Geologia Croatica	55/1	39 - 44	2 Figs.	4 Tabs.		ZAGREB 2002

Discriminant Function Analysis of Miocene Volcaniclastic Rocks from North-Western Croatia Based on Geochemical Data

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Key words: Volcaniclastic rocks, Discriminant function analysis, Geochemical data, Miocene, Pannonian Basin, Croatia.

Abstract

Preliminary results of discriminant function analysis of geochemical data of Miocene volcanic and volcaniclastic rocks revealed that it is possible to distinguish rocks of different ages, namely Egerian - Eggenburgian, Karpatian and Badenian. On the basis of calculated coefficients of classification functions, presented in the paper, it is possible to indicate the age of Miocene volcanic and volcaniclastic rocks if their trace element content is known. The analysis also showed that, especially in the case of volcaniclastic rocks, the mineral and petrological composition of the rocks should also be considered. Most of the investigated volcaniclastic rocks from the Možđenec and Kalnik areas, the age of which was unknown, are, according to discriminant function analysis, of Egerian - Eggenburgian age.

1. INTRODUCTION

In the north-western part of Croatia, belonging to the South Pannonian Basin, numerous small occurrences of Miocene volcanic and volcaniclastic rocks have been discovered (ŠIMUNIĆ et al., 1981; ANIČIĆ & JURIŠA, 1985; PAMIĆ, 1997 and references therein). According to the comprehensive work of PAMIĆ (1997), Neogene volcanic rocks could be divided into four groups: Egerian - Eggenburgian, Karpatian, Badenian and post-Badenian.

The age of volcanic and volcaniclastic rocks could be determined by radiometric methods or on the basis of field relationships with associated sediments. Radiometric methods are still not easily available, while scarce and poor exposures, due to the vegetation cover and tectonic deformation, often make it difficult to establish the correlation between sediments and volcanic rocks. The aim of this work (which forms a part of a detailed investigation of volcaniclastic rocks in the area) was to see if any significant difference in geochemical characteristics of the rocks of different ages exists, i.e. to determine the geochemical fingerprint of rocks of different ages. The theoretical background for the analysis lies in the fact that the composition of volcanic rocks depends on the geotectonic settings which changed during the evolution of Pannonian basin, and therefore should be recorded in the chemical composition of the rocks. Positive results could help distinguish rocks of unknown age.

For this purpose we used statistical methods, principally the discriminant function analysis, which is a powerful technique for classifying individual cases (samples) into previously defined groups on the basis of multiple variables, and one which has a broad application in determining solutions for geoscience problematics (DAVIS, 1986).

2. MATERIALS AND METHODS

In the scope of our research we investigated Miocene volcanic and volcaniclastic rocks, as well as rocks for which they were the origin, e.g. bentonites, that crop out in north-western Croatia, along the easternmost segment of Periadriatic fault system, from the Slovenian border to the Varaždinske Toplice. We analysed andesites from Cerovec (sample T-6-94B) and Lepoglava, dacites from Trlično (T-5-93-17) and Donje Jesenje (T-6-93-17E), bentonites from Poljanska Luka and Šaša, and tuffs (*sensu lato*) from the areas of Hromec, Jesenje - Cerje Jesensko, Lapornica - Šeprun, Jamno, Vuglovec, Podrute, Možđenec, and Kalnik Mountain (Fig. 1). In addition to these newly collected samples we analysed samples of rocks from Možđenec, described by KIŠPATIĆ (1909), that are deposited in the Croatian Natural History Museum (catalogue numbers 600: ZAG; 7113 and 7115: MP1). According to available data, the samples from Poljanska Luka are Badenian (ANIČIĆ & JURIŠA, 1985), those from Trlično, Hromec, Jesenje, Cerje Jesensko, Jamno, Lepoglava and Vuglovec are of Egerian - Eggenburgian age (ŠIMUNIĆ & PAMIĆ, 1993) as are those from Podrute (ŠIMUNIĆ et al., 1981). Volcaniclastic rocks from Šaša, Lapornica and Šeprun areas are interstratified with clas-

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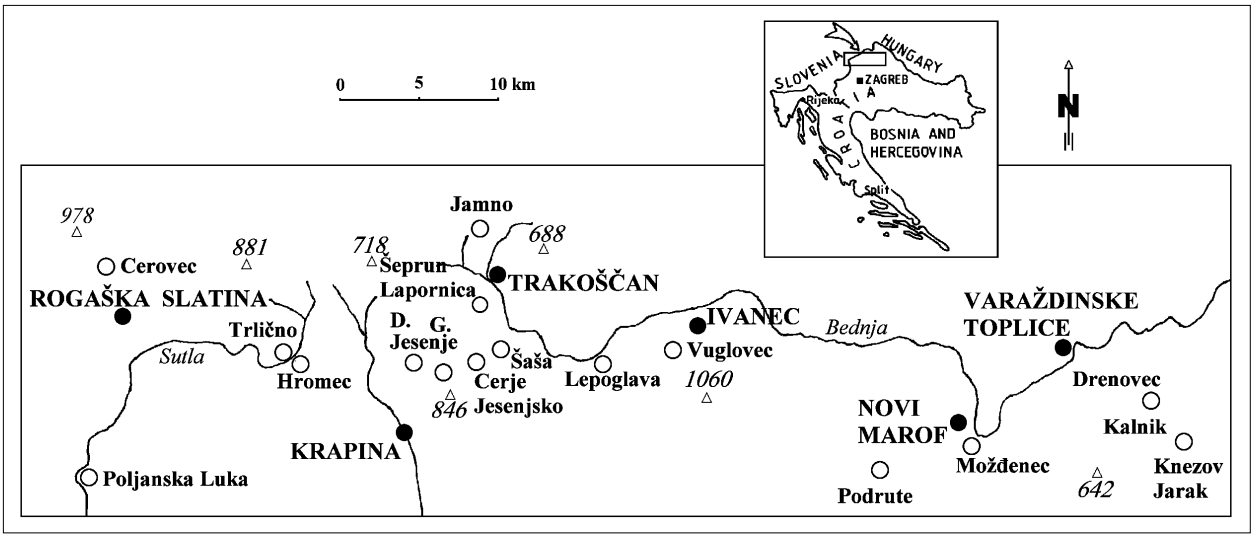

Fig. 1 Location map of investigated area. Circles represent sampling locations of volcaniclastic rocks.

tic rocks of Egerian to Karpatian age (ŠIMUNIĆ & PAMIĆ, 1993). The only published data on volcanic rocks from Možđenec area are from KIŠPATIĆ (1909), who presumed the same age for these rocks as for those from the Jesenje area. The tuffs in the Kalnik area, are, according to the unpublished fieldtrip guidebook[3], of Badenian age. Investigated samples are listed in the lower part of Table 3 on the basis of sampling locality, successively from the west to the east.

The chemical composition of the rocks was determined on an ARL 8410 X-ray fluorescence (XRF) wavelength dispersive spectrometer equipped with an Rh-tube. Glass beads, for the determination of major elements, were prepared by melting a 1:1:4 mixture of water-free sample, $Li_2B_4O_7$ and $LiBO_2$. Measured intensities were corrected for matrix effect using the empirical model of LACHANCE & TRAILL (1966). H_2O^- was determined as loss of weight after 4 hr of drying at 110°C, while loss on ignition at 1025°C was taken as H_2O^+. Trace elements were analysed on pressed powder pellets. Details on the measuring conditions are given in TIBLJAŠ (1996). Results of the chemical analyses can be obtained from the authors on request.

The computer programme STATISTICA (STATSOFT, 1995) was used to carry out the discriminant function analysis of the collected data. Additional input data (element concentrations and geological age of the rocks) for the analysis were taken from PAMIĆ (1997). It was necessary to take logarithmic values of element concentrations, except in the cases of gallium and thorium, to achieve a normal distribution of the input data, which is one of the assumptions of discriminant function analysis. All statistically analysed samples are listed in Table 3. The first 25 samples are from PAMIĆ (1997). They are marked with symbols of the type E7 where letter designates age, i.e. E is for Egerian-Eggenburgian, while the numbers correspond to the sample numbers in the tables, in his book, that contain chemical compositions of the rocks of the age concerned. Due to the fact that, according to their major elements, as well as immobile trace element content, the investigated volcaniclastic rocks are mainly acid and rarely neutral (TIBLJAŠ et al., 2000) only data for the rocks that contain >55wt. % SiO_2 were considered. Rocks of known age were assigned to three age groups (Egerian - Eggenburgian, Karpatian and Badenian) and we tried to statistically distinguish these groups on the basis of rock geochemical characteristics, and finally, to assign each newly analysed sample of unknown age to one of these predefined groups. Due to the scarce available age data for the volcaniclastic rocks from Šaša, Lapornica, Šeprun, Možđenec and Kalnik areas their age was taken as unknown. The reason why we considered only three, instead of the four age groups described by PAMIĆ (1997), was that post-Badenian rocks are basic, while, as already mentioned, investigated volcaniclastic rocks are acid to neutral.

3. RESULTS

Standardised coefficients for two discriminant functions obtained by discriminant analysis of Miocene volcaniclastic rocks, based on their trace element content, are given in Table 1 together with their eigenvalues and relative and cumulative proportion of variance extracted by each function. The plot of discriminant scores given in Fig. 2 differentiates between rocks of three different ages. Function 1 explains 80.8 % variation of the data, with a high negative loading of Ce and positive of Cu

[3] ŠIMUNIĆ, A. (1981): Vodič ekskurzije kroz Kalničko gorje i sjeverozapadni dio Dravske depresije.- Unpublished (in Croatian), Croatian Geological Society, Zagreb, 25 p.

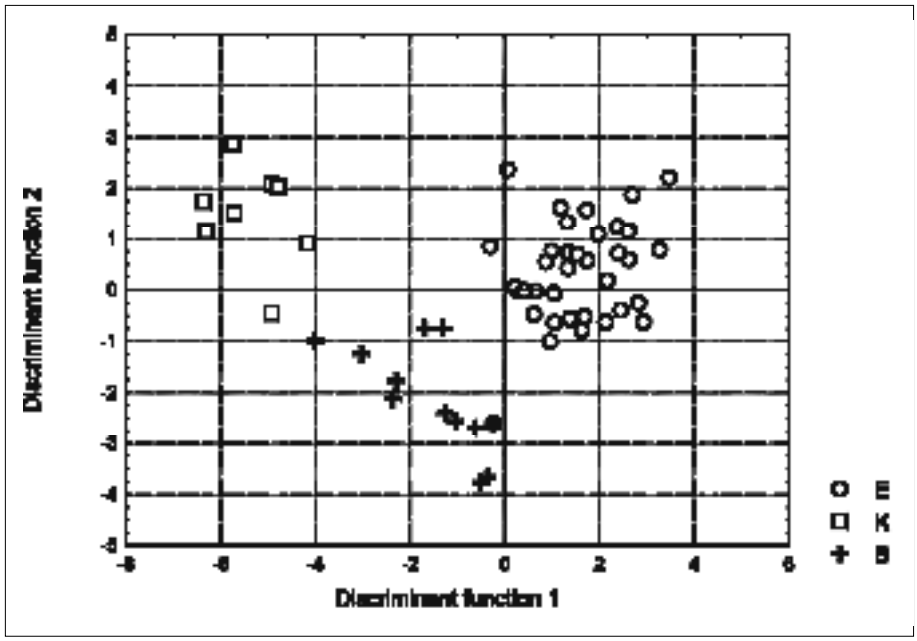

Fig. 2 Plot of discriminant scores along Function 1 versus Function 2, to discriminate volcanic and volcaniclastic rocks of different age (E = Egerian - - Eggenburgian, K = Karpatian, B = Badenian).

and Nd, and differentiates clearly between Karpatian samples and the Egerian - Eggenburgian ones, while the Badenian samples are transitional. The second function, of bipolar nature, that separates the Badenian samples from the Karpatian and Egerian - Eggenburgian ones, has a high negative loading of Cr and positive of V.

Coefficients (Ce = a_i, Cr = b_i, Cu = c_i, ..., Zr = m_i) as well as constant (C) of classification functions of a form

$$S_i = a_i x_1 + b_i x_2 + c_i x_3 + ... + m_i x_m + C \qquad (1)$$

where x_1, x_2, x_3, ..., x_m are concentrations, or their logarithms, of elements in the sample, are given in Table 2. On the basis of classification scores S_i each sample was

	Discriminant function 1	2
log Ce	-1.77543	0.1676
log Co	-0.0309	-0.50112
log Cr	-0.54651	-1.05168
log Cu	1.08006	0.71779
Ga	0.37776	-0.42432
log La	0.22753	0.05975
log Nb	0.3213	0.38883
log Nd	0.86753	-0.09416
log Ni	-0.3365	0.36198
log Pb	0.11063	-0.2135
log Rb	0.56435	0.48088
log Sc	-0.02668	0.25888
Th	0.07007	0.56928
log V	-0.60661	1.01681
log Y	-0.01791	0.38464
log Zn	-0.24478	-0.42836
log Zr	-0.26779	0.05888
Eigenvalue	6.12012	1.45174
% of variance - relative	80.83	19.17
% of variance - cumulative	80.83	100.00

Table 1 Standardized discriminant function coefficients and related statistics.

	Egerian - - Eggenburgian	Karpatian	Badenian
log Ce	449.13	558.69	492.772
log Co	-7.368	-8.292	-3.27
log Cr	-68.481	-64.002	-61.06
log Cu	-83.598	-103.009	-98.541
Ga	4.286	3.105	4.272
log La	56.803	50.776	53.417
log Nb	-61.637	-70.962	-71.916
log Nd	-62.86	-76.376	-68.161
log Ni	18.139	22.8	18.269
log Pb	-52.843	-57.491	-51.8
log Rb	-65.926	-78.378	-76.845
log Sc	-54.203	-53.004	-55.712
Th	0.023	0.056	-0.450
log V	211.827	225.997	209.631
log Y	-48.405	-45.449	-53.705
log Zn	-14.858	-11.073	-9.158
log Zr	418.166	434.039	423.642
Constant	-746.471	-918.402	-781.051

Table 2 Classification function coefficients used in formula (1) for grouping of volcaniclastic rocks according to their age.

included in the age group for which the score was highest (Table 3). The age attributed to the samples on the basis of references mentioned in the previous section is given in the second column of the table. The following three columns contains ages ascribed on the basis of discriminant analysis, ordered into the first, second, and third choice according to the posterior classification probabilities. These classification functions could be used for the classification of samples of unknown age if their chemical composition is known.

Table 4 gives a comparison between the actual and predicted number of samples in each age group. According to these results 96.5 % of samples have been classified correctly to their pre-defined groups. Misclassified samples are due to overlap in the discriminant space of Badenian samples with the Karpatian ones on one side, and Egerian - Eggenburgian on the other (Fig. 2).

4. DISCUSSION

The results of performed discriminant function analysis, presented in Tables 3 & 4 and Fig. 2, showed that Miocene volcanic rocks of different ages (Egerian - Eggenburgian, Karpatian and Badenian) could be confidently distinguished on the basis of their geochemical data. Almost all (55) of the 57 samples of known age, that were used as input data for the analysis, were classified correctly. This analysis showed that Karpatian samples could be successfully differentiated from Egerian - Eggenburgian ones. A slight overlap of Badenian samples with Karpatian and Egerian - Eggenburgian ones is in agreement with the conclusion of PAMIĆ (1997) that Egerian - Eggenburgian and Badenian rocks have similar geochemical characteristics. But in spite of that their discrimination could be performed quite successfully.

The high negative loading of Ce on discriminant function 1, that successfully discriminates the Karpatian samples is in accordance with the elevated Ce content of Karpatian volcanics (PAMIĆ, 1997). PAMIĆ (op. cit.) also noticed that Karpatian rocks have higher contents of Zr, Nb and La, and lower Sc and Y than other Tertiary rocks, but this is not obvious from standardised coefficients listed in Table 1. These coefficients indicate a higher Cu content in the Egerian - Eggenburgian samples than for the other two groups. Badenian samples are discriminated by function 2, in which Cr and V carry the main discriminatory potential.

As shown in Table 3, most of the volcaniclastic rocks from the Možđenec and Kalnik areas, of previously unknown age, are of Egerian - Eggenburgian age according to discriminant function analysis based on geochemical data. The only exception is the sample from the Kalnik area (VHK 500) which is Karpatian. Such results for the samples from the Možđenec area support the conclusions of KIŠPATIĆ (1909), based on petrographic investigations, about the contemporaneous age of the rocks from the Možđenec and Jesenje areas. Equivocal results for volcaniclastic rocks from Kalnik could indicate volcanic activity in both Egerian - Eggenburgian and Karpatian times, but such results are probably a consequence of problems encountered during investigations of the chemical composition of any volcaniclastic rock. The original chemical composition of volcaniclastic rocks is a consequence of magma composition, which depends mostly on geotectonic environment, and could be strongly modified by: (1) separation during transport of pyroclastic material from the volcanic vent to place of deposition, (2) alteration and (3) admixing of epiclastic or any other detrital material. Because of (3) we excluded from the analysis all of the samples that were an obvious mixture of volcanic and other detrital material. A Karpatian age obtained for the sample VHK 500 from the Kalnik area is probably the result of separation during transport. This is a sample of crystal tuff (*sensu lato*), and probably, its modal and, consequently, chemical compositions were strongly modified by processes of separation. The obtained chemical composition is thus probably nonrepresentative for the magma and the result for this sample should be treated cautiously. The Egerian - Eggenburgian age for samples from Kalnik is not in accordance with available data from ŠIMUNIĆ (1981)[3]. We also encountered the problem of modified chemical composition due to alteration, or rather, due to the product of alteration of volcanic glass. All of the samples with authigenic zeolites (clinoptilolite and/or mordenite) have relatively elevated contents of barium and strontium. These higher contents are the result of zeolite selectivity for these elements. Therefore we have to exclude these elements from the discriminant model, and the conclusion of PAMIĆ (1997) that Rb/Ba and Rb/Sr contents could differentiate Egerian - Eggenburgian and Badenian rocks could not be confirmed.

It is obvious that, for distinguishing volcaniclastic rocks of different age on the basis of geochemistry, it is necessary to know their chemical composition but also their mineral and petrographic composition.

The statistical analysis was carried out on a limited number of samples and therefore their results should be taken cautiously and should be tested by further investigation. In addition, the available chemical analyses were occasionally incomplete. Also, comparison of the literature and our own data, mainly because of different experimental methods was problematical and should be acknowledged.

5. CONCLUSIONS

The discriminant function analysis of geochemical data, which was carried out on a relatively limited number of samples of Miocene volcanic rocks from the Sava-Drava interfluve, enabled the following preliminary conclusions to be made.

Sample (locality)	Age according to literature data	Age according to discriminant function analysis Probability		
		1	2	3
E7	E	E	B	K
E8	E	E	B	K
E9	E	E	B	K
E11	E	E	B	K
E18*	E	B	E	K
E19	E	E	B	K
E20	E	E	B	K
K1	K	K	B	E
K3	K	K	B	E
K4	K	K	B	E
K7	K	K	B	E
K12	K	K	B	E
K15	K	K	B	E
K17	K	K	B	E
K20	K	K	B	E
B9	B	B	E	K
B25	B	B	E	K
B31	B	B	E	K
B35	B	B	E	K
B36	B	B	E	K
B40	B	B	E	K
B42	B	B	K	E
B43	B	B	E	K
B46*	B	K	B	E
B51	B	B	E	K
KREM (Poljanska Luka)	B	B	E	K
SIVA (Poljanska Luka)	B	B	E	K
T-6-94-4B (Cerovec)	E	E	B	K
T-5-93-17 (Trlično)	E	E	B	K
T-5-93-21 (Hromec)	E	E	B	K
T-5-93-18 (Hromec)	E	E	B	K
T-6-93-17E (Donje Jesenje)	E	E	B	K
T-7-90-K2 (Donje Jesenje)	E	E	B	K
T-790-K5 (Donje Jesenje)	E	E	B	K
T-7-90-K18 (Donje Jesenje)	E	E	B	K
T-7-90-K22 (Donje Jesenje)	E	E	B	K
T-7-90-K27 (Donje Jesenje)	E	E	B	K
T-7-90-K27G (Donje Jesenje)	E	E	B	K
T-7-90-15 (Donje Jesenje)	E	E	B	K
T-7-90-30 (Gornje Jesenje)	E	E	B	K
T-7-90-33 (Gornje Jesenje)	E	E	B	K
T-4-98-1 (Gornje Jesenje)	E	E	B	K
T-7-90-2 (Cerje Jesensko)	E	E	B	K
T-7-90-4B (Cerje Jesensko)	E	E	B	K
T-7-90-7 (Cerje Jesensko)	E	E	B	K
T-7-90-8 (Cerje Jesensko)	E	E	B	K
T-7-90-57 (Jamno)	E	E	B	K
T-7-90-62 (Jamno)	E	E	B	K
T-6-93-14 (Jamno)	E	E	B	K
LEPOGLAVA	E	E	B	K
T-4-99-8 (Vuglovec)	E	E	B	K
T-4-99-9 (Vuglovec)	E	E	B	K
T-4-99-10 (Vuglovec)	E	E	B	K
T-4-99-11 (Vuglovec)	E	E	B	K
PODRUTE	E	E	B	K
HMPM7110 (Jesenje)	-	E	B	K
T-7-90-Š1 (Šaša)	-	E	B	K
T-3-90-1 (Lapornica)	-	E	B	K
ŠEPRUN3	-	E	B	K
HMPM7113 (Možđenec)	-	E	B	K
HMPM7115 (Možđenec)	-	E	B	K
T-4-99-3 (Možđenec)	-	E	B	K
T-4-99-7 (Možđenec)	-	E	B	K
T-4-99-5S (Možđenec)	-	E	B	K
T-4-99-2A (Možđenec)	-	E	B	K
T-4-99-4 (Možđenec)	-	E	B	K
VHK500 (Kalnik - Drenovec)	-	K	B	E
T-5-99-1 (Kalnik - Knezov jarak)	-	E	B	K
KALNIK (Knezov jarak)	-	E	B	K
VHK227 (Kalnik - Knezov jarak)	-	E	B	K

Table 3 Classification of samples on the basis of discriminant function analysis. E = Egerian-Eggenburgian, K = Karpatian, B = Badenian. Incorrect classifications are marked with *. Samples from PAMIĆ (1997) are listed at the top, followed by newly analysed samples of known age, and finally by newly analysed samples of unknown age.

	Percent correct	E	K	B
E	97.3	36	0	1
K	100.0	0	8	0
B	91.7	0	1	11
Total	**96.5**	**36**	**9**	**12**

Table 4 Classification matrix; rows contains number of samples in each observed group while in columns number of samples in predicted groups are given.

1) It is possible to obtain an indication about the age of Miocene volcanic and volcaniclastic rocks on the basis of their chemical composition.
2) Most of the investigated volcaniclastic rocks from Možđenec and Kalnik areas, whose age was unknown, are, according to discriminant function analysis of Egerian - Eggenburgian age.

It must be stressed that such conclusions are only preliminary and should be confirmed or refuted by further investigations on more samples.

Acknowledgements

We are grateful to Marta CRNJAKOVIĆ for rock specimens from Croatian Natural History Museum, to Josip HALAMIĆ, Franjo PERCELA and Emil BUKVIĆ for help during sampling, and to Slobodan MIKO for his help in statistical analysis. We are indebted to anonymous referee for comments that greatly improved the manuscript. Thanks also go to Julie ROBSON for language editing. The study has been financially supported by the Ministry of Science and Technology of the Republic of Croatia (Project 119304).

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Manuscript received February 12, 2001.
Revised manuscript accepted May 20, 2002.