subcontinental lithospheric mantle source that was isolated >1.1 Ga (minimum T_{DM}) before the partial melting event that led to their formation occurred.

Relative to Pieniny BA rocks, the Pieniny MKA samples have older and restricted Nd isotopic T_{DM} age of 1.3 Ga. This suggests that parental magmas of these evolved rocks have originated from an older (>1.3 Ga) portion of the metasomatized subcontinental lithospheric mantle.

We already observed that Pieniny rocks have geochemical features very similar to the adakite-like lavas in the Mts Apuseni. According to Defant and Drummond (1990), adakites are subduction-related rocks of andesitic-dacitic to sodic rhyolitic compositions derived by partial melting of hydrated mafic source

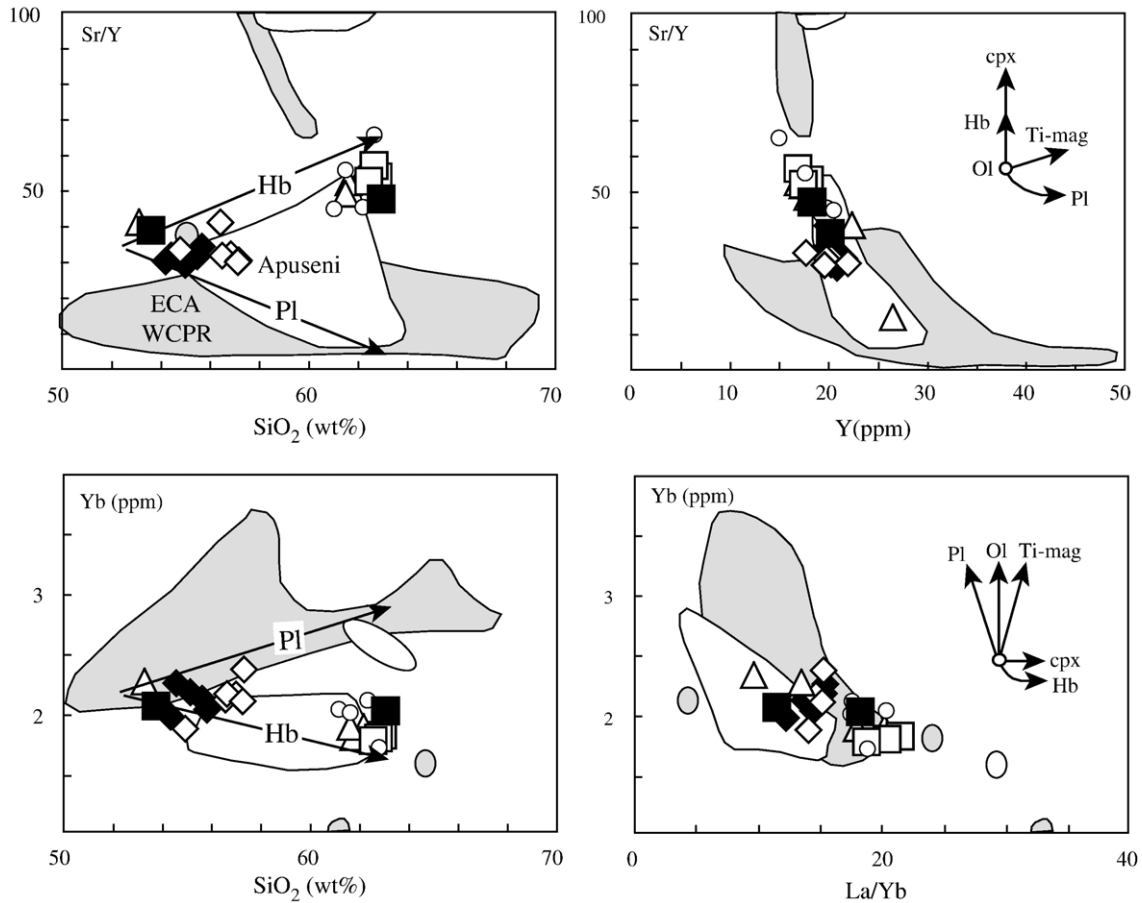


Fig. 10. Sr/Y vs SiO_2 and Y, and Yb vs SiO_2 and La/Yb for Mts. Pieniny samples. Data sources as in Fig. 3. Crystal fractionation paths of primary minerals are from Castillo et al. (1999). See text for further discussion.

rocks in the form of eclogite or garnet amphibolite. This melting may occur either in the basaltic crust of the downgoing oceanic slab or at the base of crust above the mantle wedge (Defant and Drummond, 1990; Kay and Kay, 1993). Alternatively, some rocks with adakitic compositional features have been considered to originate by AFC processes involving basaltic magmas (Castillo et al., 1999).

None of the Pieniny rocks classify as adakites, since their LREE/HREE fractionation is not sufficiently strong and their Y and Yb contents are not as low as those of proper adakites ($\text{La}/\text{Yb} > 20$, $\text{Y} < 18$ and $\text{Yb} < 1.9$ ppm in adakites; see Samaniego et al. (2002) and references therein). Furthermore, we have already discussed the impossibility to explain the isotopic signatures of Pieniny rocks through AFC processes. Finally, radiogenic enriched Sr–Nd–Pb isotope compositions of Pieniny rocks exclude melting of oceanic crust (or lower crust) material to have played a role in the petrogenesis of their parental

magmas (Figs. 8 and 9). An old lithosphere seems therefore the most likely source for the parental magmas of Pieniny rocks.

6.3. Source region mineralogy

The high abundances of Sr (from 600 up to 1000 ppm) in Pieniny BA samples and the lack of significant Eu anomalies indicate that the source was plagioclase free and therefore probably located in the mantle. Furthermore, the formation of parental Pieniny magmas by variable partial melting of garnet bearing source is precluded by the small range (from 11 up to 15) of La/Yb ratio in Pieniny BA rocks (Fig. 11). Yet, the degree of LREE enrichment is uncorrelated with $\text{Mg}_{\#}$ ($\text{Mg}_{\#} = \text{Mg}/(\text{Mg} + \text{Fe}^{2+})$, with $\text{Fe}^{3+}/\text{Fe}^{2+}$ as suggested by Middlemost, 1989). In fact, some of the highest $\text{Mg}_{\#}$ Pieniny rocks have the highest La/Yb (Fig. 11) again suggesting that partial melting and regional source variations exerted the dominant

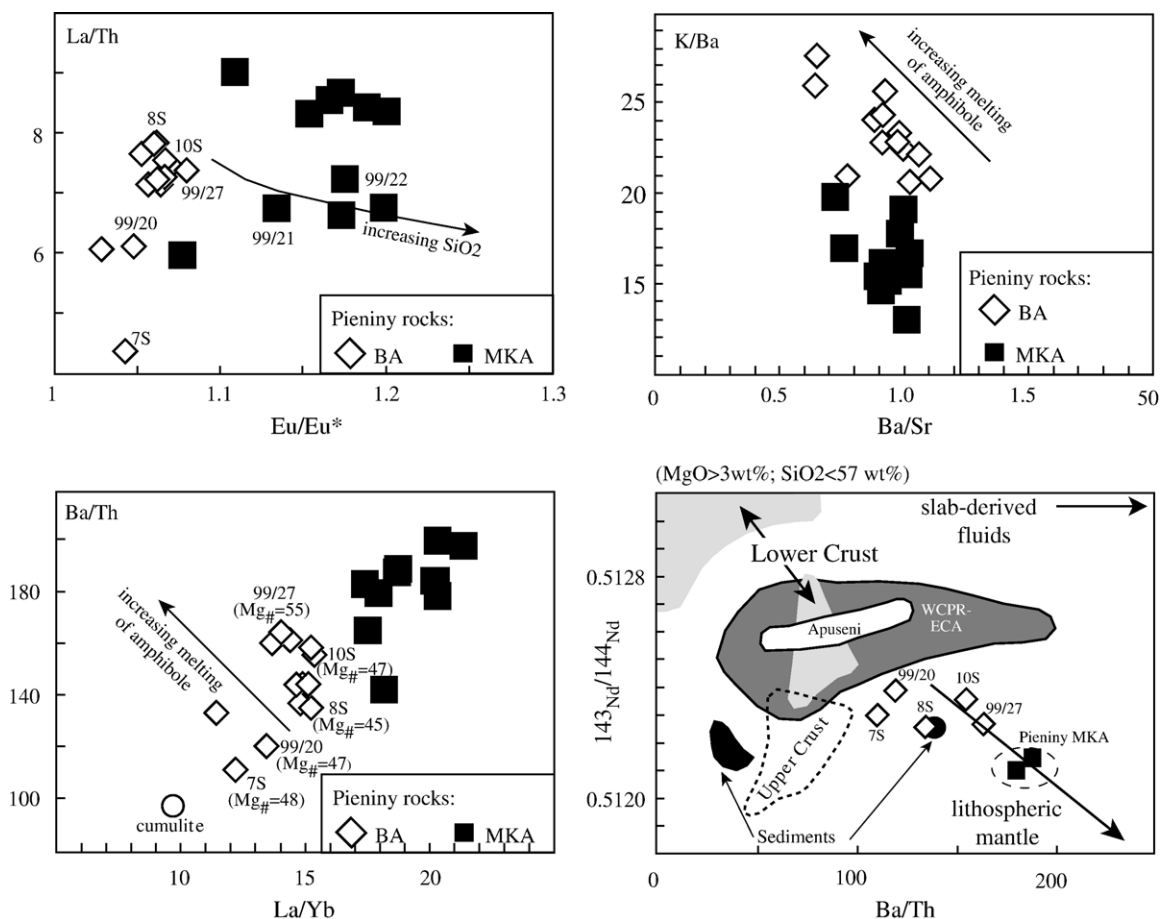


Fig. 11. Selected trace element ratios and $^{143}\text{Nd}/^{144}\text{Nd}$ ratios used to identify the source region mineralogy of Mt. Pieniny rocks. Signed samples as in Fig. 4. Partial melting arrows of amphibole are shown for reference. They have been obtained by using: amphibole composition from Dalpé and Baker (2000) and Brenan et al. (1995a) (only for Th); distribution coefficients from Brenan et al. (1995b) and Adam et al. (1993) (only for La). Slab derived fluid component in $^{143}\text{Nd}/^{144}\text{Nd}$ vs Ba/Th diagram is from Ishizuka et al. (2003). BA = basaltic andesites; MKA = medium-K andesites. See text for further discussion.

control on the trace element variability within Pieniny magmas.

The relatively high $\text{Na}_2\text{O}/\text{K}_2\text{O}$ (1.9–2.4) and low Rb/Sr (0.06–0.09) ratios in Pieniny BA rocks and their hydrous oxidizing mineralogy are consistent with hydrous minerals (amphibole, phlogopite) being present in their mantle source. Although the exact mineralogy of such source cannot be unambiguously estimated from geochemical parameters, we can argue that amphibole, rather than phlogopite, is present during partial melting of the Pieniny mantle source. This conclusion is based on the observation that melts in equilibrium with phlogopite (see Furman and Graham, 1999) are expected to have higher Rb/Sr (>0.1) and Rb/Ba (>0.7) ratios than those observed in Pieniny BA rocks. Additional support for the presence of stable amphibole in the mantle source of parental Pieniny magmas is

confirmed by selected useful trace element ratios (Fig. 11). The already observed variation of the Ba/Th ratio among the Pieniny BA rocks could be explained with the presence during partial melting of the source of mineral phase that preferentially retains Ba over Th, most likely amphibole. Moreover, the distinct trends that these basic rocks define in Fig. 11 cannot result from a single source but require involvement of a heterogeneous source in term of amphibole abundance.

A veined mantle lithosphere seems the more likely source to explain the geochemical and isotopic characteristics of Pieniny rocks. The ancient (>1.1 Ga) subduction-related enrichments, deduced by isotopic data, might have resulted in amphibole-bearing pyroxenite veins in a wall-rock peridotite. Moreover, the identification of different Nd isotopic T_{DM} ages for Pieniny BA and MKA implies that metasomatic events

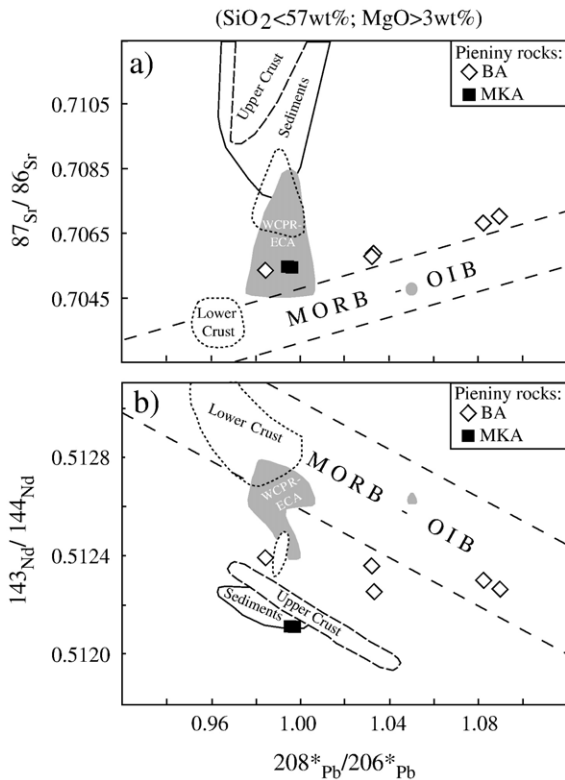


Fig. 12. $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{143}\text{Nd}/^{144}\text{Nd}$ vs $^{208}\text{Pb}^*/^{206}\text{Pb}^*$ for Mts. Pieniny samples. MORB–OIB field from Rogers (1992). BA = basaltic andesites; MKA = medium-K andesites. See text for further discussion.

occurred at different times in the lithospheric mantle of this region. The veins could have been imported with the incompatible element features observed in Pieniny BA rocks and, with time, developed the radiogenic isotopic signatures observed in the Pieniny BA or in MKA rocks. Melting of these veins would form the parental magmas of Pieniny rocks, which although erupted through continental crust, preserved the original lithospheric Sr–Nd–Pb isotope signature. Obviously, these isotopically different Pieniny parental magmas have been subsequently affected by fractional crystallization to generate the Pieniny rocks. However, it is difficult to model the fractional crystallization process because primitive basalts that can be used as parental compositions for the Pieniny rocks are lacking.

6.4. Geodynamic implications

Since Early Miocene, the CPR was affected by a complex tectonic regime (Sperner et al., 2002; Seghedi et al., 2004 and references therein). During that time, the

subduction of a land-locked basin started generating the convergence of two continental fragments with the European foreland. The collision with the European continental margin occurred firstly in the area of the present-day Western Carpathian Arc, about 16 Ma ago. Then, a change in the direction of subduction occurred, from southwestward to northeastward and finally eastward, leading to an oblique closure of the basin and a progressive change of subduction to collision eastward along the Carpathian Arc. The end of collision occurred during the Pannonian (11.5–6.2 Ma) in the southeastern corner of the Carpathian Arc. Distribution of the Neogene–Quaternary CA magmatism within the CPR is directly related in space and time to the complex tectonic processes affecting this area in that time: subduction, collision, post-collision and extension (Nemčok et al., 1998a,b; Seghedi et al., 1998, 2004). Several authors agree that this CA magmatism is related to melting of a heterogeneous asthenospheric mantle source modified by addition of fluids and sediment (see Seghedi et al., 2004 and references therein). Petrogenetic modeling of trace elements and isotopic ratios suggests that the source of the Mts Pieniny CA rocks cannot be the asthenospheric metasomatized mantle wedge. Rather, these rocks appear to be a product of a metasomatized lithospheric mantle. The Middle Miocene lithospheric mantle delamination of the European plate occurred below the WCP (Seghedi et al., 1998; Sperner et al., 2002), where lithospheric root is lacking, represents a key element to resolve the apparently enigmatic origin of the Mts Pieniny magmatism. The delamination process probably favoured upwelling of younger asthenospheric material, which replaced a part of the removed oceanic lithospheric root. When the hotter asthenospheric material rose, it impinged upon the mantle lithosphere of the northern part of the overriding Alcapa micro-plate, which can be geologically correlated to the Austroalpine units (Sperner et al., 2002). The resulting thermal perturbation induced melting of domains within the mantle lithosphere that were metasomatized and hydrated during ancient (>1.1 Ga) subduction-related events, generating the parental magmas of Pieniny BA rocks.

7. Summary and conclusions

The petrochemical features of the Pieniny CA rocks shed new light on the genesis of the outermost post-collisional volcanic arc of the Carpathian orogen. These rocks, which range from BA to MKA in composition, have an arc signature similar to that observed in the Neogene–Quaternary CA rocks erupted on the nearby

CPR. Nevertheless, trace elements and Sr–Nd–Pb isotopic data of Pieniny CA rocks suggest a petrogenetic scenario different from that of these latter. Their isotopic ratios and certain features of trace element systematic require a petrogenetic model involving partial melting of amphibole-bearing pyroxenite veins located in the ancient metasomatized lithospheric mantle. We suggest that the partial melting process was triggered by the flux of heat coming from the rising asthenospheric material once the delamination of the subducting European oceanic plate occurred in this sector of the CPR.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.lithos.2006.01.001](https://doi.org/10.1016/j.lithos.2006.01.001).

References

- Adam, J., Green, T.H., Sie, S.H., 1993. Proton microprobe determined partitioning of Rb, Sr, Ba, Y, Zr, Nb and Ta between experimentally produced amphiboles and silicate melts with variable F content. *Chem. Geol.* 109, 29–49.
- Birkenmajer, K., 1983. Strike-slip faults in the northern boundary zone of the Pieniny Klippen Belt, Carpathians. *Stud. Geol. Pol.* 77, 89–112.
- Birkenmajer, K., 1984. Interrelation of Neogene tectonics and volcanism in the Pieniny Klippen Belt of Poland. *Acta Geod. Geophys. Montan. Hung.* 19, 37–48.
- Birkenmajer, K., 1986. Stages of structural evolution of the Pieniny Klippen Belt, Carpathians. *Stud. Geol. Pol.* 88, 7–32.
- Birkenmajer, K., Pécskay, Z., 1999. K–Ar dating of the Miocene andesite intrusions, Pieniny Mts, West Carpathians. *Bull. Pol. Acad. Sci., Earth Sci.* 47, 155–169.
- Birkenmajer, K., Pécskay, Z., 2000. K–Ar dating of the Miocene andesite intrusions, Pieniny Mts, West Carpathians, Poland: a supplement. *Stud. Geol. Pol.* 117, 7–25.
- Brenan, J.M., Shaw, H.F., Ryerson, F.J., Phinney, D.L., 1995a. Mineral–aqueous fluid partitioning of trace elements at 900 °C and 2.0 Gpa: constraints on the trace element chemistry of mantle and deep crustal fluids. *Geochim. Cosmochim. Acta* 59, 3331–3350.
- Brenan, J.M., Shaw, H.F., Ryerson, F.J., Phinney, D.L., 1995b. Experimental determination of trace-element partitioning between pargasite and a synthetic hydrous andesitic melt. *Earth Planet. Sci. Lett.* 135, 1–11.
- Castillo, P.R., Janney, P.E., Solidum, R.U., 1999. Petrology and geochemistry of Camiguin Island, southern Philippines: insights to the source of adakites and other lavas in a complex arc setting. *Contrib. Mineral. Petrol.* 134, 33–51.
- Chesley, J., Ruiz, J., Righter, K., Ferrari, L., Gomez-Tuena, A., 2002. Source contamination versus assimilation: an example from the Trans-Mexican Volcanic Arc. *Earth Planet. Sci. Lett.* 195, 211–221.
- Dalpé, C., Baker, D.R., 2000. Experimental investigation of large-ion-lithophile-element-, high-field-strength-element- and rare-earth-element-partitioning between calcic amphibole and basaltic melt: the effects of pressure and oxygen fugacity. *Contrib. Mineral. Petrol.* 140, 233–250.
- Deer, W.A., Howie, R.A., Zussman, J., 1997. *Rock-forming minerals: double-chain silicates*. The Geological Society of London. Published by. 764 pp.
- Defant, M.J., Drummond, M.S., 1990. Derivation of some modern arc magmas by melting of young subducted lithosphere. *Nature* 347, 662–665.
- Downes, H., Pantó, G., Póka, T., Matthey, 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.
- Furman, T., Graham, D., 1999. Erosion of lithospheric mantle beneath the East African Rift system: geochemical evidence from the Kivu volcanic province. *Lithos* 48, 237–262.
- Ishizuka, O., Taylor, R.N., Milton, J.A., Nesbitt, R.W., 2003. Fluid–mantle interaction in an intra-oceanic arc: constraints from high-precision Pb isotopes. *Earth Planet. Sci. Lett.* 211, 221–236.
- Kardymowicz, I., 1957. Inclusions in the andesites of the Pieniny region (in Polish, English summary) *Biul. Inst. Geol. (Warszawa)* 117–152.
- Kay, R.W., Kay, S.M., 1993. Delamination and delamination magmatism. *Tectonophysics* 219, 177–189.
- Kempton, P.D., Downes, H., Embey-Isztin, A., 1997. Mafic granulite xenoliths in Neogene alkali basalts from the Western Pannonian Basin: insights into the lower crust of a collapsed orogen. *J. Petrol.* 38, 941–970.
- Le Maitre, R.W., 1989. A classification of Igneous Rocks and Glossary of Terms. In: Le Maitre, R.W. (Ed.), *Recommendations of the International Union of Geological Sciences, Subcommittee on Systematics of Igneous Rocks*. Blackwell Sci. Publ. 193 pp.
- Malkowski, S., 1921. Les andesites des environs de Piénines. *Trav. Sér. Géol. Pol.* 1, 3–67.
- Malkowski, S., 1958. Volcanic processes in the geologic history of the Pieniny Mts area. *Pr. Muz. Ziemi (Warszawa)* 1, 11–55.
- Mason, P.R.D., Downes, H., Thirlwall, M.F., Seghedi, I., Szakács, A., Lowry, D., Matthey, D., 1996. Crystal assimilation as a major petrogenetic process in the East Carpathian Neogene and Quaternary Continental Margin Arc, Romania. *J. Petrol.* 37, 927–959.
- Middlemost, E.A.K., 1989. Iron oxidation ratios, norms and the classification of volcanic rocks. *Chem. Geol.* 77, 19–26.
- Morimoto, N., 1988. Nomenclature of pyroxenes. *Mineral. Petrol.* 39, 55–76.
- Nemčok, H., Kovac, P., Marko, F., Coward, M.P., Madaras, J., Houghton, J.J., Bezak, V., 1998a. Tertiary extension development and extension/compression interplay in the West Carpathian mountain belt. *Tectonophysics* 290, 137–167.
- Nemčok, M., Pospisil, L., Lexa, J., Donelick, R.A., 1998b. Tertiary subduction and slab break-off model of the Carpathian–Pannonian region. *Tectonophysics* 295, 307–340.

- Peccerillo, A., Taylor, S.R., 1976. Geochemistry of Eocene calc-alkaline volcanic rocks from the Kastamonu area, northern Turkey. *Contr. Mineral. Petrol.* 58, 63–81.
- Rogers, N.W., 1992. Potassic magmatism as a key to trace-element enrichment processes in the upper mantle. *J. Volcanol. Geotherm. Res.* 50, 85–99.
- Salters, V.J.M., Hart, S.R., Pantó, G., 1988. Origin of late cenozoic volcanic rocks of the Carpathian arc, Hungary. In: Royden, L., Horvath, F. (Eds.), *The Pannonian Basin: a Study in Basin Evolution*. AAPG Memoir, vol. 45, pp. 279–292.
- Samaniego, P., Martin, H., Robin, C., Monzier, M., 2002. Transition from calc-alkalic to adakitic magmatism at Cayambe volcano, Ecuador: insights into slab melts and mantle wedge interactions. *Geology* 30, 967–970.
- Seghedi, I., Balintoni, I., Szakács, A., 1998. Interplay of tectonics and Neogene post-collisional magmatism in the Intercarpathian region. *Lithos* 45, 483–497.
- Seghedi, I., Downes, H., Pécskay, Z., Thirwall, M.F., Szakács, A., Prychodko, M., Matthey, D., 2001. Magmagenesis in a subduction-related post-collisional volcanic arc segment: the Ukrainian Carpathians. *Lithos* 57, 237–262.
- Seghedi, I., Downes, H., Szakács, A., Mason, P.R.D., Thirwall, M.F., Rosu, E., Pécskay, Z., Márton, E., Panaiotu, C., 2004. Neogene–Quaternary magmatism and geodynamics in the Carpathian–Pannonian region: a synthesis. *Lithos* 72, 117–146.
- Sperner, B., Ratschbacher, L., Nemčok, M., 2002. Interplay between subduction retreat and lateral extrusion: tectonics of the Western Carpathians. *Tectonics* 21 (6), 1051. doi:10.1029/2001TC901028.
- Stacey, J.S., Kramers, J.D., 1975. Approximation of terrestrial lead isotope evolution by a two-stage model. *Earth Planet. Sci. Lett.* 26, 207–221.
- Sun, S.S., McDonough, W.F., 1989. In: Saunders, A.D., Norry, M.J. (Eds.), *Magmatism in the Ocean Basins*. Geol. Soc. Lond., Spec. Publ., vol. 42, pp. 313–345.
- Turner, S., Hawkesworth, C., van Calsteren, P., Heath, E., Macdonald, R., Black, S., 1996. U-series isotopes and destructive plate margin magma genesis in the Lesser Antilles. *Earth Planet. Sci. Lett.* 142, 191–207.
- Vroon, P.Z., van Bergen, M.J., White, W.M., Varekamp, J.C., 1993. Sr–Nd–Pb isotope systematics of the Banda Arc, Indonesia: combined subduction and assimilation of continental material. *J. Geophys. Res.* 98, 22349–22366.
- Wortel, M.J.R., Sparkman, W., 2000. Subduction and slab detachment in the Mediterranean–Carpathian region. *Science* 290, 1910–1917.
- Youssef, M.M.M., 1978. Large-scale geological survey of the Mt. Wzar andesites, Pieniny Mts., Poland, vol. LVI. *Polska Akademia Nauk*, pp. 1–30.