

Boron and chlorine concentration of volcanic rocks: An application of prompt gamma activation analysis

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Boron and chlorine concentrations in geological standards and in representative volcanic rock samples were determined by prompt gamma activation analysis (PGAA). The results of the GSJ standard measurements proved the high precision of PGAA in measuring the boron, chlorine, other trace elements (Sc, Nd, Sm, and Gd) and the major element contents of the samples. The rock samples originate from the western part of the Northern-Pannonian Volcanic Field (NPVF), which includes the Central Slovakian Volcanic Field (CSVF), the Börzsöny and the Visegrád Mts. (VMt.). The oldest 16–13.5 Ma samples as the first products of the Miocene calc-alkaline volcanism are the most enriched in B (11–29 µg/g), whereas the primitive basaltic andesites (from CSVF), the latest products (9 Ma) of the volcanic activity have lower B content (8–9 µg/g). The measured B concentrations correlate positively with fluid-mobile elements, and the trace element pattern of the samples show subduction related signatures. The chlorine content of the investigated samples shows wide variation between 42.62 and 1148.45 µg/g. The 9 Ma samples from the CSVF show Cl contents between 150–160 µg/g. In agreement with the latest geodynamic models of the Neogene calc-alkaline volcanism^{1,2} in the NPVF during the shallow, prograding subduction, the fluid-mobile elements metasomatized the mantle wedge. Thus the oldest volcanic rocks have relatively higher B (>11 µg/g) and high but variable Cl contents. As the subduction waned and extension proceeded, the magma generation region changed to a not thoroughly metasomatized mantle by the former subduction event, resulting in lower B, low and stable Cl content of the younger (9 Ma) volcanic rocks.

Introduction

The most complex petrogenetic processes of igneous systems occur at active continental margins. Convergent plate margins are the sites of substantial mass transfer back into the upper mantle.^{3,4} Oceanic lithosphere consisting of hydrothermally altered mafic crust and sediments are recycled back into the Earth's mantle.⁵ During subduction, the downgoing formations dehydrate^{6,7} and, under certain conditions,^{1,8–10} can also melt partially. Fluids and melts are transferred to the overlying mantle wedge¹¹ which they metasomatize^{12–14} (Fig. 1). Upwelling of hydrous peridotite results in partial melting, forming primitive high-Al basaltic magmas. Although it is now generally accepted that subduction-related volcanic rocks contain components of the slab, the exact nature of the mechanisms that transfer these components from the slab to the mantle are not well understood. The important constraints on the transfer mechanism can be derived from the studies of light elements, such as lithium, beryllium, chlorine and boron. This paper tries, therefore, to give an insight to one of the geological applicability of Budapest PGAA, which allows us to measure the precise B, Cl, few other trace and all major element contents of whole rocks. We have found relation between the subduction processes and the calc-alkaline volcanic products in the Northern-Pannonian Volcanic Field based on the variation in B and Cl concentrations.

Boron is a good tracer of fluids and recycled, subducted materials^{15–24} of the Earth, because it has low mineral/fluid and low mineral/melt distribution coefficients, i.e., B is a highly fluid-mobile and incompatible trace element. Chlorine is also a fluid-mobile element. Both B and Cl concentration are high in sediments and altered oceanic basalt (average 80–120 µg/g B,²⁵ and 100–3000 µg/g Cl)^{26,27} due to the interaction with sea-water, whereas they have low values in the mantle (0.1 µg/g B,^{28,29} 2–8 µg/g Cl).²⁷ Indeed, mantle-derived basaltic rocks have low B concentrations, except for subduction related volcanic arcs. These show significantly greater B concentrations (1–35 µg/g)^{18,30–34} than MORBs (0.6–2 µg/g)^{18,35} (i.e., mid-ocean ridge basalts, which are thought to represent primitive partial melts of un-metasomatized upper mantle).¹⁸ However, chlorine concentrations are largely variable, the average Cl content of MORB's (40–1100 µg/g Cl)^{26,36} is lower compared to arc-volcanic basalts, which are influenced by slab-derived components (400–4000 µg/g Cl).^{37,38} Chlorine is an important trace element in the subduction related magmatic systems, even though the Cl content of the mantle is quite inhomogeneous. However, the Cl content of the subducting slab decreases progressively due to the metamorphic reactions^{27,38} the original Cl content of the slab can also be inhomogeneous. Thus the Cl behavior is even more complex in magmatic systems, than that of B.

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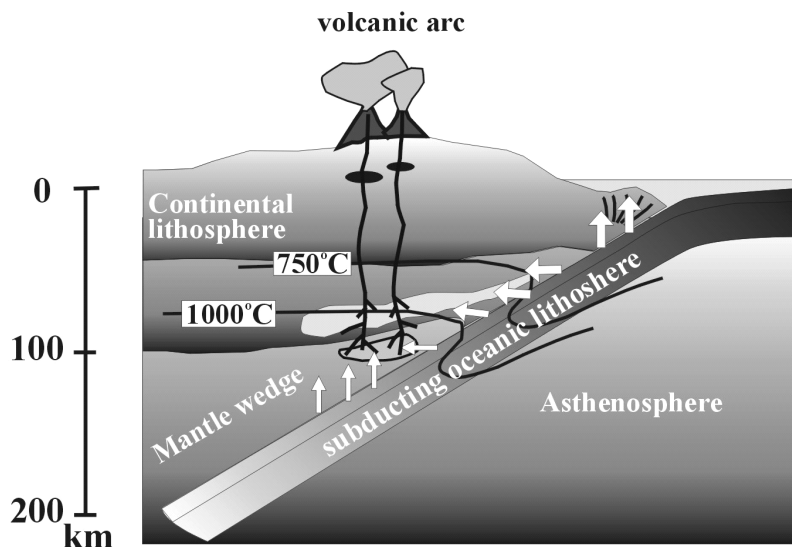


Fig. 1. Model of a subducting oceanic lithosphere under continental lithosphere. The arrows are demonstrating the fluid-mobile element transport during dehydration and metamorphism

Data from subduction-related metamorphic and igneous rocks show that B and Cl are efficiently removed from the slab during subduction by progressive metamorphic reactions^{16,27,39–43} and transferred into the mantle wedge via aqueous fluids.^{27,38,44,45} The upwelling magmatic melt can suffer crustal contamination, but the average boron content of the crust is quite low (5 and 10 $\mu\text{g/g}$, lower- and upper crust, respectively)⁴⁶ to influence the boron content of the volcanic rocks significantly. However, dehydration melting of amphibolite-grade meta-pelites, which can contain muscovite, biotite and tourmaline (B-bearing minerals), mixing with ascending mantle melts would contribute to higher B concentration, especially in evolved rocks, which we exclude from this study. Systematic decreases of B concentrations behind the volcanic front of several arcs^{19,41} (e.g., Kamchatka arc, Kurile-Kamchatka Trench and Kurile arc) suggest that the B input to the magma source region decreases from arc to back-arc, i.e., the boron concentration of slab-derived fluids decreases with increasing slab depth. Exact behavior of B in magmatic systems is fairly unknown to this day. This rather unsatisfying situation is mainly due to the fact that the measurement of precise B content in whole rock is difficult and time consuming or even impossible with analytical methods frequently used in geochemistry (XRF, ICP-AES, -MS, TIMS etc.).

Because of the difficulties in measuring B with conventional compared to nuclear analytical techniques, and the essential geological information carried by B, a promising co-operation can be expected between nuclear physicists and igneous geologists. Prompt gamma activation analysis offers an excellent way to measure B

in volcanic rock samples through the detection of prompt gamma-photons from $^{10}\text{B}(n,\alpha\gamma)^7\text{Li}^*$ nuclear reaction. In this manner, joint research started in 2002 between the scientists and students of the Department of Petrology and Geochemistry, Eötvös University and the Nuclear Research Department of the Institute of Isotopes and Surface Chemistry in the framework of the Hungarian Scientific Research Fund (OTKA, T037974).

The remembered head of the Department, Prof. Gábor MOLNÁR, being a broad-minded physicist, immediately realized the applicability of the prompt gamma activation analysis method in geology. Being sharp-sighted and interested in other scientific fields, he came up with numerous good and new ideas. The first author is especially thankful to him for the support during her MSc studies and for the encouragement to work at his department as a Ph.D. student. The aim of this paper is to give an overview of the results of our joint research.

Geological background of the investigated samples

We have measured the B concentrations of Miocene calc-alkaline volcanic rocks occurring in the Carpathian-Pannonian Region (CPR), Eastern-Central Europe. In the CPR a wide range of volcanic rocks can be found that formed during the last 20 Ma.⁴⁷ This region was formed during the Neogene by combined processes of large-scale block translation, subduction and extension. All of these are related to the collision of the European and African plates. One of the consequences of the plate convergence was the escape of the so called ALCAPA block from the Alpine orogenic belt.⁴⁸ This rigid crustal

block moved northeast-eastward, where an oceanic basin presumably with oceanic lithosphere was situated. Subduction of this oceanic lithosphere occurred along the curvilinear belt of the present Outer-Carpathians. Termination of subduction was graded from west to east-southeast from Middle Miocene to Pliocene.⁴⁹ Behind the subduction zone, a back arc basin (the Pannonian Basin) was formed by lithospheric extension (Fig. 2). The southward subduction and roll-back of the weakened southern edge of the European plate under the ALCAPA terrain^{50–53} and suction exerted by this subducting plate may have enhanced lithospheric stretching in the back-arc region.^{48,54,55} At the Northern Pannonian Basin subduction commenced at approximately 20 Ma without coexisting volcanism and terminated at about 16 Ma.⁵⁶

The Miocene calc-alkaline volcanism occurred mainly parallel to the Carpathian range, with the total

length of more than 700 kilometres. In addition to this more or less continuous belt, calc-alkaline volcanic formations are found, mostly buried, in the Pannonian Basin (Fig. 2a). The calc-alkaline volcanic complexes (Fig. 2a) can be divided into four groups based on spatial distribution (northern-, eastern-, south-western- and inner-Pannonian calc-alkaline volcanic fields).⁴⁷ The Northern-Pannonian Volcanic Field (NPVF) (Fig. 2b) occurs roughly perpendicular to the Carpathian Arc, extending as far as 200–300 km from the assumed suture zone. It includes the Visegrád Mts. (VMt.), the Börzsöny and the Central Slovakian Volcanic Field (CSVF), the Cserhát, the Mátra and the Tokaj-Slanske Volcanic Field. This study focuses on the western part of the NPVF (i.e., Central Slovakian Volcanic Field, Börzsöny and Visegrád Mt.) where the volcanic activity started at 16.5 Ma and terminated at 9 Ma.⁵⁶

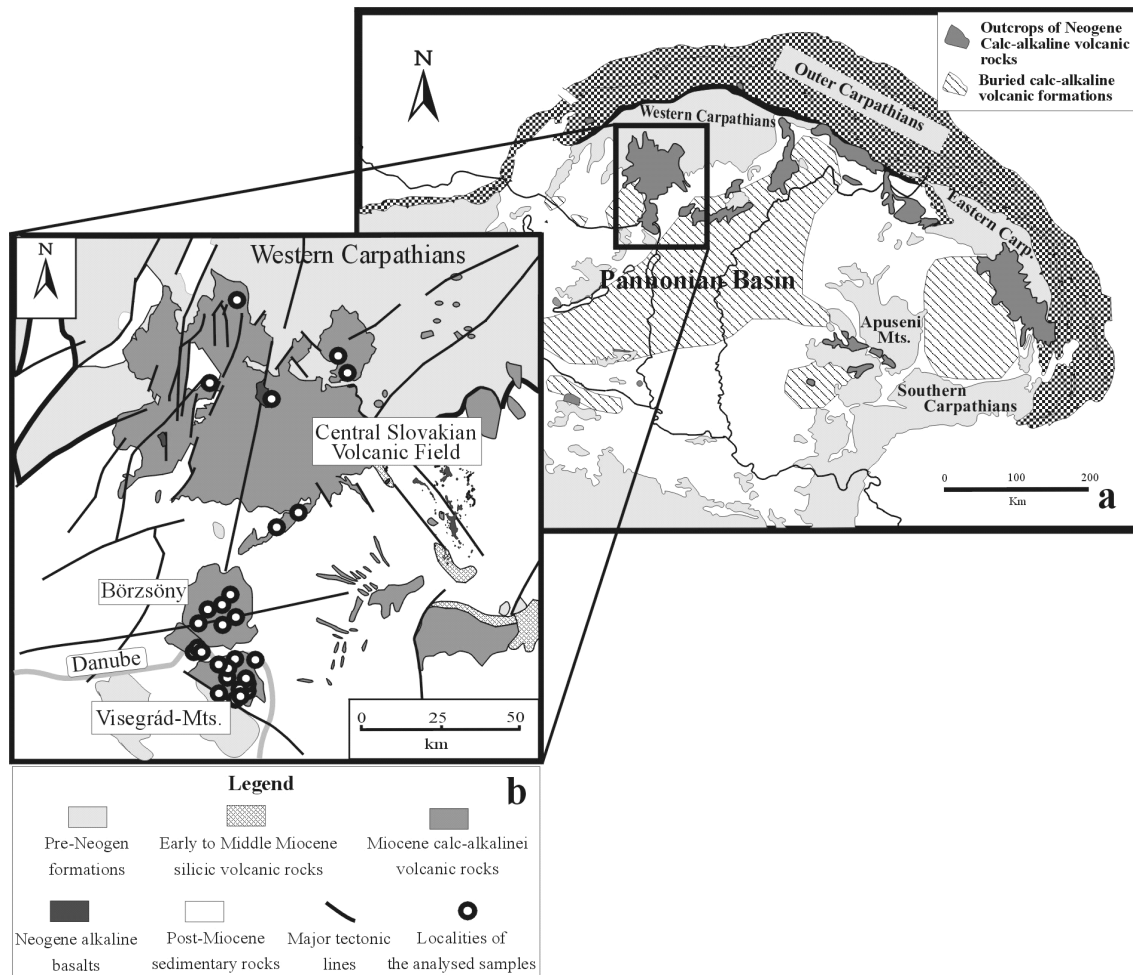


Fig. 2. Geological map of the Carpathian Pannonian Region (CPR); (a) occurrence of the calc-alkaline volcanic rocks in the CPR,²⁸ (b) Western segments of the Northern Pannonian Volcanic Field (NPVF)³⁸

The studied calc-alkaline volcanic rocks are dominantly andesites and basaltic andesites, and follow a north-south section with 130 km length and 7 million years temporal variation. The samples belong to different volcanic facies, such as lava flows (CSVF) and pyroclastic breccias (Visegrád Mts.). GSJ (Geological Survey of Japan) standards were also investigated, which are covering the geochemical variability of the investigated rock series (three basalts: JB-1A, JB-2, JB-3; two andesites: JA-2, JA-3; and additionally two rhyolites: JR-1, JR-2 with high B content).

Analytical methods and sample preparation

Determination of B, Cl and some other trace elements (Sc, Sm and Gd) together with major elements were carried out using prompt gamma activation analysis (PGAA) facility at the 10 MW Budapest Research Reactor (BRR), Hungary. A cold (20 K) neutron beam is transported from the reactor core by a 35 m long, slightly curved neutron guide, where the PGAA apparatus is located. The powdered rock samples were dried at 105 °C for 8 hours and 2–3 g of each were heat-sealed in fluorinated ethylene propylene (FEP) film (size of 2.5×3.5 cm²). The samples were placed directly into the cold neutron beam of $5 \cdot 10^7 \text{ n} \cdot \text{cm}^{-2} \cdot \text{s}^{-1}$ thermal equivalent flux. The beam was collimated to an area of 2×2 cm², and the typical irradiation time lasted for 90–120 minutes. The prompt gamma spectrometer consists of a Canberra high purity Ge detector (HPGe), bismuth-germanate scintillator detectors (BGO), lead shielding and a multichannel analyzer system operated by a personal computer. For the spectrum evaluation we used the Hypermet PC software.⁵⁷ More detailed description of the PGAA system is given elsewhere.^{58–63}

The investigated volcanic rock samples from the NPVF have been previously analyzed by XRF and ICP-AES, -MS and MC-TIMS at the Royal Holloway University of London. The experimental conditions of the latter measurements were described by MASON et al.⁶⁴ and HARANGI et al.⁶⁵ Therefore, results of PGAA measurements could have been directly compared with the results of other analytical techniques.

Results

Boron concentration measured with PGAA (Budapest)

The B data of volcanic rock series from geological standards, measured by PGAA show very good correlation with concentrations given by GSJ⁶⁶ for B contents in the interval between 5 and 50 µg/g (JB-1A, JB-2, JB-3, JA-2, JA-3, Fig. 3). However, the B contents of the rhyolite standards measured with PGAA are about 16–20% higher than the standard values published by IMAI et al.⁶⁶ (average of the results of different methods). SANO et al.⁶⁷ had the same experience measuring the B content of the JR-1, JR-2 standards with PGAA at JAERI. They found a discrepancy between their results and those of IMAI et al.⁶⁶ Our experiments support the suggestion of SANO et al.⁶⁷ that the published B content of rhyolite standards (JR-1, JR-2) should be reconsidered (Table 1). However, in this study we focus on the basaltic andesites and andesites having B contents lower than 50 µg/g. In this range the standard results agree well with the reported GSJ values. The major element contents of the geological standards measured by PGAA also concur with the published data (Table 2).

Volcanic rocks previously analyzed with XRF, ICP-AES and -MS were measured by PGAA to compare our results with that of other analytical techniques (Fig. 4). The major elements show good agreement, having the same values within the uncertainty limit. The uncertainties of PGAA measurements for all the analyzed elements do not exceed 5%, are generally between 1 and 2%. In the case of TiO₂, Fe₂O₃, MnO, Na₂O and K₂O we measured slightly higher values than those determined by XRF, whereas we had the opposite experiences with SiO₂, Mg- and Ca-oxide, where the PGAA slightly underestimated the XRF results. The reason for that bias is being investigated. Among major elements, only the P₂O₅ concentration cannot be measured with PGAA, due to the relatively low sensitivity of P, of the trace elements B, Cl, Sc, Gd and Sm can be measured effectively by PGAA.

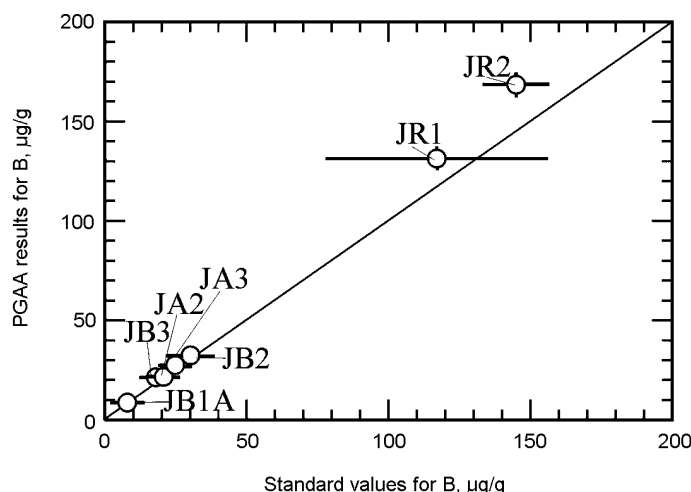


Fig. 3. Boron concentration of the GSJ volcanic rock standards measured by PGAA show good correlation with the standard values⁶⁶

Table 1. Boron concentration of the GSJ volcanic rock standards.

Recommended values by IMAI et al.⁶⁶ and Sano et al.,⁶⁷ and the results of the present study

Standard	B, µg/g (recommended)	B, µg/g (PGAA-JAERI)	B, µg/g (PGAA-BRR)
	IMAI et al. (1995)	Sano et al. (1999)	Present study
JB-1A	7.88	7.75	8.68
JB-2	30.20	31.70	31.72
JB-3	18.00	20.40	21.50
JA-2	20.70	22.30	21.38
JA-3	24.80	26.50	27.52
JR-1	117.00	134.00	132.78
JR-2	145.00	156.00	168.40

Table 2. Major and few trace element contents of the GSJ volcanic rock standards measured by PGAA and their published⁶⁶ values

%	JB1A	PGAA	JB2	PGAA	JB3	PGAA	JA2	PGAA	JA3	PGAA	JR1	PGAA	JR2	PGAA
SiO ₂	52.41	51.89	53.25	52.97	50.96	50.82	56.42	57.59	62.27	61.56	75.45	75.15	75.69	74.89
TiO ₂	1.28	1.30	1.19	1.22	1.44	1.47	0.66	0.69	0.70	0.72	0.11	0.12	0.07	0.07
Al ₂ O ₃	14.45	14.53	14.64	14.21	17.20	17.10	15.41	15.39	15.56	15.56	12.83	12.53	12.72	12.86
Fe ₂ O ₃	9.05	9.01	14.24	14.44	11.82	11.95	6.21	6.21	6.60	6.79	0.89	0.83	0.77	0.74
MnO	0.15	0.17	0.22	0.26	0.18	0.21	0.11	0.12	0.10	0.13	0.10	0.11	0.11	0.13
MgO	7.83	7.50	4.62	4.69	5.19	4.82	7.60	7.22	3.72	3.43	0.12		0.04	
CaO	9.31	9.14	9.82	9.06	9.79	9.28	6.29	5.98	6.24	5.99	0.67	0.70	0.50	0.46
Na ₂ O	2.73	2.79	2.04	2.19	2.73	2.83	3.11	3.17	3.19	3.42	4.02	4.28	3.99	4.23
K ₂ O	1.40	1.48	0.42	0.44	0.78	0.83	1.81	1.91	1.41	1.53	4.41	4.72	4.45	4.97
H ₂ O	1.84	1.86	0.25	0.35	0.25	0.27	1.12	1.71	0.31	0.52	1.16	1.41	1.41	1.50
mg/g														
B	7.88	8.61	30.20	30.76	18.00	21.40	20.70	21.06	24.80	27.52	117.00	131.59	145.00	168.40
Cl	171.00	169.42	281.00	304.46	259.00	320.00		7.77			920.00	1005.68		
Sm	5.07	3.62	2.31	1.58	4.27	2.95	3.11	2.07			6.03	3.91		
Gd	4.67	4.63	3.28	3.01	4.67	4.52	3.06	2.86	2.96	3.27	5.06	5.81	5.83	5.80

Table 3. The investigated volcanic rock samples type, locality, distance from the subduction suture zone, eruption age and major element (in wt.%), boron, chlorine (in µg/g) and few other trace element (in µg/g) concentration

Sample	Locality	Rock type	Distance from subduction zone, km	Age, M	SiO ₂ wt%	TiO ₂ wt%	Al ₂ O ₃ wt%	Fe ₂ O ₃ wt%	MnO wt%	MgO wt%	CaO wt%	Na ₂ O wt%	K ₂ O wt%	H ₂ O wt%	B ₂ µg/g	Cl µg/g	Se µg/g	Sm µg/g	Cd µg/g
Central Slovakian Volcanic Field																			
SB1	Breziny, quarry	gt andesite	14	16.00	59.50	0.77	17.49	7.07	0.16	2.11	5.60	3.43	2.22	1.58	19.22	155.75	17.37	3.23	4.02
SK5	Vlci vrch	ol-px bas andesite	84	9.00	51.63	1.08	18.25	9.35	0.19	4.34	8.61	3.47	1.87	1.13	8.80	153.47	29.07	5.18	6.12
SK8	Ziar nad Hronom	high-Al basalt	104	9.00	51.59	1.20	17.69	10.11	0.21	4.49	8.85	3.11	1.66	1.03	8.56	158.58	38.65	3.57	4.83
SP4	Pol'ana SW	px andesite	99	16.00	58.12	0.88	17.41	7.71	0.14	3.03	5.93	3.05	2.25	1.42	11.20	96.44	31.10	3.56	4.47
SP5	Rochy W	px andesite	106	16.00	56.28	1.19	17.57	8.60	0.19	2.64	6.63	3.16	2.10	1.58	15.99	117.47	21.45	3.68	4.93
SV1	Hrusov SE, Csmakova	andesite	134	16.00	56.11	0.78	17.07	7.70	0.13	4.44	7.57	3.09	1.70	1.35	19.72	66.71	29.42	2.69	3.71
SV4	Celovce quarry	px andesite	129	16.00	56.88	0.92	16.73	7.43	0.15	4.46	6.88	2.38	2.55	1.54	24.85	366.46	38.73	3.33	4.36
Börzsöny																			
B134	Fekete-p, Szarvask	andesite	170	14.00	58.53	0.88	18.12	6.15	0.12	2.46	6.54	3.51	2.23	1.38	10.96	271.77	27.66	3.33	4.41
B144	Nagy-Mána hegy	andesite	170	14.00	56.98	0.76	18.29	7.61	0.14	2.82	6.35	3.16	2.40	1.44	21.23	112.39	23.60	3.39	4.22
B24A	Tar-Péter hegy	red andesite	180	14.00	57.72	0.64	17.49	7.16	0.19	2.41	6.64	3.23	2.90	1.58	20.76	263.24	20.78	3.84	4.58
B3	Nagyhíd hegy	andesite	174	13.50	54.57	0.96	18.44	8.47	0.19	3.01	7.30	3.39	1.90	1.71	12.30	97.91	23.03	3.48	4.81
B72	Hegyes hegy	vesicular andesite	175	13.50	55.30	0.90	17.84	8.61	0.20	2.74	6.82	2.99	2.59	1.87	29.82	839.87	21.16	3.98	5.07
Visegrádi Mts.																			
VH121	Dobogókő, Szerzőkő	andesite	210	14.00	50.99	0.75	18.79	8.45	0.18	5.31	8.75	2.38	1.30	2.93	15.29	1002.63	37.73	2.87	3.58
VH122	Dömbökapu	andesite	212	13.50	56.03	0.96	17.99	7.86	0.14	3.52	7.65	2.54	2.14	1.09	12.67	293.86	34.58	4.14	5.07
VH302	Vadállókő	red andesite	208	14.00	58.52	0.65	17.74	7.05	0.15	3.07	6.67	3.19	2.05	0.83	23.47	191.43	23.42	2.96	3.58
VHCS3	Kis-Csikóvár hegy	andesite	215	15.00	57.86	0.78	18.40	7.14	0.15	2.27	6.53	3.05	1.91	1.85	15.82	234.95	19.50	2.92	3.95
VHCS4	Nagy-Csikóvár hegy	andesite	215	15.00	57.85	0.67	17.81	6.78	0.17	3.30	6.37	3.03	2.13	1.78	21.07	812.24	14.33	2.70	3.61
VHH2	Holtvilágok	andesite	215	16.00	58.32	0.73	18.63	7.05	0.10	1.50	6.24	3.25	2.16	1.98	11.12	120.40	22.92	3.28	4.31
VHL2	Malom völgy, quarry	andesite	204	15.40	58.29	0.66	17.65	6.37	0.08	2.86	5.80	3.13	2.17	2.95	13.43	42.62	12.00	2.87	3.62
VHPR1	Prépost hegy	bas andesite	206	14.00	54.64	0.83	18.76	7.45	0.13	3.94	7.83	3.19	1.79	1.37	16.71	95.47	29.49	2.61	3.46
VHS10	Hídfelelős kereszt	andesite	183	14.00	57.67	0.51	18.23	6.12	0.14	3.23	7.23	2.80	2.04	1.86	24.75	1148.45	18.65	2.30	2.87
VHS3B	Szamar hegy	bas andesite	183	14.00	53.78	0.85	18.73	7.87	0.12	3.41	8.00	2.89	1.77	2.52	15.28	138.87	27.75	2.68	3.63
VHS4	Hídfelelős kereszt	bas andesite	183	14.00	56.14	0.78	18.05	8.15	0.15	3.01	7.18	3.00	1.95	1.54	18.17	114.06	28.05	2.85	2.80

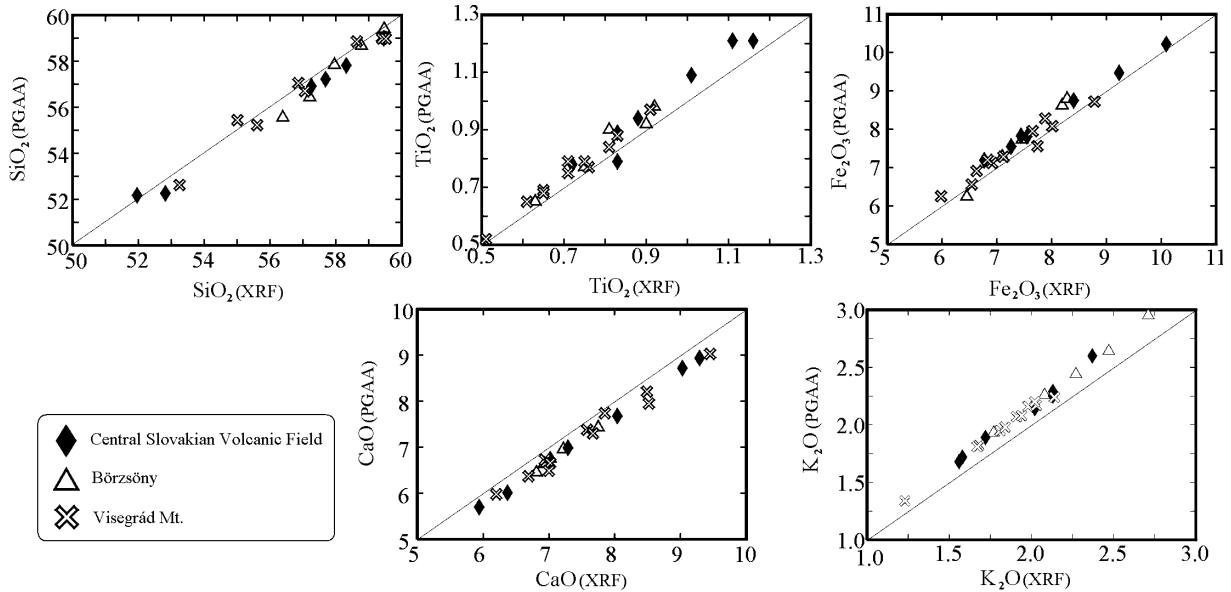


Fig. 4. Comparison of results from XRF and PGAA for selected major elements

In summary, based on the analysis of geological rock standards (Table 2) and volcanic rock samples (Table 3) previously analyzed by other analytical techniques, we conclude that the Budapest PGAA gives satisfactory results with high precision for major elements and some trace elements, especially for B. Similar results were obtained for metamorphic rocks.⁶⁸

Major element, boron and chlorine composition of the NPVF samples

Mineral/melt partition coefficients of B for the most important rock forming minerals are about 0.01. Therefore, it is a strongly incompatible element, which is concentrated in the residual liquids during magmatic differentiation. In order to minimize the influence of magmatic differentiation, our study focuses on the least evolved rocks of the studied area, i.e., basaltic andesites and andesites ($\text{SiO}_2 < 60$ wt.%). The SiO_2 contents of the measured volcanic rock samples (Table 3) vary between 50.99 and 59.50 wt.%. The most mafic rocks are the youngest (9 Ma) from the Central Slovakian Volcanic Field (CSVF). All the examined rocks fall in the high-K calc-alkaline series. Samples from the Börzsöny are more K-rich than those from the Visegrád Mts. (VMt.). The trace element composition of the andesitic rocks (Fig. 5) show enrichment in large ion lithophile elements

(LILE, e.g., Rb, Ba, Cs, K) and depletion in high field strength elements (HFSE, e.g., Nb, Ti), showing pattern typical of subduction related volcanic rocks. The basaltic andesites have lower B contents and higher HFSE contents than the andesites.

B content in the NPVF ranges from 8.56 to 29.82 $\mu\text{g/g}$ (Table 3). The highest B contents were measured in andesites and the lowest B values from basaltic andesites (CSVF), which are the youngest (9 Ma) among the studied samples. The B content of the andesites ranges between 11.12 and 29.82 $\mu\text{g/g}$. B contents of the basaltic andesites and andesites from the Visegrád Mt. did not show strong correlation with other major or trace elements. The strongest correlation can be seen between the B contents and some major and trace element concentrations of the CSVF samples. The B contents of these samples from the CSVF correlate positively with K_2O and slightly with H_2O (fluid-mobile elements) and negatively with TiO_2 , Al_2O_3 , Fe_2O_3 , Na_2O , Gd and Nb (fluid-immobile trace elements) (Fig. 6). Note that Nb and the $^{87}\text{Sr}/^{86}\text{Sr}$ isotope ratio, which are important for geological interpretations and used in this study, are impossible to detect with the present sensitivity of the Budapest PGAA system. Therefore, we obtain these data from ICP-AES and MS measurements, respectively.^{47,69}

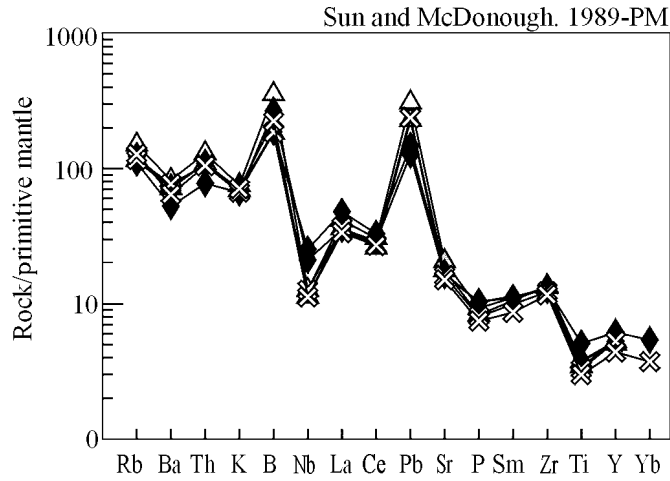


Fig. 5. Primitive mantle normalized trace element distribution of the Neogene volcanic rocks from the NPVF

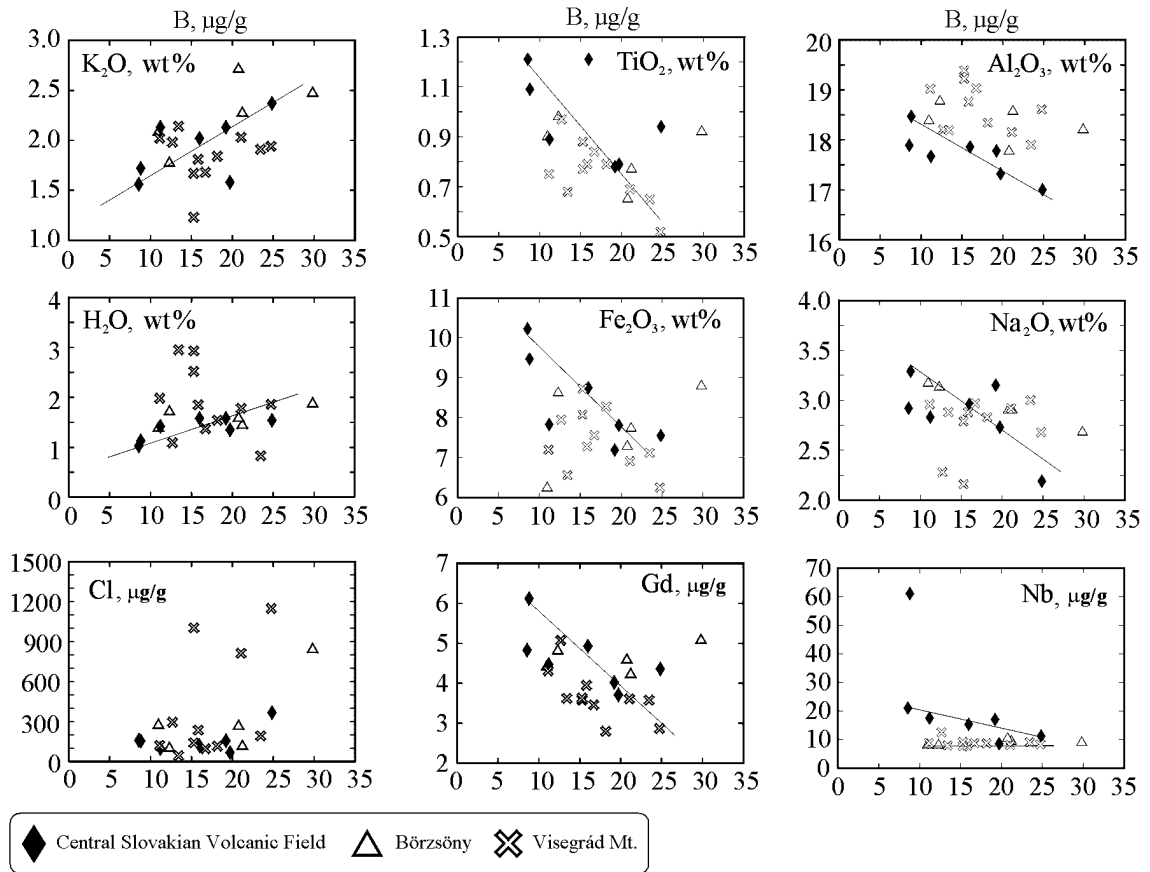


Fig. 6. Boron concentration of the CSVF samples shows positive correlation with K_2O , H_2O and negative correlation with Al_2O_3 , TiO_2 , Fe_2O_3 , Na_2O , Gd and Nb

Chlorine concentrations of the investigated samples are between 42.62 and 1148.45 $\mu\text{g/g}$ (Table 3). Both the highest and lowest Cl contents were measured in

andesites from the Visegrád Mts. (14–15 Ma). Cl contents of the rocks have no correlation with other trace and major elements. Cl contents of the samples from the

CSVF are relatively stable with variable SiO_2 , Fe_2O_3 and Na_2O content (Fig. 7). The 9 Ma basaltic andesite samples have the highest Fe_2O_3 concentration. Nb concentrations in the CSVF samples are much higher, while the Cl concentrations are lower than in the rest of the investigated area. Moreover, there is no correlation between the B and the Cl concentration of the volcanic samples (Fig. 6).

The B concentrations in the CSVF increase (8.56–24.85 $\mu\text{g/g}$) with growing distance (84–134 km) from the presumed subduction suture zone. However, no similar correlation can be observed in the Börzsöny-Visegrád Mts. (BVMts.). The samples Cl contents do not vary systematically with the distance from the presumed suture zone or with the age of the samples.

The Sm/Nb ratios are lower (<0.25) in the volcanic rocks at the CSVF than in the Börzsöny-Visegrád Mts. (BVMts.) but correlates positively with the B/Nb ratio at the CSVF (Fig. 8a). The B/Nb ratios are also higher (above 1.25) at the BVMts. than at the CSVF (Fig. 8a). The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of the whole rocks range from 0.7048 (CSVF) to 0.7103 (VMt.)⁷⁰ (Figs 8b and c). There is a slight positive correlation between the $^{87}\text{Sr}/^{86}\text{Sr}$ vs. B concentration in the CSVF, but no correlation can be observed in the BVMts. (Fig. 8b). While the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of the CSVF samples show wide variation, the Cl concentrations are stable. No correlation can be observed in the case of the BVMts. samples. Two samples (VHS10 and VH121) from the VMt. and one (B72) from the Börzsöny have much higher Cl content than the other samples have.

Discussion

The B concentration of the studied samples fall into the range shown by subduction-related volcanic rocks (average 2–35 $\mu\text{g/g}$).^{18,30–34} During subduction of oceanic slab, metasomatic processes strongly influence the fluid-mobile element enrichment in the magma source region.^{70,71} Boron and chlorine are enriched in source region during aqueous fluid metasomatism, due to their fluid-mobile behavior. In addition, B enters preferentially into the magmas, because of its incompatible character. During magmatic differentiation B shows enrichment in the evolving liquids. Thus, relatively high B concentration may be due to intense aqueous fluid metasomatism in the mantle source region of the melts, or due to magmatic differentiation. As B is not much enriched in the lower continental crust, the crustal contamination cannot increase significantly the B content of the rising magma, which forms less evolved rocks. This feature can be used to distinguish between slab derived fluid and material contamination and crustal contamination, respectively. However, Cl is an important trace element in the subduction related magmatic systems its complex behavior is not well understood yet. In our study the Cl content of the samples is quite variable and does not show significant correlation with any other elements or elemental ratios to draw further conclusions.

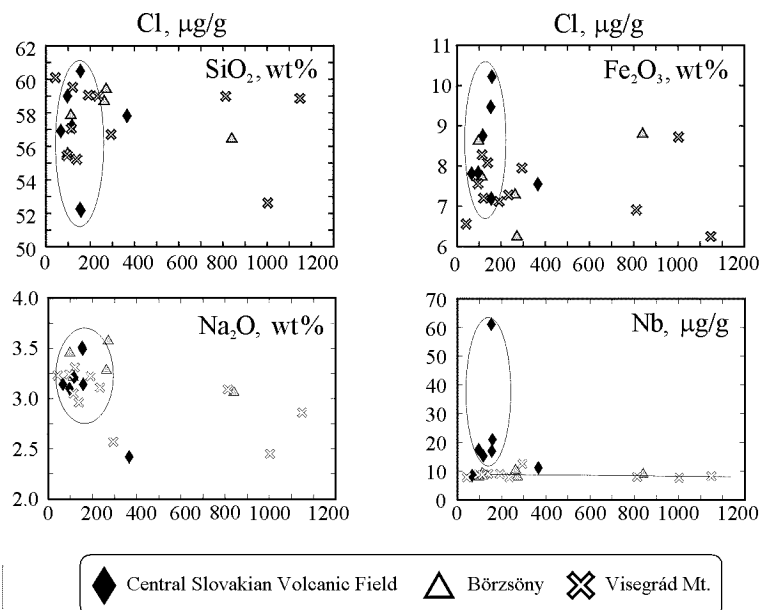


Fig. 7. Chlorine concentration of the CSVF samples shows narrow variation compare to the SiO_2 , Fe_2O_3 , Na_2O and Nb concentrations

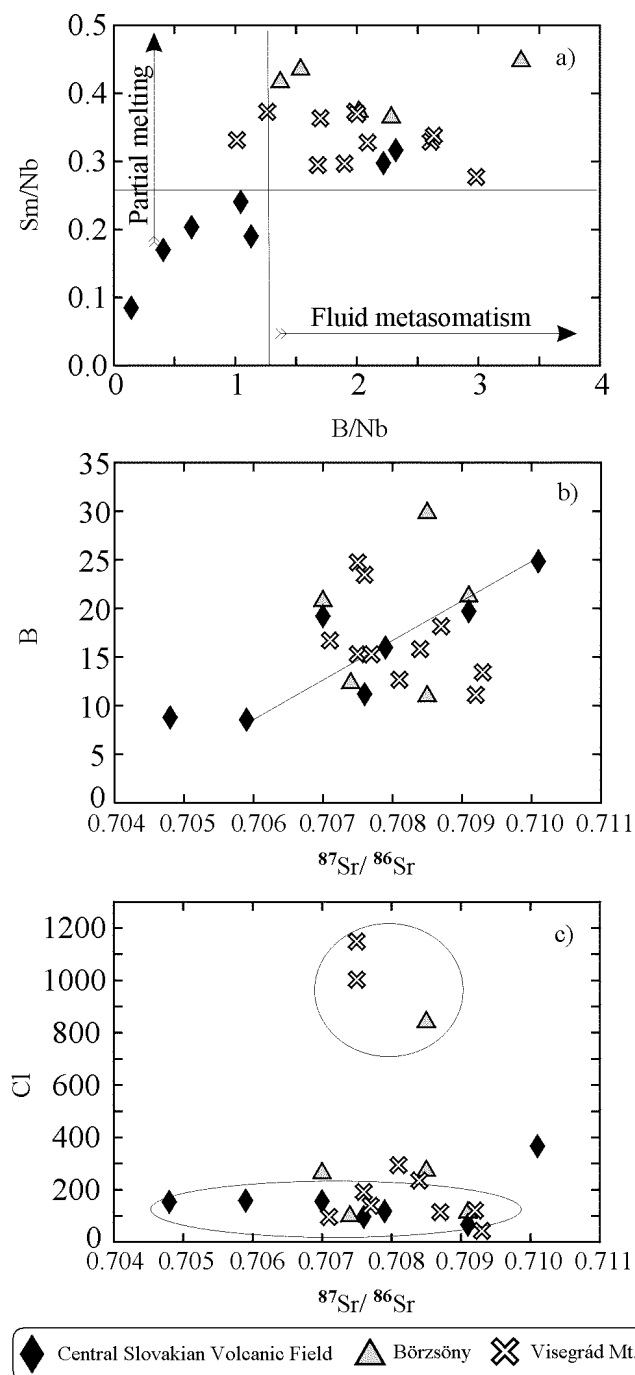


Fig. 8. Trace element and isotopic ratio diagrams of the basaltic andesite and andesite samples from the NPVF (a) B/Nb vs. Sm/Nb; (b) Sr-isotopic ratio plotted against B content; (c) Sr-isotopic ratio plotted against Cl content

In igneous systems, Nb behaves similar to B, i.e., they have similar low mineral/melt partition coefficients. Boron is mobile in aqueous fluids, whereas Nb is fluid-immobile trace element.⁷² Therefore, B/Nb ratio should be constant during partial melting and magmatic differentiation processes and it is influenced only by aqueous fluid transport mechanism. The B/Nb ratio is

commonly used as a sensitive indicator of aqueous fluid mechanism in the source region of subduction-related magmas.^{24,41,73–75} So, we used B/Nb ratios (Fig. 8a), which show great variation in the NPVF, to demonstrate the wide variation of fluid addition to the source region of the magmas under the investigated area. The variation of B/Nb ratio (0.5–3.5) in the samples is indicative of variable fluid addition. Sm/Nb ratio indicates the degree of partial melting, because Sm is less incompatible than B and Nb. The higher B/Nb and Sm/Nb ratios at the BVMts. indicate more significant fluid addition and relatively higher Sm/Nb ratios refer to possibly higher degree of partial melting (Fig. 8a) than at the CSVF. However, at the beginning of volcanism the degree of partial melting and fluid addition to the CSVF could be similar to that under the BVMts.

The B concentration correlates positively with the $^{87}\text{Sr}/^{86}\text{Sr}$ isotope ratios in the CSVF samples (Fig. 8b). Variation in the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio can be explained by various crustal components in the samples. High $^{87}\text{Sr}/^{86}\text{Sr}$ isotopic ratios imply strong crustal contamination during the ascent of magmas or source contamination by fluid released from subducted sediments. HARANGI et al.⁴⁷ suggested that involvement of lower crustal rocks could have been significant in the genesis of the early-stage volcanic rocks of the NPVF. However, lower crustal rocks have typically low B concentration ($\sim 5 \mu\text{g/g}$) as shown by LEEMAN et al.³⁹ Thus, if we exclude significant upper crustal (average $10 \mu\text{g/g}$) contamination processes,³⁹ the positive correlation between the $^{87}\text{Sr}/^{86}\text{Sr}$ and B could help quantify the degree of involvement of subducted sediment-derived fluids in the genesis of the NPVF rocks. The Cl contents do not change significantly with the growing $^{87}\text{Sr}/^{86}\text{Sr}$ ratios, except for a few samples from the BVMts. which have extremely high Cl content compared to the rest of the samples. This seems to indicate that in the NPVF the crustal contamination did not influence the Cl content of the volcanic rocks. High Cl content of the above mentioned samples (VHS10, VH121 and B72) might originate from the inhomogeneity of the slab and/or the different rate of Cl-enriched fluid addition to the source region.

In the NPVF the B and Cl contents do not correlate with the distance of the samples from the assumed suture zone of the former subduction. In the Börzsöny the distance between the samples is only 10 km, but the variation in the B content is wide (11–29.8 $\mu\text{g/g}$). In the CSVF we observed a positive correlation between the B content and distance from the subduction suture zone, which is related to the age difference of 7 million years between the samples. The basaltic andesite lavas with the lowest B content, formed in the final volcanic stage (9 Ma) are situated closer to the proposed suture zone of subduction. The age difference of the volcanic rocks in the NPVF is large, ranging from 9 to 16 Ma with B

concentrations (8.56–29.82 µg/g), the youngest samples having the lowest boron content.

Conclusions

On the basis of PGAA measurements of international geological standards and comparing our results with previous XRF and ICM-AES data on the same samples, we recommend the Budapest PGAA facility for investigation of especially B, some other trace (Cl, Sm, Gd, Nd and Sc) and major element compositions of geological samples as it gives satisfactory results with high precision.

It is important to measure the B concentration of the volcanic rocks, because it suggests the contribution of oceanic sediments and the subducted slab to arc magma genesis. B concentrations of the volcanic samples from the NPVF in the Carpathian-Pannonian Region are in the typical range of subduction-related volcanic rocks. The wide variation of B and Cl concentration of the studied samples suggest various degrees of fluid addition to the magma source regions. At the NPVF due to delayed volcanism (started 16.5 Ma) compared to the beginning of the subduction, (19–20 Ma) long-term fluid addition (2.5–3.5 million years) and sediment contamination occurred and caused metasomatism of the magma sources region. The BVMts are different from the CSVF in the aspects of source contamination by slab-derived fluids and sediments. The possible lower crustal contamination⁴⁷ did not influence the B and Cl content of the samples. The B content decreases with the age of the volcanic rocks. However, B as well as Cl concentrations do not show any relationship with the spatial distribution of the samples, i.e., with the distance from the assumed subduction zone. This may indicate that the fluid-mobile B and Cl already released from the slab closer to the suture zone or the B enrichment does not relate to active subduction but was due to a former subduction event.

These geochemical characters are consistent with the model proposed by LEXA and KONEČNY,^{76,77} HARANGI⁴⁷ and SEGHEDI et al.¹ who suggested that the Miocene calc-alkaline volcanism was associated with extension of the Pannonian Basin that followed shallow angle subduction.

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