

Boron concentration measurements by prompt gamma activation analysis: Application on miocene-quaternary volcanics of the Carpathian-Pannonian Region

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Prompt gamma activation analysis is a highly powerful analytical method in geology, due to its applicability to determine the concentration of all major and few trace elements in whole rock samples. Furthermore, the boron concentration can be determined with proper accuracy without time consuming sample preparation. The reliability of this method was checked on geological standards¹ and on other volcanic rocks, which were analyzed previously by XRF and TIMS for many major and trace element components and Sr-isotopes.² Boron concentrations of volcanic rock samples from the East Carpathian Volcanic Field (Eastern-Central Europe) are reported here for the first time. The boron concentrations were measured for an improved definition of the petrogenesis of these rocks and to understand the fluid addition processes during subduction-related volcanism in this region.

Introduction

Recently prompt gamma activation analysis (PGAA) has become a more often used analytical method in geology, due to its high sensitivity for boron. The average abundance of boron is very low (at $\mu\text{g/g}$ level), thus in most cases it is below the detection limits of most analytical techniques (XRF, ICP, EMPA, etc.). In a series of test measurements on international standards, performed at the PGAA facility of the Budapest Research Reactor (BRR),¹ the detection limit for boron was found as low as $0.3 \mu\text{g/g}$. Besides the major components, PGAA is also suitable to determine other geologically important trace elements, such as chlorine, samarium, hydrogen and gadolinium.

Boron as an incompatible, highly fluid-mobile trace element can provide geochemical information about the fluid cycles of subduction zones and subduction related volcanic systems.^{3–8} Boron is a relatively rare element in nature. It is concentrated mostly in altered oceanic crusts and sediments ($80\text{--}120 \mu\text{g/g}$).^{5,9–10} In the upper continental crust the average boron content is $\sim 10 \mu\text{g/g}$, whereas the lower crust appears to be significantly depleted ($\sim 5 \mu\text{g/g}$) due to boron mobilization during high-grade metamorphism. The boron content is an order of magnitude lower in the upper mantle ($\sim 0.1\text{--}0.3 \mu\text{g/g}$).¹¹ In contrast, the volcanic arc rocks are enriched in boron (average $35 \mu\text{g/g}$), which indicates an involvement of fluid components derived from the subducted oceanic crust and sediments during the genesis of the magma. As subduction proceeds, the down-going oceanic lithosphere undergoes progressive metamorphism and dehydration. Boron is a highly fluid-mobile element, consequently showing strong affinity to

different aqueous fluids such as those liberated during the devolatilization of subducting slab. These fluids penetrate and metasomatize the mantle wedge above the subducted slab.¹² In addition, boron is an incompatible element as it preferably stays in the melt phase than in minerals, thus it enriches in the melt during partial melting. Therefore, boron is a useful geochemical tracer of subduction-related processes. The concentration of boron in subduction related volcanic rocks (arc volcanic rocks) also depends on the conditions of the subduction and the boron input.⁹ Thus, variation of boron concentration across an arc may well indicate characteristics of the subduction process. The other advantage in the determination of the boron concentration in volcanic arc rocks is that, the boron concentration of the lower crustal rocks is relatively low, hence, the assimilation of such material during the ascent of the magma will not influence the boron content. On the other hand, the Sr isotope ratio can refer to crustal contamination.¹³

One of the most exciting questions in the genesis of the calc-alkaline volcanic rocks in the Carpathian-Pannonian Basin (Eastern-Central Europe, Fig. 1a) is the relationship between the boron content and the series of subduction and extension events, respectively, and the crustal contamination effects. In this study we have focused on the east-southeast segments of the Inner-Carpathian calc-alkaline volcanic arc, i.e., the East Carpathian Volcanic Field (ECVF, Fig. 1b) and analyzed more than 20 volcanic rock samples. The variation of the boron concentrations (in the range of $5\text{--}80 \mu\text{g/g}$) was determined as a function of age, since the volcanic formations in the ECVF towards the south are younger. Boron concentration as a function of Sr isotope ratio (measured by MC-TIMS)² has also been

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investigated. In combination with previous experimental result, our measured boron concentrations allowed us to distinguish between the formation and evolution of the calc-alkaline volcanic rocks in the East Carpathian Volcanic Field (ECVF).

Geodynamic evolution and volcanism at the Carpathian-Pannonian Basin in the last 20 million years

For a better understanding of the geological problems, raising questions, and our conclusions from the measured data, we hereby summarize our present knowledge of the last 20 million years of geological evolution of the Carpathian-Pannonian Region.

The Carpathian-Pannonian Region was formed during the Neogene-Quaternary by the 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.¹⁴ This rigid crustal block moved northeastward-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. The termination of the subduction was graded from west to east-southeast.¹⁵ Behind the subduction zone, a back arc basin (i.e., the

Pannonian Basin, Fig. 1a) was formed by lithospheric extension. The southward subduction and roll-back of the weakened south edge of the European plate under the ALCAPA terrain¹⁶ and suction exerted by this subduction could have helped the formation of the lithospheric stretching in the back arc region.¹⁷

Experimental

PGAA apparatus

The determination of boron and some other trace elements (Cl, Sc, Sm and Gd) together with major components was carried out using the prompt gamma activation analysis (PGAA) facility at the Budapest Research Reactor (Hungary). The principle of the PGAA method is the detection of prompt γ -rays which originate from the (n,γ) -reactions. The prompt gamma radiation is characteristic, hence, qualitative and quantitative analysis is possible from the prompt gamma spectrum, considering the energies and intensities of the peaks. From the core of the 10 MW research reactor a beam of so-called “cold neutrons” is guided to the PGAA apparatus. The cold neutron beam has a $5 \cdot 10^7 \text{ n} \cdot \text{cm}^{-2} \cdot \text{s}^{-1}$ thermal equivalent flux at the sample position. The neutron beam during these measurements was collimated to an area of $2 \times 2 \text{ cm}^2$, and the typical irradiation time lasted for 90–120 minutes.

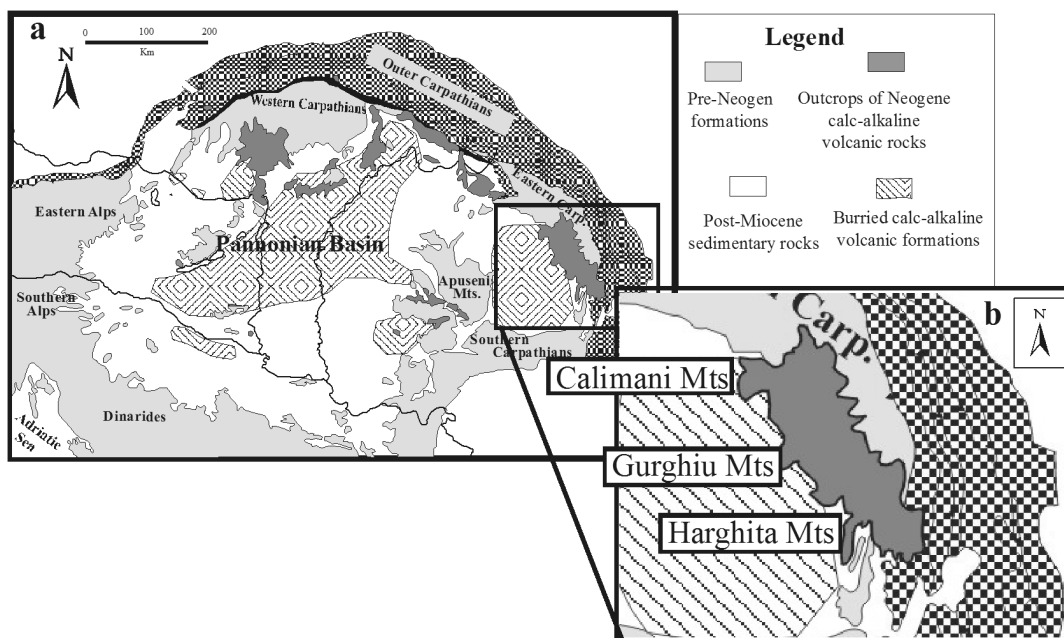


Fig. 1. Geological map of the Carpathian Pannonian Region (CPR); Occurrence of the calc-alkaline volcanic rocks in the CPR (a); Eastern Carpathian Volcanic Field (ECVF) (b)

The prompt gamma spectrometer consists of a Canberra high purity Ge (HP Ge) detector, a bismuth-germanate (BGO) Compton guard, and lead shielding. The signals of the detectors are processed with standard electronics and the spectra were collected with a multichannel analyzer connected to a personal computer.^{18–20} For the spectrum evaluation we used the Hypermet PC software.²¹ The Doppler-broadened boron peak at 477.6 keV were fitted with an improved model by SZENTMIKLÓSI et al.²²

Analyzing volcanic rocks and geological standards by PGAA

The reliability of PGAA measurements for geological samples was checked on international geological standards,¹ and on volcanic rocks, which have previously been measured by XRF and TIMS.² The SiO₂ contents of the examined basalt, basaltic andesite and andesite samples fall in the range of 51 to 63 wt.%, thus we chose to investigate volcanic rock standards from the Geological Survey of Japan (GSJ) in the same SiO₂ range, i.e., basalts: JB-1A, JB-2, JB-3 and andesites: JA-2, JA-3. The powdered rock samples were dried at 105 °C for 8 hours and 2–3 g of each sample was heat-sealed in fluorinated ethylene propylene (FEP) film (size of 2.5×3.5 cm²).

The sensitivity and the equivalent detection limit of PGAA vary over a wide range for different elements. For each element, we can determine the detection limit c_L from the measured spectra according to:

$$c_L = \frac{3\sigma_B \cdot \text{FWHM}}{S \cdot t} \quad (1)$$

where σ_B is the standard deviation of the baseline (background) counts in the spectrum and FWHM is the typical full-width-half-maximum value of the significant γ -ray line. The detection limit is inversely proportional to the measurement time, t and to the sensitivity of boron, S . These must be individually determined for every measurement. The detection limit gives the amount of boron that can produce a significant identifiable peak in the measured spectrum. The contribution of the background to the boron peak, which originates from the B₄C containing neutron shielding, was subtracted. Obviously, one can improve the sensitivity with the increasing measurement time and the amount of the samples.²³ According to Eq. (1), the detection limit for boron was 0.3 $\mu\text{g/g}$ for 2–3 g samples after 1.5–2 hours of measurement time.

The volcanic rocks, which were previously investigated by MASON et al.,² for major, trace element concentrations and Sr isotope ratios with XRF and TIMS were also measured by PGAA. The main objective was to obtain their boron concentration, but in addition we determined all major and few trace element

concentrations of these rocks. Thus we were able to compare major element data obtained by XRF with those of the PGAA.

Results and discussion

The boron data of geological standards measured with PGAA agree well with the given GSJ values.²⁴ As Fig. 2. shows, the PGAA results for major components in the geochemical reference samples agree well with the given values²⁴ within the uncertainty limit. In the cases of CaO, Na₂O and K₂O, we found systematic differences. MgO and CaO concentrations measured with PGAA are lower than the standard values, whereas the amount of Na₂O and K₂O seemed to be overestimated by the present measurements. The reason of the bias is under investigation.

Similarly to the comparison of standards, the XRF and PGAA results of volcanic rocks agree well with each other (Fig. 3). However, these data show larger deviations than the PGAA/standard value ratios, due to the higher uncertainty of XRF measurements.²⁴

The main objective in measuring the volcanic rocks by PGAA is to obtain the boron concentration of different samples. As mentioned in the introduction the boron concentration of the volcanic rocks implies subduction processes. In order to have significant information about boron enrichment itself via metasomatism, excluding the effect of magma differentiation, mixing and mingling, we examined only basaltic andesite and andesite samples (SiO₂ 51–63 wt.%). The boron concentrations vary in the range of 4.9–79.9 $\mu\text{g/g}$ in the ECVF. The highest and the largest variation of the boron content were obtained among the Northern-Harghita Mts. (NHMTs) samples.

The H₂O content of the samples does not change much (Fig. 4a), although the largest variation obtained in the Northern-Harghita Mts samples, correlates positively with the boron content (Fig. 4a). This implies massive fluid addition under the area.

Variation in the ⁸⁷Sr/⁸⁶Sr ratio can be explained by various crustal components in the samples. High ⁸⁷Sr/⁸⁶Sr isotope ratios may imply strong crustal contamination during the ascent of magmas or source contamination by fluids released from subducted sediments. The ⁸⁷Sr/⁸⁶Sr ratios in the ECVF are relatively low (<0.707) and do not change much referring to no or low scale crustal contamination (Fig. 4b). However, the boron concentration alters more significantly indicating the involvement of subducted sediment-derived fluids in the genesis of these rocks, especially the NHMTs samples.

A complex metasomatic fingerprint (enrichment in fluid-mobile and incompatible elements like B, K, Rb, Ba, etc.) can be detected in the ECVF. The ECVF is parallel with the oblique subduction zone, thus we can

not measure the variation of boron content across arc, even though boron is systematically increasing towards the south (Fig. 4c) i.e., towards the younger samples.

The only exceptions are the youngest samples (0.2 million years old) from the Southern-Harghita Mts., which have relatively low boron content (Fig. 4c).

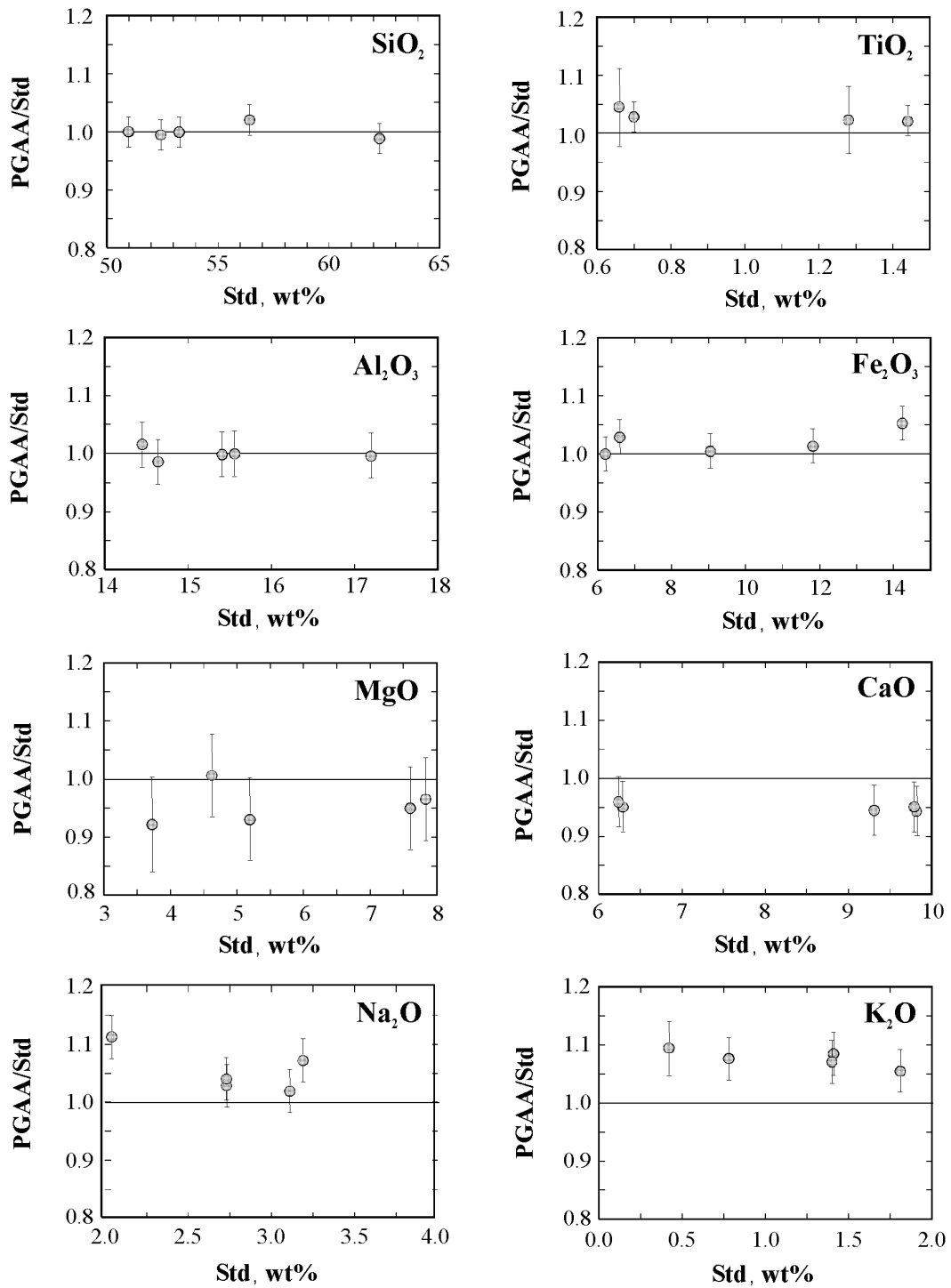


Fig. 2. Ratio of the PGAA concentrations and standard values²⁴ vs. major element content of volcanic rock standards (Geological Survey of Japan (GSJ)).²⁴ The given uncertainties of the data are $\pm 1\sigma$

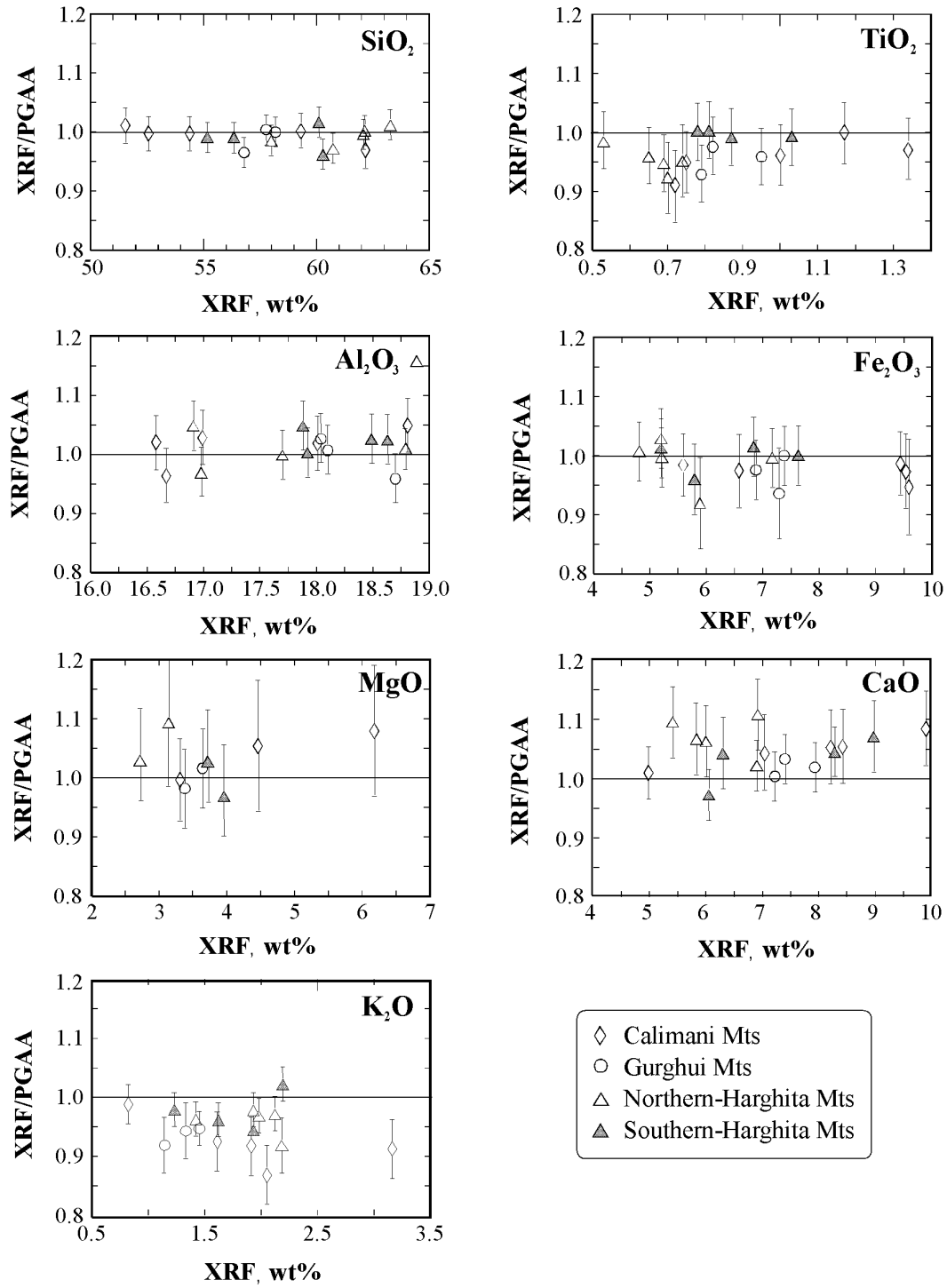


Fig. 3. Major component ratios of volcanic rocks measured with XRF² and PGAA vs. the wt.% of the elements of interest

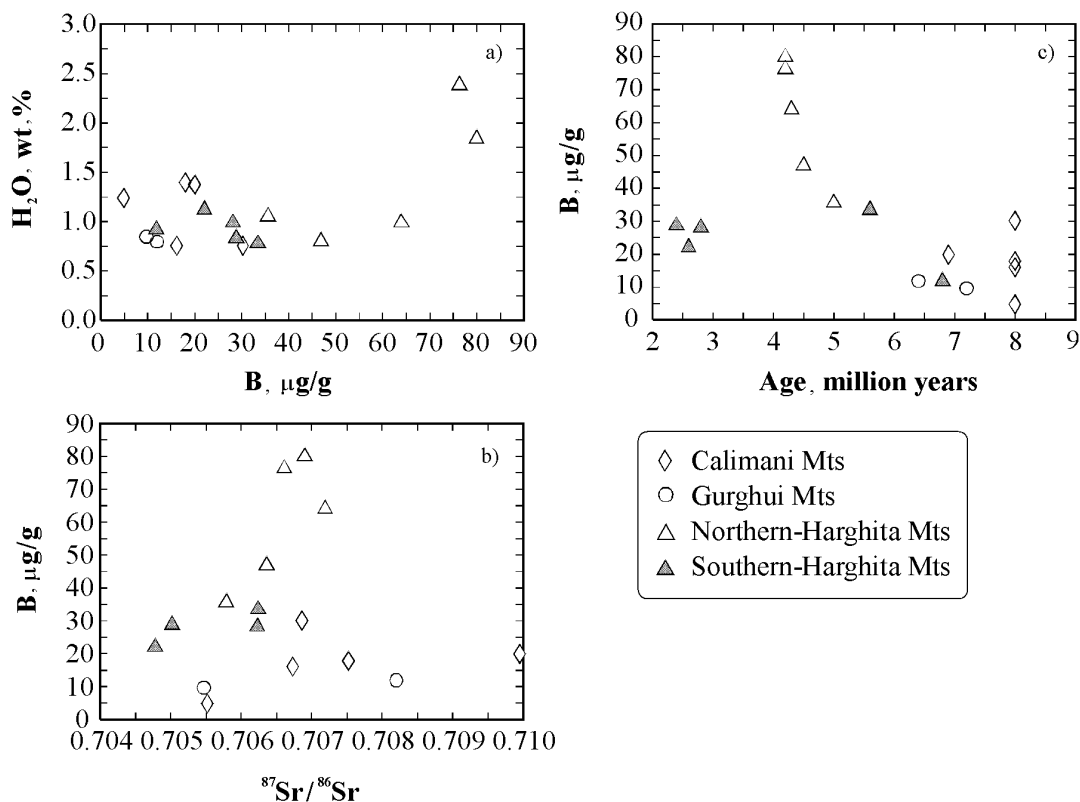


Fig. 4. Boron concentration data of the examined Eastern Carpathian volcanics plotted against: H₂O concentration (a); ⁸⁷Sr/⁸⁶Sr ratio (b); the age (million years) of the samples (c)

Conclusions

Based on measurements of geological standards, we can conclude that prompt gamma activation analysis gives satisfactory results with proper accuracy and reliability for major elements and some trace elements (Cl, Gd, Sm, Sc, V), especially for boron. However, without sample preparation it has insufficient sensitivity for other, geologically important trace elements (e.g., Pb, La, Nb, Ba, Be) and isotope ratios (e.g., ⁸⁷Sr/⁸⁶Sr, ¹⁴³Nd/¹⁴⁴Nd, ²⁰⁶Pb/²⁰⁴Pb). Nevertheless, PGAA is an easy-to-use method for the determination of boron in whole rock samples, making it an essential complementary method in geochemical analysis.

Measuring the boron concentration in the volcanic rocks from the east-southeastern part of the Inner-Carpathian Neogene Volcanic Arc (East Carpathian Volcanic Field, Eastern-Central Europe) is valuable for further information about the fluid addition to the magma source regions and the relation to subduction events under the volcanic mountains.

The strongest fluid addition in the examined areas occurred beneath the NHMts (35–80 μg/g). In the rest of the ECVF the fluid addition was also variable (5–35 μg/g) but significantly lower. The melt generation

regions beneath the volcanoes were variably enriched and more or less contaminated with slab-derived fluids. A complex metasomatic fingerprint can be detected in the volcanic rocks of the ECVF. The ECVF is parallel with the oblique subduction zone and the magmatic activity migrated towards the south with time. The boron concentration increases with the decreasing age of volcanism, whereas it is low at the end of volcanism in the Southern-Harghita Mts (SHMts). The magma source region of the SHMts changed when the slab breakoff propagated southward and got closer to the subduction suture zone. It is possible that most fluids left the slab before reaching the arc. The other probable explanation is that the fluids just had time to reach the arc, but due to the slab breakoff and asthenospheric mantle upwelling and mixing with the depleted melt,²⁵ the boron content of the magma decreased.

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References

1. K. GMÉLING, SZ. HARANGI, ZS. KASZTOVSZKY, J. Radioanal. Nucl. Chem., 265 (2005) 201.
2. P. R. D. MASON, H. DOWNES, M. THIRLWALL, I. SEGHEDI, A. SZAKÁCS, D. LOWRY, D. MATTEY, J. Petrol., 37 (1996) 927.
3. J. SPIVACK, J. M. EDMOND, Geochim. Cosmochim. Acta, 51 (1987) 1033.
4. G. E. BEBOUT, M. D. BARTON, Chem. Geol., 108 (1993) 61.
5. J.G. RYAN, C. LANGMUIR, Geochim. Cosmochim. Acta, 57 (1993) 1489.
6. T. ISHIKAWA, E. NAKAMURA, Nature, 370 (1993) 205.
7. C. F. YOU, A. J. SPIVACK, J. H. SMITH, J. M. GIESKES, Geol., 21 (1993) 207.
8. S. TONARINI, W. P. LEEMAN, L. CIVETTA, M. D'ANTONIO, G. FERRARA, A. NECCO, J. Volc. Geoth. R., 3022 (2003) 1.
9. W. P. LEEMAN, V. B. SISSON, M. R. REID, Geochim. Cosmochim. Acta, 56 (1992) 775.
10. F. TERA, L. BROWN, J. MORRIS, I. S. SACKS, J. KLEIN, R. MIDDLETON, Geochim. Cosmochim. Acta, 50 (1986) 535.
11. M. CHAUSSIDON, G. LIBOUREL, Geochim. Cosmochim. Acta, 57 (1993) 5053.
12. C. F. YOU, A. J. SPIVACK, J. M. GIESKES, R. ROSENBAUER, J. L. BISCHOFF, Geochim. Cosmochim. Acta, 59 (1995) 2435.
13. SZ. HARANGI, Acta Geol. Hung., 44 (2001) 223.
14. L. CSONTOS, A. NAGYMAROSY, F. HORVÁTH, M. KOVÁC, Tectonophys., 208 (1992) 221.
15. J. E. MEULENKAMP, M., KOVAC, I. CICHA, Tectonophys., 266 (1996) 301.
16. L. FODOR, L. CSONTOS, G. BADA, I. GYÖRFI, L. BENKOVICS, Geol. Soc., London, Spec. Publ., 156 (1999) 295, in: The Mediterranean Basins: Tertiary Extension within the Alpine Orogen, B. DURAND, L. JOLIVET, F. HORVÁTH, M. SÉRANNE (Eds).
17. G. TARI, P. DÖVÉNYI, F. HORVÁTH, I. DUNKL, L. LENKEY, M. STEFANESCU, P. SZAFIÁN, T. TÓTH, Geol. Soc., London, Spec. Publ., 156 (1999) 215, in: The Mediterranean Basins: Tertiary extension within the Alpine orogen, B. DURAND, L. JOLIVET, F. HORVÁTH, M. SÉRANNE (Eds).
18. G. L. MOLNÁR, T. BELGYA, L. DABOLCZI, B. FAZEKAS, Á. VERES, I. BIKIT, Z. KIS, J. ÖSTÖR, J. Radioanal. Nucl. Chem., 215 (1997) 111.
19. ZS. RÉVAY, T. BELGYA, ZS. KASZTOVSZKY, J. L. WEIL, G. L. MOLNÁR, Nucl. Instr. Meth. Phys. Res., B213 (2004) 385.
20. ZS. KASZTOVSZKY, ZS. RÉVAY, T. BELGYA, B. FAZEKAS, J. ÖSTÖR, G. L. MOLNÁR, J. BOROSSAY, J. Anal. Atomic Spectr., 14 (1999) 593.
21. ZS. RÉVAY, T. BELGYA, P. P. EMBER, G.L. MOLNÁR, J. Radioanal. Nucl. Chem., 248 (2001) 401.
22. L. SZENTMIKLÓSI, K. GMÉLING, ZS. RÉVAY, J. Radioanal. Nucl. Chem., 271 (2007) 447.
23. GY. SZAKMÁNY, ZS. KASZTOVSZKY, Eur. J. Mineral. 16 (2004) 285.
24. S. TERASHIMA, N. IMAI, S. ITOH, A. ANDO, N. MITA, Bull. Geol. Surv. Japan, 45 (1994) 305.
25. I. SEGHEDI, H. DOWNES, A. SZAKÁCS, P. R. D. MASON, M. F. THIRLWALL, E. ROSU, Z. PÉCSKAY, E. MÁRTON, C. PANAIOTU, Lithos, 72 (2004) 117.