

Geochemical Characteristics of Basaltic Andesites from Baranja (Croatia, Yugoslavia)

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Miocene basaltic andesites from Baranja are composed of plagioclase (An_{61-42}), augite ($Mg\# = 77.5-71.5$) or titanian augite/titanian hedenbergite ($Mg\# = 38.3-30.8$), olivine ($Mg = 85.1-62.3$), titanian magnetite and apatite. Olivine phenocrysts are cumulate grains in the rock samples containing exceptional high Ni. Titanium-rich clinopyroxene phenocrysts are not in equilibrium with their host lava and show chemical features similar to clinopyroxenes accommodated in alkaline volcanics from within-plate setting. On the contrary, bulk rock chemical composition is typical of calc-alkaline volcanic rocks from destructive plate boundaries. Such a geochemical characteristics are not surprising for the volcanic rocks generated in a post-subduction continental back-arc basin.

1. Introduction

Between the towns of Beli Manastir and Batina in Baranja (Eastern Croatia, near Hungarian border) extrusive and pyroclastic rocks crop out under a cover of loess deposits. The best outcrops are found in the area of the village of Popovac and in the vicinity of Batina. Petrographic descriptions and chemical analyses of these rocks were already given by Mauritz (1920) and Golub (1957) and these authors classified the rocks as basalt-andesite. Additional geological and geochemical data were given in a recent paper by Pamić and Pikija (1987). These authors concluded that the rocks are basic andesites and were extruded in Miocene (Badenian) time as »a result of geodynamic processes connected with post-subduction uplift of upper mantle in the basement of the Pannonian basin«.

Although the previous papers on these extrusives give valuable data and petrogenetic interpretations, we collected new samples with the intention to give more reliable data, especially on mineral compositions which still have been missing. Five of the freshest samples of our collection which represent extruded melt were selected for major and trace element chemical analyses and three of them for microprobe analysis of minerals. The petrological meaning of these data will be discussed and possible geodynamic implications will be given. We will show that significant differences in geochemical character exist between the Batina-Beli Manastir volcanics on the one hand and basic to intermediate volcanics of

Ključne riječi: Baranja, Panonski bazen, kalcijsko-alkalijski bazalni andeziti, kemijski sastav minerala, poslije subdukcijski kontinentalni rubni bazen

Miocenski bazalni andeziti Baranje sastoje se od plagioklasa (61–42% An), augita ($Mg\# = 77,5-71,5$) ili titanskog augita/titanskog hedenbergita ($Mg\# = 38,3-30,8$), olivina ($Mg\# = 85,1-62,3$), titanskog magnetita i apatita. U uzorcima stijena s visokim sadržajem nikla utrusci su olivina kumulatnog porijekla. Titanom bogati utrusci augita/hedenbergita nisu u ravnoteži s taljevinom predstavljenom intergranularnom osnovom stijena. Kemijski je sastav ovih utrusaka sličan onom kojeg imaju monoklinski pirokseni sadržani u kontinentalnim alkalijskim »within-plate« efuzivima. Nasuprot, analizirane stijene imaju kemijski sastav kojim se inače odlikuju kalcijsko-alkalijski efuzivi razaralačkih rubova ploča. Ovakve ukupne geokemijske osobine uobičajene su u vulkanskim stijenama nastalim u poslije subdukcijskim kontinentalnim rubnim (»back-arc«) bazenima.

Cenozoic age from Mts. Papuk and Krndija in Slavonia (Tajder, 1956; Golub and Marić, 1968; Lugović, 1983) and those from Bár in the Hungarian part of Baranja (Szederkényi, 1980) on the other hand.

2. Geology and Petrography

Golub (1957) assumed that the extrusives which crop out between Beli Manastir and Batina form a single sheet-like body extending for about 20 km in length and 1 to 2 km in width. What we could see exposed on the surface is a few outcrops of extrusives overlain by loess of Upper Pleistocene age (Takšić, 1947). Near the village of Popovac some dikes occur cutting sedimentary rocks of Badenian age (Pamić and Pikija, 1987). On the basis of this field relationship and two K-Ar dates on one of the dikes (14.5 Ma) and on an irregular extrusive body in cold contact with Badenian sediments (13.8 Ma) Pamić and Pikija (1987) concluded that the volcanic rocks are of Badenian age. The same age is quoted by these authors for pyroclastic rocks (volcanic breccias) which are widespread near Batina. However, a younger (Lower Pannonian) age for these volcanics was deduced by Lóczy (1914).

Samples investigated show holocrystalline porphyritic texture. Plagioclase with glassy and cryptocrystalline inclusions, fresh or altered (iddingsite) olivine, and rare clinopyroxene are the phenocrysts which are embedded in an intergranular groundmass of

plagioclase, clinopyroxene, Ti-magnetite and apatite. Phenocryst clusters which are a common characteristic of extrusive rock fragments incorporated in volcanic breccias (sample BB-2A; Table 5) were not observed in the lava samples (BP-1, BP-3, BP-6, BP-T; Table 5). The lavas frequently contain xenoliths of thermally metamorphosed sediments. One xenolith found in sample BP-6, for example, has the assemblage plagioclase + spinel + sillimanite + olivine. Similar xenoliths with spinel, sillimanite, vesuvianite, plagioclase, and apatite were already mentioned by Golub (1957).

3. Mineral Chemistry

3.1. Olivine

Chemical analyses of phenocrystic olivine are given in Table 1. Individual grains show fairly uniform compositions with only minor Fe enrichment towards the rims. The core Mg# (= Mg-number = $100 \cdot \text{mol. Mg}/(\text{Mg} + \text{Fe}^{2+})$) of the individual olivine grains in sample BP-3 ranges from 72.8 to 62.3 giving a mean value of 67.0 ($n=5$) which is close to the average core Mg# of olivine in sample BP-6 (69.5). A significantly higher average Mg# of 85.1 (cores and rims) was obtained on olivines of sample BB-2A representing a lava fragment within a volcanic breccia.

Table 1. Selected microprobe analyses of olivines

Sample	BP-3	BP-3	BP-3	BP-6	BP-6	BB-2A	BB-2A	BB-2A
	1(c)	1(r)	2(c)	3(c)	3(r)	4(c)	5(r)	5(c)
SiO ₂	37.62	37.83	36.48	37.34	36.91	39.61	39.05	38.93
FeO	24.78	24.85	32.71	27.33	30.26	14.86	14.18	14.16
MnO	.43	.39	.52	.38	.49	.13	.36	.24
MgO	37.16	36.94	30.30	34.95	32.34	45.40	46.40	46.67
Number of cations on the basis of 4 oxygens								
Si	.992	.997	1.000	.996	.999	.994	.980	.976
Fe ²⁺	.546	.547	.750	.610	.685	.312	.298	.297
Mn	.010	.009	.012	.009	.011	.003	.008	.005
Mg	1.460	1.451	1.238	1.390	1.305	1.698	1.735	1.745
	3.008	3.004	3.000	3.005	3.000	3.007	3.021	3.023
Mg#	72.8	72.6	62.3	69.5	65.6	84.5	85.4	85.5

Mg# = Mg-number = $100 \cdot \text{mol. Mg}/(\text{Mg} + \text{Fe}^{2+})$. Analysis number corresponds to the individual grain; (c) = core; (r) = rim. Analyses are recalculated to 100 weight % after formula calculation.

3.2. Clinopyroxene

Microprobe analyses of clinopyroxenes are given in Table 2. Clinopyroxenes from samples BP-3 and BP-6 are fairly homogeneous and show very similar compositions. Mg#, for example, range from 77.7 to 71.5 and from 75.1 to 72.5, respectively. These values contrast markedly to those obtained for the clinopyroxenes of sample BB-2A which are significantly lower (38.8–30.8). Furthermore, the clinopyroxenes of this sample are extremely rich in Ti and relatively rich in Al and Na (Table 2).

All clinopyroxenes belong to the Quad or Ca-Mg-Fe pyroxene group of Morimoto (1988). As can be seen from Fig. 1 clinopyroxenes of samples BP-2 and BP-6 are classified as augites, whereas the phenocrysts of sample BB-2A are titanian augites to titanian hedenbergites.

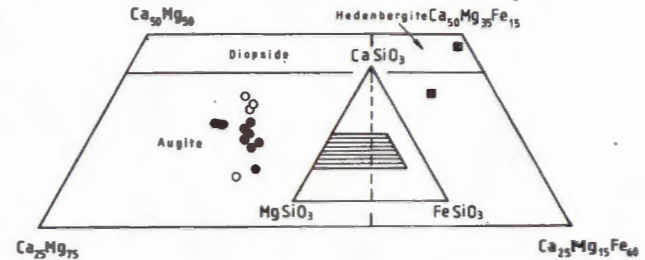


Fig. 1. Pyroxene compositions of Baranja basaltic andesites plotted in the Ca-Mg-Fe diagram of Morimoto (1988). Solid circles = BP-3; open circles = BP-6; solid squares = BB-2A.

3.3. Plagioclase

Analyses of both phenocrystic and groundmass plagioclase are given in Table 3. Anorthite contents of plagioclase from samples BP-3 and BP-6 range from about 61 (phenocryst cores) to about 42 (groundmass grains). In contrast to the lava samples, sample BB-2A shows nearly homogeneous plagioclase compositions. As can be seen from Table 2, there are no significant differences in anorthite contents between either phenocryst cores and rims or between phenocrysts and groundmass plagioclase for this sample.

3.4. Spinel in Metamorphic Xenolith

One of the spinel grains clustered in the inner part of a metasedimentary xenolith in sample BP-6 was analyzed (Table 4). The spinel grain shows a relatively uniform composition. The average R₁ site occupancy by Mg is 60% and the average R₂ occupancy by Al is 98%, typical for pleonast (Deer et al., 1962).

4. Bulk Rock Chemistry

Bulk rock chemical analyses are given in Table 5. The rocks generally show a basaltic andesite composition (Fig. 2). Three of the samples (BP-3, BP-6, BP-T) have a fairly uniform composition. Relative to these three samples, sample BP-1 shows higher Al₂O₃ and CaO but lower K₂O, total Fe and MgO. Sample BB-2A is also rich in CaO but poor in K₂O.

CIPW norms (not given in table) were calculated on a volatile-free basis (normalized to 100 wt.%) and assuming that total Fe is FeO. Normative anorthite ranges from 43.1 to 49.5 and the colour index lies between 22.4 to 31.0. All rocks are Q-normative with an average value of 3.1. The samples BP-1 and BB-2A show relatively high di (10.6–13.0) and hy (8.2–14.8); the other three samples are low in di (1.6–2.8) but high in hy (22.0–22.1).

The concentrations of the compatible elements Cr and Ni are variably high and do not correlate with

Table 2. Microprobe analyses of clinopyroxenes

Sample	BP-3	BP-3	BP-3	BP-3	BP-3	BP-3	BP-3	BP-3	Sample	BP-3	BP-6	BP-6	BP-6	BP-6	BB-2A	BB-2A
	1(c)	2(c)	3(c)	4(c)	4(r)	5(c)	5(r)	6(c)		7(c)	8(c)	9(c)	10(c)	11(c)	12(c)	13(c)
SiO ₂	52.54	54.11	50.86	50.33	50.62	51.20	51.28	50.75	SiO ₂	51.32	51.99	52.90	51.77	52.17	45.45	47.69
TiO ₂	1.60	.95	1.95	1.76	1.63	1.46	1.21	1.62	TiO ₂	1.51	1.23	.84	1.10	1.22	5.99	5.51
Al ₂ O ₃	2.28	1.49	2.75	2.22	2.20	1.69	1.69	1.82	Al ₂ O ₃	1.50	1.63	.90	1.62	1.59	4.12	5.36
Cr ₂ O ₃	.16	.04	.25	n.d.	n.d.	n.d.	n.d.	n.d.	Cr ₂ O ₃	n.d.	.14	.14	.08	.10	n.d.	n.d.
Fe ₂ O ₃	.00	.00	.28	2.47	2.56	1.45	2.12	2.46	Fe ₂ O ₃	1.55	.40	.50	1.17	.00	.00	.00
FeO	8.18	8.25	9.76	8.93	8.74	10.83	9.93	8.47	FeO	11.59	8.69	11.38	8.77	9.73	19.08	17.31
MnO	.25	.30	.34	n.d.	n.d.	n.d.	n.d.	n.d.	MnO	n.d.	.27	.36	.36	.32	n.d.	n.d.
MgO	16.29	16.23	15.46	15.91	16.12	15.58	16.17	15.64	MgO	16.34	15.16	17.53	15.12	14.86	6.64	4.32
CaO	18.33	18.21	17.92	18.09	17.74	17.44	17.27	18.90	CaO	15.81	20.18	15.57	19.67	19.73	17.68	18.29
Na ₂ O	.37	.43	.42	.28	.39	.34	.33	.35	Na ₂ O	.38	.31	.23	.35	.28	1.03	1.52
Number of cations on the basis of 6 oxygens and 4 cations									Number of cations on the basis of 6 oxygens and 4 cations							
Si	1.934	1.985	1.893	1.877	1.884	1.914	1.911	1.893	Si	1.917	1.933	1.961	1.929	1.943	1.782	1.845
Al ^{IV}	.066	.015	.107	.098	.097	.074	.074	.080	Al ^{IV}	.066	.067	.039	.071	.057	.190	.155
T	2.000	2.000	2.000	1.975	1.981	1.988	1.985	1.973	T	1.983	2.000	2.000	2.000	2.000	1.972	2.000
Al ^{VI}	.032	.049	.013	.000	.000	.000	.000	.000	Al ^{VI}	.000	.005	.000	.000	.013	.000	.089
Fe ³⁺	.000	.000	.008	.069	.072	.041	.059	.069	Fe ³⁺	.044	.011	.004	.033	.000	.000	.000
Cr	.005	.001	.007	-	-	-	-	-	Cr	-	.004	.004	.002	.003	-	-
Ti	.044	.026	.055	.049	.046	.041	.034	.046	Ti	.042	.034	.023	.031	.034	.177	.160
Mg	.894	.887	.858	.885	.894	.868	.899	.869	Mg	.910	.840	.969	.840	.825	.388	.249
Fe ²⁺	.252	.253	.304	.279	.272	.339	.310	.264	Fe ²⁺	.362	.270	.353	.273	.303	.626	.560
Mn	.008	.009	.011	-	-	-	-	-	Mn	-	.009	.011	.011	.010	-	-
Ca	.723	.715	.714	.723	.707	.698	.689	.755	Ca	.632	.804	.618	.785	.787	.743	.758
Na	.026	.031	.030	.020	.028	.025	.024	.025	Na	.027	.022	.017	.025	.020	.078	.114
M	1.984	1.971	2.000	2.025	2.019	2.012	2.015	2.028	M	2.017	1.999	1.999	2.000	1.995	2.012	1.930
Mg#	77.5	77.2	73.2	76.1	76.7	72.0	74.4	76.7	Mg#	71.5	75.1	72.7	74.7	72.5	38.3	30.8

Table 3. Selected microprobe analyses of plagioclases

Sample	BP-3	BP-3	BP-3	BP-3	BP-6	BB-2A	BB-2A	BB-2A
	1(g)	2(c)	2(r)	3(c)	4(c)	5(g)	6(c)	6(r)
SiO ₂	57.19	55.08	54.39	52.69	56.57	55.85	55.61	55.95
Al ₂ O ₃	27.21	29.06	29.65	30.12	26.85	26.62	27.57	27.21
Fe ₂ O ₃	.98	.36	.16	.35	.40	.57	.63	.57
CaO	7.92	10.06	10.55	12.16	9.82	12.49	11.61	11.29
Na ₂ O	6.30	5.14	5.02	4.43	5.98	4.47	4.59	4.98
K ₂ O	.40	.30	.23	.25	.38	n.d.	n.d.	n.d.
Number of cations on the basis of 8 oxygens								
Si	2.564	2.477	2.449	2.388	2.548	2.523	2.506	2.521
Al	1.438	1.540	1.573	1.609	1.425	1.417	1.464	1.445
Fe ³⁺	.033	.012	.005	.012	.014	.019	.021	.019
T	4.035	4.029	4.027	4.009	3.987	3.959	3.991	3.985
Ca	.380	.485	.509	.590	.474	.605	.560	.545
Na	.548	.448	.438	.389	.522	.391	.401	.435
K	.023	.017	.013	.014	.022	-	-	-
X	.951	.950	.960	.993	1.018	.996	.961	.980
An	42.6	51.9	54.4	60.6	45.6	52.1	52.3	50.4

Analysis number corresponds to the individual grain; (c) = phenocryst core; (r) = phenocryst rim; (g) = groundmass plagioclase. Total iron is assumed as Fe³⁺ and assigned to the tetrahedral site. Anorthite content (An) is expressed as $100 \cdot (\text{Ca} + \text{Fe}^{3+} + \text{Al} - 1) / 2$. Analyses are recalculated to 100 weight % after formula calculation.

Mg# = Mg-number = $100 \cdot \text{mol. Mg} / (\text{Mg} + \text{Fe}^{2+})$. Analysis number corresponds to the individual grain; (c) = core; (r) = rim. Analyses are recalculated to 100 weight % after formula calculation.

Table 4. Microprobe analyses of spinel from metasedimentary xenolith

Sample	BP-6	BP-6	Sample	BP-6	BP-6
	1(c)	1(r)		1(c)	1(r)
TiO ₂	.36	.34	FeO	18.65	17.81
Al ₂ O ₃	63.27	64.87	MnO	.14	.17
Cr ₂ O ₃	.16	.07	MgO	15.39	16.08
Fe ₂ O ₃	2.03	.66			
Number of cations on the basis of 4 oxygens and 3 cations					
Ti	.007	.007	Fe ²⁺	.406	.384
Al	1.943	1.973	Mn	.003	.004
Cr	.003	.001	Mg	.598	.618
Fe ³⁺	.040	.013			
R ₂	1.993	1.994	R ₁	1.007	1.006

(c) = core; (r) = rim. Analyses are recalculated to 100 weight % after formula calculation.

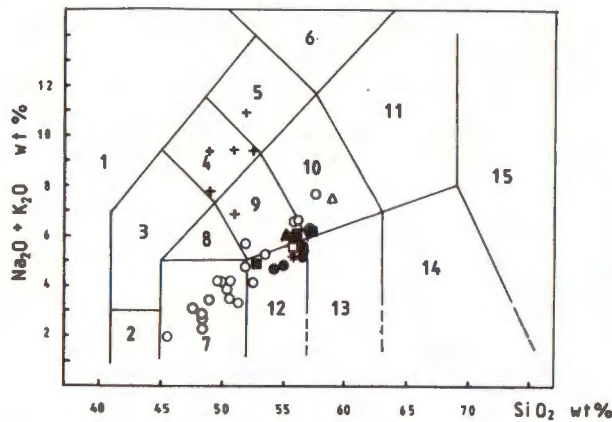


Fig. 2. Total alkali-silica (TAS) diagram for classification of volcanic rocks after Le Bas et al. (1986). Field 1 = Foidite; 2 = Picrobasalt; 3 = Tephrite/Basanite; 4 = Phonotephrite; 5 = Tephriphonolite; 6 = Phonolite; 7 = Basalt; 8 = Trachybasalt; 9 = Basaltic trachyandesite; 10 = Trachyandesite; 11 = Trachyte/Trachydacite; 12 = Basaltic andesite; 13 = Andesite; 14 = Dacite; 15 = Rhyolite. Solid symbols represent Baranja extrusives: circles = this work; squares = selected analyses from Pamić and Pikića (1987); triangle = Golub (1957); asterisk = Mauritz (1920). Open circles = Neogene basic and intermediate extrusives from Mt. Papuk (Lugović, 1983); open square = andesite from Mt. Papuk (Tajder, 1956); open triangle = Q-trachyandesite from Mt. Krndija (Golub and Marić, 1968); crosses = alkaline basalts from Bár in Hungarian part of Baranja (Szederkényi, 1980). All analyses are recalculated on a volatile-free basis and normalized to 100 weight %.

Mg#. The abundances of Rb, Ba, Pb, Th, Zr, and Nb show some correlation with K_2O contents and samples high in CaO have the highest Sr contents.

5. Discussion

5.1. Bulk Rock Chemical Compositions

The extrusive rocks of Beli Manastir-Batina were formerly classified as andesite-basalt, basalt-andesites and andesites. In this paper we follow the IUGS classification scheme (Le Bas et al., 1986). In Fig. 2 our analyses and selected (according to reliability) analyses from the literature are plotted. The majority of the analyses plot into the field of basaltic andesites with some transitions to the (basaltic) trachyandesite fields. Miocene volcanics from Mts. Papuk and Krndija (Slavonia) display basaltic to trachyandesitic compositions. Cenozoic (Pliocene to Quaternary?) extrusives from Bár (Hungarian part of Baranja) are strongly alkaline and plot into the fields of phonotephrites-tephriphonolites and basaltic trachyandesites (Fig. 2). Our intention is not to correlate the Beli Manastir-Batina volcanics with these other occurrences but, instead, to stress significant compositional differences between the three groups.

In the diagram Al-(Fe+Ti)-Mg (Jensen 1976; Fig. 3) the Beli Manastir-Batina volcanics plot into the field of calc-alkaline rocks, whereas the volcanics from the Slavonian Mts. show a tendency towards Fe-enrichment and partially plot into the tholeiitic field.

In Fig. 4, the rocks are plotted into the Zr-Ti-Y diagram of Pearce and Cann (1973) which discri-

Table 5. Bulk rock chemical analyses

Sample	BP-1	BP-3	BP-6	BP-T	BB-2A
SiO ₂	52.4	55.7	55.4	55.9	53.0
TiO ₂	1.38	1.17	1.15	1.18	1.28
Al ₂ O ₃	19.2	17.6	17.4	17.6	17.9
Fe ₂ O ₃	5.25	2.39	2.20	2.01	4.22
FeO	.65	4.28	4.57	4.60	2.78
MnO	.09	.09	.09	.09	.08
MgO	2.05	4.94	5.01	5.04	4.23
CaO	9.44	6.12	6.09	6.10	9.36
Na ₂ O	3.95	3.71	3.93	3.85	3.96
K ₂ O	.62	1.58	1.59	1.61	.62
P ₂ O ₅	.31	.26	.26	.26	.28
H ₂ O	3.09	1.12	1.04	1.00	1.60
CO ₂	.17	<.05	<.05	<.05	.10
Total	98.60	98.96	98.73	99.24	99.41
Mg#	44.4	61.7	61.6	60.1	57.4
Cr	176	191	146	193	237
Co	22	25	25	26	28
Ni	53	476	22	515	505
Cu	41	20	22	21	43
Zn	64	72	76	75	63
Ga	17	18	18	19	16
Rb	13	48	49	50	14
Sr	564	406	411	405	676
Ba	408	529	479	570	422
Pb	8	11	11	13	6
Th	4	8	8	9	3
Zr	177	220	222	226	166
Nb	8	12	12	12	7
Y	29	30	33	32	27

Major elements (in weight %) and trace elements (in ppm) obtained by XRF on fusion tablets and powder pressed tablets, respectively; Fe²⁺ by manganometric titration; H₂O titrimetric (Karl-Fischer); CO₂ by IR gas absorption spectroscopy. Sample powders were dried at 110°C for several hours prior to analyses. Mg#s are calculated assuming FeO = 0.85 · FeO_{tot}.

minates basalts erupted at different geotectonic settings. Although this discrimination diagram is constructed for basalts it shows some tolerance for moderately fractionated rocks because Ti, Zr, and Y all increase simultaneously during the earlier stages of crystal fractionation, i.e. the ratios of these elements do not change significantly. As we are dealing with basaltic andesites, i.e. moderately fractionated rocks, we may therefore use this discrimination diagram. All analyses plot into field C, that is the field of calc-alkaline basalts from destructive plate boundaries.

In the normalized concentration diagram of Pearce (1980) in which element abundances are normalized to a model MORB concentrations (Fig. 5), the Beli Manastir-Batina volcanics are characterized by high normalized abundances of large ion lithophile elements (LILE) and relatively low normalized abundances of high field strength elements (HFSE). In these characteristics they compare well with calc-alkaline rocks as, for example, basaltic andesites from northern Turkey (Peccerillo and Taylor, 1976). Magmas from destructive plate-mar-

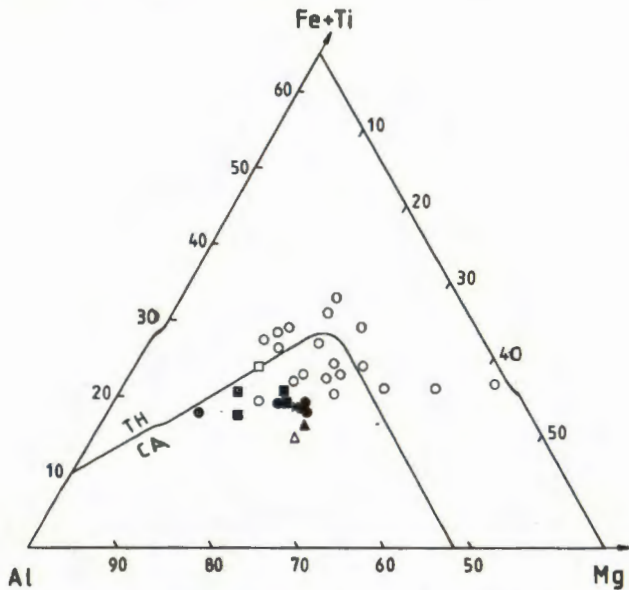


Fig. 3. Al-(Fe+Ti)-Mg diagram after Jensen (1976) for discrimination between tholeiitic (TH) and calc-alkaline (CA) volcanic rock series. Symbols as in Fig. 2. Fe = Fe²⁺ + Fe³⁺. The components are given in cation percentages.

gins in general are characterized by highly variable contents and inter-element ratios of LILEs. The exceptional high Ni abundances of samples BB-2A, BP-T, and BP-3 are certainly due to accumulation of olivine. Primary basaltic melts in equilibrium with peridotitic residues should have Mg#s around 70 and Ni abundances of about 250 ppm. As the three samples have Mg#s between 57.4 and 61.7 which are similar to that of sample BP-6 (61.6) which has a much lower Ni content (22 ppm) it seems clear that olivine accumulation has played a role. All

samples have fairly high but still normal Cr abundances between 146 and 237 ppm (Table 5).

Ba/Nb and K/Zr ratios of the investigated volcanics are high (40–60 and 29–60, respectively) whereas Nb/Th ratios are low (1.33–2.3). These characteristics are typical of volcanic rocks from destructive plate margins (e.g. Pearce, 1982; Wilson, 1989) and are never found in anorogenic magmas.

5.2. Mineral Compositions

Chemical compositions of clinopyroxene phenocrysts have repeatedly been used in the literature to discriminate between lavas of different chemical

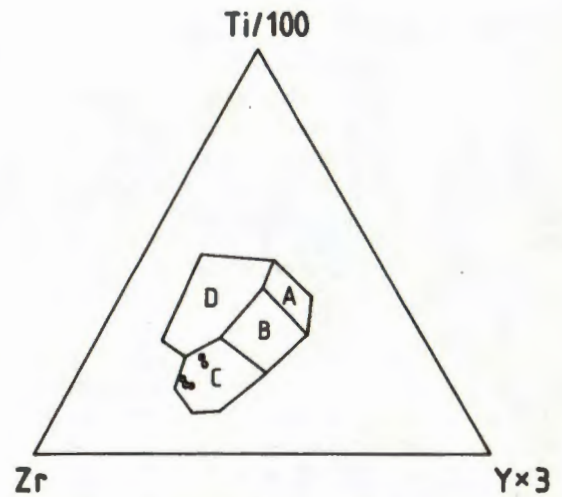
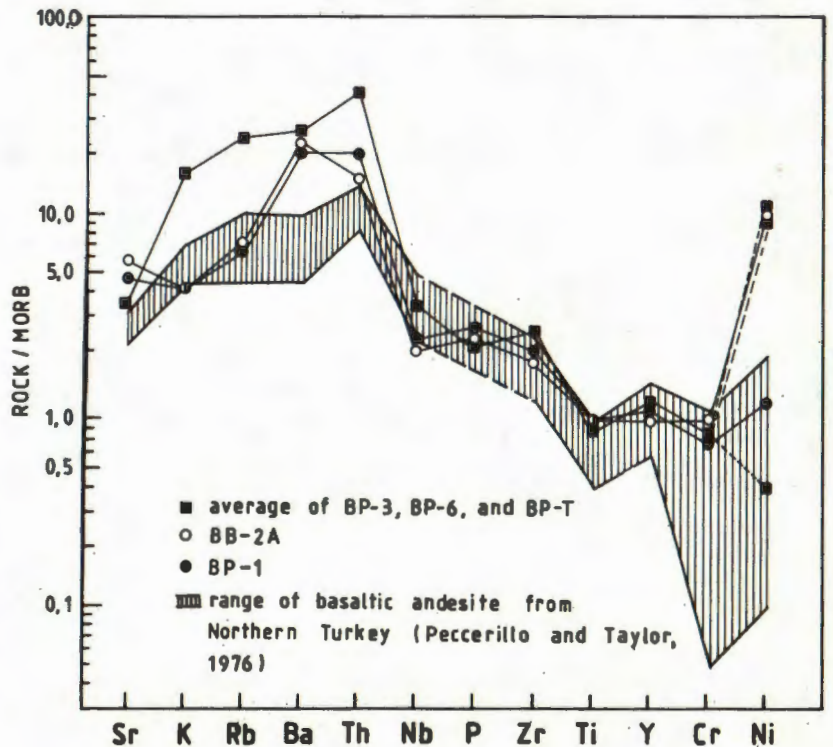


Fig. 4. Ti-Zr-Y discrimination diagram after Pearce and Cann (1973). Field A = low-potassium tholeiites; B = ocean-floor basalts; C = calcalkali basalts; D = within-plate basalts. Basaltic andesites of this work (solid circles) plot into the field of calcalkali basalts.

Fig. 5. MORB-normalized concentration diagram after Pearce (1980). Differences in Ni abundance of three averaged samples are indicated by dashed lines starting from Cr. Half solid circles = joint points of samples BP-1 and BB-2A. Hatched area represents range of subduction-related Eocene calcalkaline basaltic andesites from northern Turkey (Peccerillo and Taylor, 1976). Normalizing values and order of elements are given according to Pearce (1980).



signatures and/or different geotectonic settings (e.g., Nisbet and Pearce, 1977; Leterrier et al., 1982; Marcelot et al., 1988). We used the discrimination diagrams given by Leterrier et al. (1982) although the requirements for the use of these diagrams are not completely fulfilled. Except sample BB-2A the analyses plotted are not from clinopyroxene phenocrysts but from groundmass. Furthermore, the whole-rock silica contents of some of the samples are slightly higher than 56 weight % (on a volatile-free basis), but all samples have a differentiation index (Thornton and Tuttle, 1960) lower than 50. In the first diagram (Ti vs. (Na+Ca); Fig. 6), clinopyroxenes from alkaline basalts are discriminated from those hosted in subalkaline basalts, that is from tholeiitic and calc-alkaline basalts. Whereas clinopyroxenes from samples BP-3 and BP-6 plot into field T (tholeiitic and calc-alkali basalts), the titanian augites and hedenbergites of sample BB-2A are situated within field A (alkali basalts). The second discrimination diagram ((Ti+Cr) vs. Ca; Fig. 7) is used for clinopyroxenes from subalkaline rocks only. All clinopyroxene compositions from the two samples BP-3 and BP-6 plot into field D which stands for clinopyroxene compositions from non-orogenic tholeiites. This result, however, has to be looked at with some caution because we are not dealing with clinopyroxenes from primitive, i.e. unfractionated basalts, but, instead with those from moderately fractionated basaltic andesites. During the earlier stages of fractionation, Ti concentration of the melt increases until Ti-magnetite becomes a liquidus phase. Similarly, Ti contents of crystallizing clinopyroxenes first increase and this may cause clinopyroxenes from moderately fractionated orogenic basalts (field O in Fig. 7) to plot into field D.

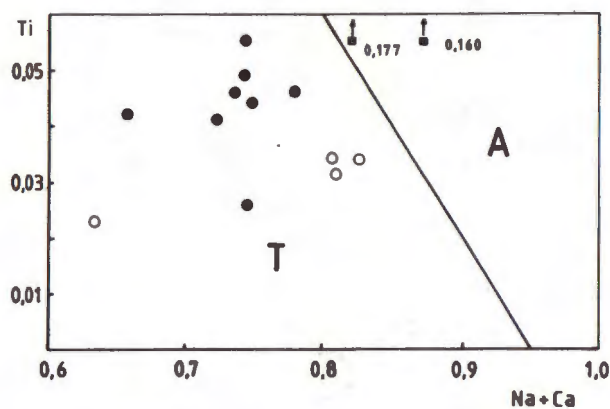


Fig. 6. Ti-(Na+Ca) clinopyroxene discrimination diagram based on cations per formula unit (after Leterrier et al., 1982). T = field of clinopyroxenes from tholeiitic and calcalkali basalts (92% confidence level); A = field of clinopyroxenes from alkalic basalts (86% confidence level). Solid circles = BP-3; open circles = BP-6; solid squares = BB-2A.

The clinopyroxene phenocrysts from sample BB-2A are most probably not in equilibrium with the melt as represented by the groundmass. The Mg# of these clinopyroxenes (38.3–30.8; Table 2) are too low when compared with the average Mg# of

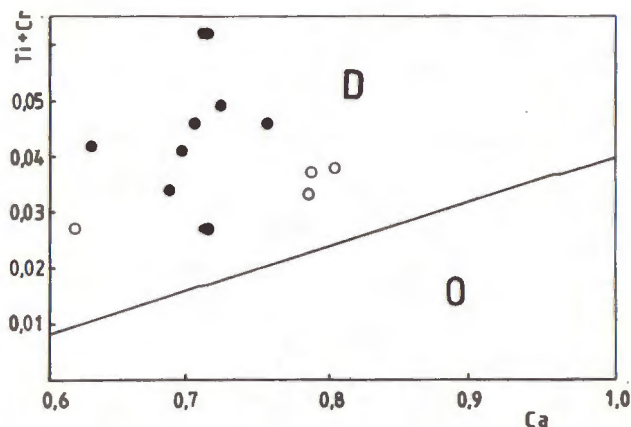


Fig. 7. (Ti+Cr)-Ca clinopyroxene discrimination diagram based on cations per formula unit (after Leterrier et al., 1982). D = field of clinopyroxenes from non-orogenic basalts (81% confidence level); O = field of clinopyroxenes from orogenic basalts (80% confidence level). Symbols as in Fig. 6.

olivine (85.5; Table 1) and the Mg# of the bulk rock (57.4; Table 5). Although sample BB-2A has whole-rock chemical characteristics of a subalkaline orogenic magma (negative Nb-anomaly) it contains clinopyroxenes rich in Na and Ti which normally can only be found in alkaline lavas. We suggest that the clinopyroxenes of this rock are in fact xenocrysts. This points either to magma mixing or to assimilation processes. The fact that all investigated rocks are slightly Q normative is not a contradiction to the observation that they all have olivine phenocrysts. At lower pressures which hold true for volcanic rocks, the system $\text{SiO}_2\text{-Mg}_2\text{SiO}_4$ is peritectic, i.e. olivine may crystallize from melts having a slight excess in silica.

5.3. Metasedimentary Xenoliths

The protoliths of the thermally metamorphosed xenoliths enclosed in some of the Baranja basaltic andesites were clayey limestones. The xenoliths have mineral assemblages typical for the pyroxene hornfels facies. Their boundaries to the enclosing groundmass are irregular and diffuse which indicates some mass transfer between the two systems. The intensity of this process was limited and is not thought to have significantly influenced the bulk rock chemical compositions of the volcanics.

5.4. Geotectonic setting

It is well known from geophysical investigations (Dragašević, 1969) and petrological evidences (Embey-Isztin, 1977) that the present-day crustal thickness in the Pannonian basin is less than 29 km. The shallow position of the Mohorovičić discontinuity in this area has been interpreted as a consequence of mantle upwelling (»mantle diapir«) and crustal extension starting in Miocene time. All these phenomena and processes have to be seen in the frame of the distinct geodynamic position of the Pannonian basin which has repeatedly been interpreted as a post-subduction continental back-arc basin (e.g., Horváth et al., 1989) characterized by Neo-

gene-Quaternary calc-alkaline and alkaline volcanic activity (e.g., Póka, 1988, Szabó and Dobosi, 1989). In such environments volcanic rocks with an alkaline or strongly alkaline major element composition but a trace element subduction signature like, for instance rocks of the shoshonite series, may be generated. However, in the interior of the Pannonian basin rhyolites, rhyodacites and their tuffs are found (Póka, 1988). The youngest rhyolite tuffs are dated at about 14 Ma (Hámor et al., 1976), i.e. at the very similar age to the Baranja basaltic andesites (Pamić and Pikija, 1987).

It is thus not surprising that the rocks investigated by us have bulk-rock compositions similar to those of volcanics from destructive plate margins but, on the other hand show some mineralogical features which are more typical of alkaline rocks from extensional tectonic (within-plate) settings.

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REFERENCES

- Deer, W. A., Howie, R. A. & Zussman, J. (1962): *Rock Forming Minerals*, Vol. 5. Longmans, London, 371 pp.
- Dragašević, T. (1969): Investigation of the structural characteristics of the Mohorovičić discontinuity in the area of Yugoslavia. *Boll. Geofiz. teor. apl.*, 11, 58–70.
- Embey-Isztin, A. (1977): The Sziliget amphibolite/lherzolite compound xenolith as an evidence for diapiric uprise in the mantle below Hungary. *Ann. Hist.-nat. Mus. Nat. Hung.*, 69, 5–11, Budapest.
- Golub, Lj. (1957): Bazalt-andezit kod Popovca u Baranji. *Geol. vjesnik*, 10, 111–122, Zagreb.
- Golub, Lj. & Marić, L. (1968): Kvarcni trahandezit s Lončarskog visa (Krndija). *Geol. vjesnik*, 21, 255–271, Zagreb.
- Hámor, G., Balogh, K. & Ravaszné Baranyai, L. (1976): Radioactive age of the tertiary formation in North Hungary. *MÁFI Évi. Jel.*, 15, 61–76.
- Horváth, F., Rumpler, J., Tari, G. & Dövény, P. (1989): Structural evolution of the Pannonian basin. *Terra Abstracts*, 1, p. 51.
- Jensen, L. S. (1976): A new cation plot for classifying subalkalic volcanic rocks. *Can. J. Earth Sci.*, 8, 523–548.
- Letterier, J., Maury, R. C., Thonon, P., Girard, D. & Marchal, M. (1982): Clinopyroxene composition as a method of identification of the magmatic affinities of paleo-volcanic series. *Earth Planet. Sci. Lett.*, 59, 139–154.
- Le Bas, M. J., Le Maitre, R. W., Streckeisen, A. & Zanettin, B. (1986): A chemical classification of volcanic rocks based on the total alkali-silica diagram. *J. Petrol.*, 27, 745–750.
- Lóczy, L. Jr. (1914): A Báni hegység (Baranya) geológiai viszonyai. *Ann. Rep. Hung. Roy. Geol. Survey*, 353–360.
- Lugović, B. (1983): Efuzivne stijene sjeverozapadnog dijela Papuka. *Geol. vjesnik*, 36, 131–156, Zagreb.
- Marcelot, G., Bardintzeff, J. M., Maury, R. C. & Raçon, J. P. (1988): Chemical trends of early-formed clinopyroxene phenocrysts from some alkaline and orogenic basic lavas. *Bull. Soc. geol. France*, 4, 851–859.
- Mauritz, B. (1920): A Báni hegység bazalt-szerfűközetei. *Mat. Term. Tud. Ért.*, 37, 62–65.
- Morimoto, N. (1988): Nomenclature of pyroxenes. *Schweiz. Mineral. Petrogr. Mitt.*, 68, 95–111.
- Nisbet, E. G. & Pearce, J. A. (1977): Clinopyroxene composition in mafic lavas from different tectonic setting. *Contrib. Mineral. Petrol.*, 63, 149–160.
- Pamić, J. & Pikija, M. (1987): Badenian andesites and pyroclastics from Baranja in northern Croatia (Yugoslavia). *Acta Geol. Hungarica*, 30, 111–132, Budapest.
- Pearce, J. A. (1980): Geochemical evidence for the genesis and eruptive setting of lavas from Tethyan ophiolites. In: Panayiotou, A. (Ed.): *Ophiolites. Proc. Int. Ophiol. Symp., Cyprus 1979*, 261–272, Nicosia.
- Pearce, J. A. (1982): Trace element characteristics of lavas from destructive plate boundaries. In: Thorpe, R. S. (Ed.): *Andesites. Orogenic Andesites and Related Rocks*. J. Wiley & Sons, Chichester, 525–548.
- Pearce, J. A. & Cann, J. R. (1973): Tectonic setting of basic volcanic rocks determined using trace element analyses. *Earth Planet. Sci. Lett.*, 19, 290–300.
- Peccerillo, A. & Taylor, S. R. (1976): Geochemistry of Eocene calc-alkaline volcanic rocks from Kastamonu area, northern Turkey. *Contrib. Mineral. Petrol.*, 58, 63–81.
- Póka, T. (1988): Neogene and Quaternary volcanism of the Carpathian-Pannonian region: changes in chemical composition and its relationship to Basin formation. In: Royden, L. H. & Horvath, F. (Eds.): *The Pannonian Basin. A Study in Basin Evolution*. AAPG Memoir, 45, 257–277.
- Szabó, Cs. & Dobosi, G. (1989): Neogene volcanism of the Carpathian-Pannonian area. *Terra Abstracts*, 1, p. 52.
- Szederkényi, T. (1980): Petrological and geochemical character of the Bár basalts, Baranya County, South Hungary. *Acta Mineral. Petrogr.*, 24, 235–244, Szeged.
- Tajder, M. (1956): Albitski efuzivi okolice Vočina i njihova geneza. *Acta geol. JAZU*, 1, 35–48, Zagreb.
- Takšić, A. (1947): Prinos poznavanju prapora Istočne Hrvatske. *Geol. vjesnik*, 1, 202–231, Zagreb.
- Thornton, C. P. & Tuttle, O. F. (1960): Chemistry of Igneous Rocks, I. Differentiation Index. *Amer. J. Sci.*, 258, 664–684.
- Wilson, M. (1989): *Igneous Petrogenesis*. Unwin Hyman Ltd, London, 466 pp.

Geokemijske osobine bazaltnih andezita Baranje

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Između Belog Manastira i Batine u Baranji nalaze se efuzivne i piroklastične stijene pod naslagama lesa gornjopliocenske starosti (Takšić, 1947). Postoje tri petrološka i geokemijska rada o ovim efuzivima (Mauritz, 1920; Golub, 1957; Pamić i Pikija, 1987). Pamić i Pikija (1987) određuju badensku starost efuziva (14.5 i 13.8 milijuna godina) i zaključuju da su oni posljedica geodinamskih procesa povezanih na poslije subdukcijско uzdizanje vanjskog plašta u Panonskom bazenu.

Pet novih uzoraka izabrano je za analizu sadržaja glavnih elemenata i elemenata u tragovima (tablica 5) i analizu kemijskog sastava minerala (tablice 1-4). Baranjski efuzivi imaju holokristalnu porfirnu strukturu s intergranularnom osnovom. Sastoje se od plagioklasa (61-42% An), augita ($Mg\# = 77,5-71,5$) ili titanskog augita/titanskog hedenbergita ($Mg\# = 38,3-30,8$), olivina ($Mg\# = 85,1-62,3$), titanskog magnetita i apatita. Postoji značajna razlika u kemijskom sastavu između feromagnezijskih minerala sadržanim u uzorcima stijena koji predstavljaju lavu (tablice 1 i 2; uzorci BP-3 i BP-6) i onih u fragmentima efuziva iz piroklastičnih stijena (tablice 1 i 2; uzorak BB-2A). Jedan uklopak kontaktno metamorfoziranog glinovitog vapnenca u uzorku BP-6 ima paragenezu karakterističnu za piroksen hornfels facijes: plagioklas, pleonast (tablica 4), silimanit i olivin.

Analizirane stijene imaju kemijski sastav bazaltnih andezita (tablica 5; sl. 2) ali s različitim sadržajem glavnih oksida. Sadržaj kompatibilnih elemenata (Cr, Ni) je visok i promjenjiv i ne korelira se s $Mg\#$. Sadržaj Rb, Ba, Pb, Th, Zr i Nb pokazuje izvjesnu korelaciju sa sadržajem K_2O .

Zajedno s bazaltnim andezitima Baranje projicirani su u sl. 2 miocenski vulkaniti Papuka i Krndije (Tajder, 1956; Golub i Marić, 1968; Lugović, 1983) i alkalijski efuzivi iz okolice Bára u mađarskom dijelu Baranje (Szederkényi, 1980) s jedinom namjerom da se istaknu značajne razlike u kemijskom sastavu koje postoje među njima. Baranjski bazaltni andeziti imaju udjel elemenata i njihovu relativnu obilnost karakteristične za efuzivne stijene kalcijsko-alkalijske svojte (sl. 3) odnosno za kalcijsko-alkalijske bazalte (sl. 4) i bazaltne andezite (sl. 5) iz

područja subdukcije. Neočekivano visok sadržaj nikla u nekim uzorcima stijena objašnjavamo kumulacijom olivina.

Kemijski sastav monoklinskih piroksena iz efuzivnih stijena može poslužiti za određivanje kemijskih osobina lava i/ili njihovog geotektonskog položaja (Nisbet i Pearce, 1977; Lettner et al., 1982; Marcelot et al., 1988). Augiti iz uzoraka BP-3 i BP-6 imaju sastav sličan monoklinskim piroksenima sadržanim u nealkalijskim bazaltima (sl. 6), tj. u toleitskim neorogenim bazaltima (sl. 7) a titanski augiti/titanski hedenbergiti u uzorku BB-2A sličnim onima iz alkalijskih bazalta kontinentalnih riftnih područja (sl. 6).

Panonski bazen je poslije subdukcijски rubni bazen («back-arc basin») nastao ekstenzijom kontinentalne kore i uzdizanjem plašta, započetim u miocenu (Horváth et al., 1989). Debljina kore ne prelazi 29 km (Dragašević, 1969) i ima tendenciju daljnjeg istanjenja. Vulkanske stijene koje su nastale za vrijeme stvaranja Panonskog bazena zastupljene su kalcijsko-alkalijskim andezitima i bazaltima miocenske i pliocenske starosti i alkalijskim bazaltima gornjeg panona i kvartara (Póka, 1988; Szabó i Dobosi, 1989). U ovakvoj geotektonskoj sredini mogu nastati i stijene, kao što su npr. šošoniti, koje su po sadržaju glavnih elemenata slične alkalijskim vulkanskim stijenama, ali im je sadržaj elemenata u tragovima karakterističan za subdukcijске vulkanite. Međutim, u unutrašnjem dijelu Panonskog bazena nalaze se rioliti, riodaciti i njihovi piroklastiti, erupcije kojih se dijelom prostorno i vremenski podudaraju s erupcijama andezita (Póka, 1988). Najmlađi riolitni tufovi imaju izotopnu starost od oko 14 milijuna godina (Hámor et al., 1976) i vremenski se podudaraju s erupcijom bazaltnih andezita Baranje.

S obzirom na ovako raznovrsnu vulkansku aktivnost unutar Panonskog bazena nije začudujuće da bazaltni andeziti Baranje imaju kemijski sastav sličan vulkanskim stijenama destruktivnih rubova ploča, a sadrže neke minerale čiji je sastav više karakterističan za alkalijske stijene ekstenzijskih («within-plate») geotektonskih sredina. Da li je, i u kolikoj mjeri, ovakav sastav rezultat i miješanja magmi i/ili procesa asimilacije ostaje za sada nepoznato.