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## PROMPT GAMMA ACTIVATION ANALYSIS (PGAA) OF THE LOWER PERMIAN RHYOLITIC ROCKS FROM THE NORTH SUDETIC BASIN

**Abstract:** The major aim of the our measurements was to compare the geochemical data obtain by XRF and ICP-MS methods with the results determined using nondestructive nuclear method – prompt gamma activation analysis (PGAA). The whole-rock samples of Lower Permian rhyolites of different genesis (ignimbrites, lava flows and subvolcanic intrusions) from the southeastern part of the North Sudetic Basin were selected for analyses. Together with major elements some trace elements (B, Nd, Sm and Gd) were also determined.

**Key words:** prompt gamma activation analysis (PGAA), boron, volcanic rocks, Świerzawa Graben, North Sudetic Basin, SW Poland

### INTRODUCTION

Prompt gamma activation analysis (PGAA) is a nuclear analytical method, which characterized by absence of contamination or evaporation problems during sample preparation (Byun *et al.* 2004). Moreover, PGAA offers unique possibility to obtain data on bulk composition without actually destroying the samples. All of these, because no needs of samples preparation for these measurements. It is crucially important that, the same samples after radioactivity decay can be studied by means of other analytical methods (INAA, ICP-MS, SIMS, etc.).

The principle of the PGAA method is the detection of prompt  $\gamma$ -radiation which originate in the (n, $\gamma$ )-reactions during neutron irradiation (Robertson, Dyar 1996; Révay, Belgya 2004). The energy and intensity of the prompt gamma radiation are directly measured by a spectrometer and qualitative and quantitative analysis of major elements and some trace elements such as transition and the light rare earth elements is possible. Moreover, hydrogen, boron and chlorine could be determined by the PGAA method with good precisions and high sensitivity, even for very low concentrations in the sample (e.g. detection limit for boron is 0.3  $\mu\text{g/g}$ ).

### SAMPLES AND ANALYTICAL METHODS

The Lower Permian calc-alkaline volcanic succession from the southeastern part of the North Sudetic Basin (Świerzawa Graben) comprises volcanic rocks of different genesis (Pańczyk 2002; 2003). Small-volume eruption of different explosivity spread from elongated fissures. Therefore, the profile of volcanic sequence comprises deposits of base surges, non-welded and welded ignimbrites, lava flows as well as subvolcanic intrusions.

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Because of the possible effects of particle sorting and fractionation during the emplacement the deposition of base surges and pyroclastic falls were excluded, and only the lava flows and welded ignimbrites were chosen for analyses. Therefore, 3 samples of high-grade ignimbrites (the Świny ignimbrites), 5 samples of the Świny lavas; 5 samples of moderate-grade ignimbrites (the Popielowa ignimbrites), 4 samples of the Popielowa lavas and 2 samples of the subvolcanic intrusion from the Świerzawa Graben were measured with PGAA at the Budapest Research Reactor (BRR), Hungary. Almost all of the volcanic samples have been previously analysed with X-ray fluorescence spectrometry (XRF) and inductively coupled plasma-mass spectrometry (ICP-MS) in the Geochemical Laboratory of the Institute of Mineralogy, TU-Bergakademie Freiberg.

The 2-3 g of the whole rock samples were heat-sealed in fluorinated ethylene propylene (FEP) film. From the core of the 10 MW research reactor (Budapest) a cold neutron beam is guided to the PGAA apparatus. The cold neutron beam (20 K) has a  $5 \times 10^7 \text{ cm}^{-2} \text{ s}^{-1}$  thermal equivalent flux at the sample position. The neutron beam during these measurements was collimated to an area of 2x2 cm and the typical irradiation time lasted for 60-90 minutes. The prompt gamma spectrometer consists of a Canberra high purity Ge detector (HPGe), bismuth-germanate scintillator detectors (BGO), lead shielding and a multichannel analyser system operated by a personal computer. For the spectrum evaluation, we used the Hypermet PC software developed at the Nuclear Research Department, Institute of Isotopes of the Hungarian Academy of Sciences (Révay *et al.* 2001). The Doppler-broadened peak of boron at 477.6 keV was fitted with an improved model of Szentmiklósi *et al.* (2005).

## RESULTS, DISCUSSION AND CONCLUSIONS

The determination of almost all the major element oxides was possible, excluding CaO, MgO and P<sub>2</sub>O<sub>5</sub>. The concentrations of calcium, magnesium and phosphorus were under the detection limit of PGAA. Generally, the obtained results are in good agreement with previous XRF values and differences in results between the two methods are within the uncertainty limit (Table 1). The most problematic and controversial issue is the concentration of Na<sub>2</sub>O, which seems to be overestimated. However, sodium is known as a volatile element, which might be evaporated or contaminated during sample preparation and XRF measurements (Marschall *et al.* 2005). That is why the PGAA results amount to 110–130% of the XRF data (Table 1).

Unfortunately, it was impossible to quantify the transition elements such as V, Cr, Co and Ni because of their very low concentration in the rhyolitic samples, also below the detection limit of PGAA. On the other hand, among the light rare earth elements, neodymium, samarium and gadolinium could be determined with very high precision. However, the obtained contents of each of these elements are slightly higher, but still within the uncertainty limit, in comparison with ICP-MS values.

Table 1. Comparison of results obtained for selected major elements by means of XRF and PGAA.

	SiO <sub>2</sub>		TiO <sub>2</sub>		Al <sub>2</sub> O <sub>3</sub>		Na <sub>2</sub> O	
	XRF	PGAA	XRF	PGAA	XRF	PGAA	XRF	PGAA
Świny lavas	69.14	70.74	0.49	0.50	13.70	14.07	3.20	3.62
Świny ignimbrites	70.15	70.86	0.45	0.44	14.03	14.10	4.39	5.02
Popielowa lavas	69.41	71.88	0.51	0.51	13.71	13.78	3.57	3.96
Popielowa ignimbrite	71.50	72.20	0.37	0.38	13.66	13.47	3.57	3.92
Subvolcanic intrusion	71.61	72.66	0.26	0.26	12.69	13.01	0.79	0.98

Prompt gamma activation analysis due to the high neutron capture cross section of  $^{10}\text{B}$  as well as avoiding evaporation problems during the sample preparation, is an excellent method for determining boron. As a typically incompatible element (London, Morgan 1996), boron shows poorly defined increasing trend with the differentiation index ( $\text{SiO}_2$ , Fig. 1) on the Harker's variation diagram.

In general, the boron content of the measured samples varies from 9 to 56  $\mu\text{g/g}$ . Several different type of volcanites can be distinguished by their boron content. The boron concentrations range from 13 to 27  $\mu\text{g/g}$  for the lava flows (the Świny and Popielowa lavas); 12 and 20  $\mu\text{g/g}$  for high-grade ignimbrites and moderate-grade ignimbrites, respectively. The highest content of boron characterises the subvolcanic intrusions (above 40  $\mu\text{g/g}$ ).

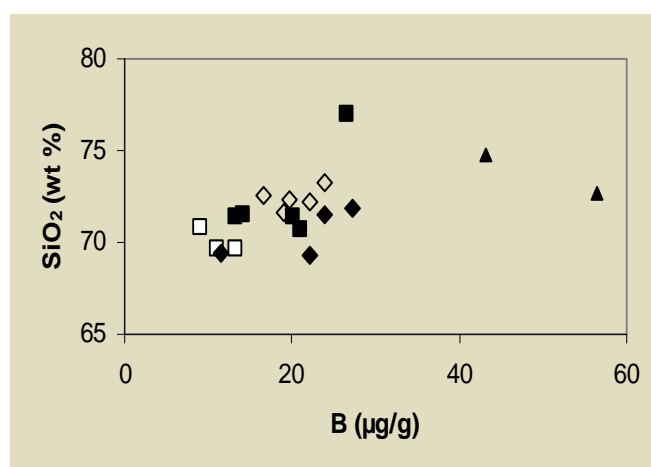


Fig. 1. The B vs.  $\text{SiO}_2$  diagram for the volcanic rocks from the North Sudetic Basin. The used symbols: squares – the Świny Lavas, empty squares – the Świny ignimbrites, diamonds – the Popielowa lavas, empty diamonds – the Popielowa ignimbrites, triangles – subvolcanic intrusion.

Most probably, the slight impoverishment in boron of both ignimbrites deposits could be the result of fractionation and in consequence losing boron during the magmatic eruption and degassing. On the contrary, the subvolcanic intrusion are strongly enriched in boron, presumably that could be explained by contamination of magma during the emplacement by metamorphic sheets.

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