Carpathian Journal of Earth and Environmental Sciences, November 2012, Vol. 7, No. 4, p. 197 - 210

MAGMATIC AND POST-MAGMATIC EVOLUTION OF THE TOKAJ MTS. INTERMEDIATE LAVA ROCKS: STATISTICAL EVALUATION OF MAJOR ELEMENT DATA

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Abstract: Over 500 bulk analyses are available in the literature about the intermediate volcanic rocks of the Tokaj Mountains, NE Hungary. Following careful selection, about 400 samples were chosen for detailed statistical analysis in order to answer some open questions concerning petrologic circumstances of the rather complex magmatic series. The most fundamental aim was to identify the essential magmatic and post-magmatic processes, one can define using the geochemical data. Based on these processes we compare the current petrographic classification scheme to the geochemical data based group structure of the samples. The final question studied concerns spatial appearance of the identified petrographic processes and the samples groups defined using geochemical data. Results of a sequence of traditional statistical methods (factor, cluster and discriminant function analyses) suggest that beside igneous differentiation different post-magmatic processes significantly determine bulk composition of the studied intermediate rocks. Due essentially to the complex alteration history, rock classes were defined using petrographic observations previously, hardly meet the group structure can be defined using geochemical data. In fact, trachyte is not an original igneous rock type; rather it is regarded as intensively metasomatised dacite and andesite. Interpolated maps of the identified magmatic and post-magmatic processes (factors) clearly mimic the spatial pattern of the known volcanic and sub-volcanic centers suggesting that alteration coincides to late dacitic activity.

Keywords: Tokaj Mts., major elements, multivariate statistics, post-magmatic evolution, volcanic centers

1. INTRODUCTION

The Tokaj Mountains, an important member of the Inner Carpathian Volcanic Belt were formed by Neogene volcanism from the Upper Badenian to the Pannonian with a paroxism in the Sarmatian (Fig. 1). Moreover, volcanic formations that are tectonic and volcanological connection with the Tokaj Mountains can be traced in Transcarpathia, Ukraine and in the basement of the Great Hungarian Plain. Volcanic formations of the mountains are represented by almost the entire calc-alkaline series from basalt to rhyolite with quite common complex post-magmatic alterations. The purpose of our study was to find the main genetic and alteration processes, which formed the andesites and dacites in the Tokaj Mts.; as well as to outline of the spatial distribution of these processes.

In order to meet these aims as many data should be involved in the analysis as possible. From the literature major element composition of over 400 analyzed lava rock samples are available, while trace elements are known only from a few dozens of them. That is why we focus on major element compositions instead of using trace elements. Normally, geochemical discriminant diagrams give meaningful results only when fresh, non-altered samples are used. In our case andesite and dacite samples with different degree of alteration shall be used. The different alteration processes changed the original igneous composition of most samples making geochemical investigation problematic.

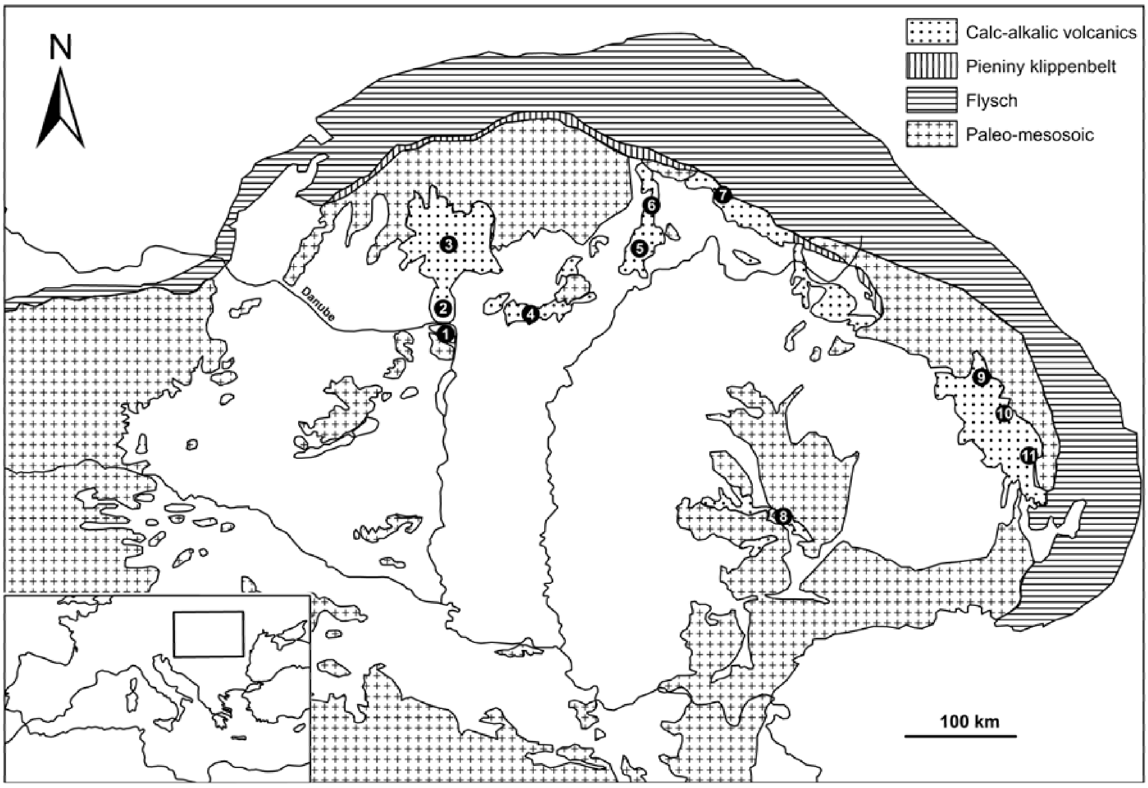

Figure 1. Geological sketch map of the Inner Carpathian Volcanic Belt. Legend: 1. Dunazug-Visegrág Mts. 2. Börzsöny Mts. 3. Central Slovakian Volcanic Field 4. Mátra Mts. 5. Tokaj Mts. 6. Slanské Mts. 7. Vihorlat-Gutâi Mts. 8. Apuseni Mts. 9. Călimani Mts. 10. Gurghiu Mts. 11. Hargitha Mts.

To avoid thidifficulty the most obvious way is to use only immobile trace elements during the geochemical study. We follow a different way. Since the samples show a complicated evolution history, a sequence of multivariate mathematical-statistical methods was applied in order to use all major elements simultaneously.

2. GEOLOGICAL SETTING

Regarding the geology of Hungary Miocene intermediate volcanism has a particular importance. This calc-alkaline acid and intermediate volcanic activity was the result of a westward and southward subduction of the oceanic crust of the Carpathian flysch. This oceanic lithosphere began to disappear in the Lower Miocene and was consumed from west to east from the Middle Miocene till the Quaternary (Royden et al., 1982; Csontos et al., 1992; Tomek & Hall, 1993), while the detached slab sank into the mantle. As the Benioff-zone came into a steeper position, a dome in the astenosphere was formed that caused extensional stress (Szabó et al., 1992). This tectonic evolution was accompanied by widespread volcanic activity; from about 21 to about 14 Ma explosive eruptions of silicic magmas were dominant (Pécskay et al., 1995; Harangi et al., 2005). Calc-alkaline volcanic activity started at 16.5 Ma in the northern part of the Pannonian Basin with garnet-bearing andesites and rhyodacites (Harangi et al., 2001) and was followed by mostly andesites and dacites up to 9 Ma (Konečný et al., 1995; Harangi, 2001). In the eastern part of the region, calc-alkaline volcanic activity started at about 14 Ma, and became gradually younger and younger towards the southeast. The final stages of this magmatism are as young as about 13 ka (Mason et al., 1996, 1998). As a result, a more or less continuous chain of volcanic ranges, the so-called Inner Carpathian Volcanic Belt, was formed. Moreover, andesitic masses of great extent are buried in the NE part of the Pannonian Basin (Széky-Fux and Kozák, 1984), and sporadic occurrences in the southern part are also known (Pécskay et al., 1995, Harangi, 2001). The calc-alkaline volcanism was followed by eruptions of alkaline mafic rocks forming monogenetic volcanic fields mostly in the inner part of the Pannonian Basin (Embey-Isztin et al., 1993). Recently, "Eastern" and "Western" segments of Tertiary igneous rocks have been distinguished, and it is suggested that subduction-related geochemical character of the much more complex Western segment (running from the Tokaj Mts. to Styrian basin) is an inherited feature, where metasomatism happened before the Miocene (Kovács & Szabó, 2008). The volcanic complex of the Tokaj Mountains is the southern part of the Prešov-Tokaj Mountains (Fig. 1). This approximately N-S striking mountain chain forms an about 100 km long and maximum 30 km wide arc. The orientation of the mountains is determined by two structural lineaments (Fig. 2). The older, NW-SE striking Szamos Lineament and the younger, NNE-SSW striking Hernád Lineament provide the eastern and the western delimitation of the mountains, respectively (Gyarmati, 1977).

The volcanism started in the Upper Badenian with the extrusion of rhyolite-rhyodacite flood tuff, and then it became intermediate in composition. At the same time intense subsidence and transgression set in and resulted in the development of a volcanotectonic graben in the northern part of the mountains (Pantó, 1968). Hence, considerable portion of the volcanics was erupted in subaqueous conditions. Badenian volcanic rocks of more than 1000 m in thickness are exposed only in the northeastern part of the mountains; elsewhere they are covered by younger formations. In the Sarmatian, the area became an archipelago, and volcanic rocks were dominantly formed on land or in subvolcanic bodies. Volcanism started with the production of silicic volcanic rocks, and continued with intermediate ones.

The most typical rock type of this stage is the so-called acid pyroxene andesite with an average SiO_2 content of 62% (Gyarmati, 1977). Volcanic activity terminated in the Pannonian. In a borehole near Sárospatak olivine basalt as a product of the final activity was found. Its age is about 9.4 Ma, i.e. the estimated duration of the volcanic activity is about 5 million years (Pécskay et al., 1986).

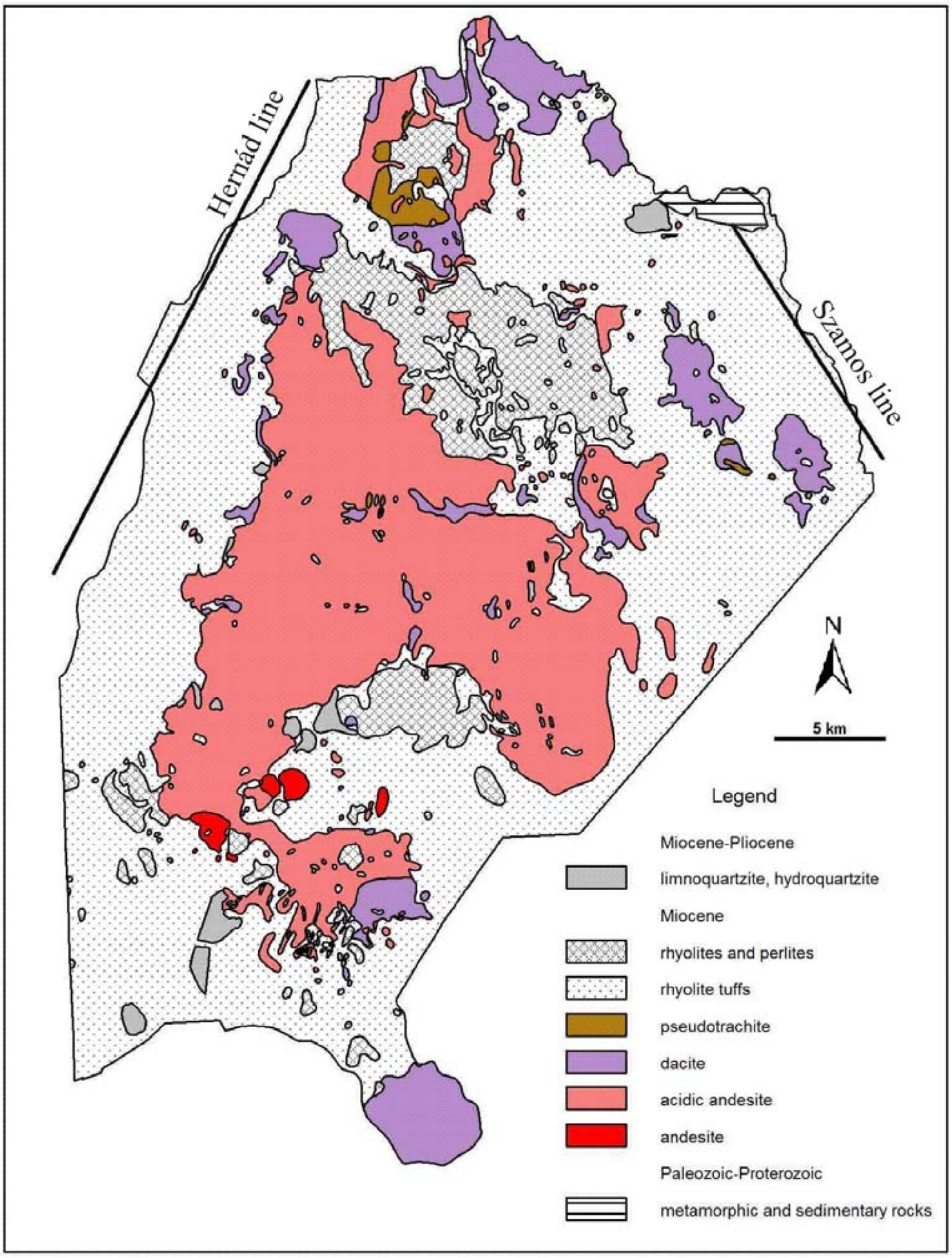

Fig. 2. Geological sketch map of the Tokaj Mountains (after Gyarmati 1977)

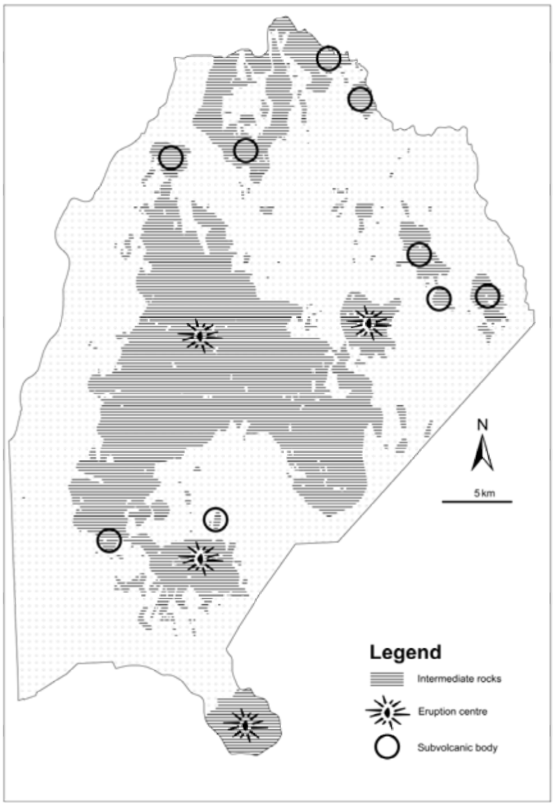

Figure 3. Volcanic and subvolcanic centres of the Tokaj Mountains composed or dominantly composed by intermediate rocks (after Gyarmati, 1977). The stripped areas sign the surface extension of the studied intermediate rocks.

The magmatism was associated with significant hydrothermal activity. Mineralized zones represent typical low-sulphidation-type environments (Molnár et al., 1999). Adularia-sericite alteration exposed in the northern, eastern, and central part of the mountains is characteristic for the zones eroded to greatest depth, and formed within andesitic-dacitic volcanic centers and subvolcanic intrusions between 13.0 and 12.2 Ma. Shallower, acid-sulphate steam-heated alteration zones predominate the southern part of the mountains, and developed in relation to different magmatic systems between 12.1 and 10.4 Ma (Pécskay & Molnár, 2002). Products of the non-eroded, distal hydrothermal environments (limnic siliceous and clayey deposits) are widespread in several parts of the range.

The vast volcanic complex of the Tokaj Mountains is built up by flood-tuffs, subvolcanic bodies, extrusive domes, volcanic cones, calderas and remnants of large lava flows. Although it is difficult to reconstruct the volcanic forms because of the complexity and denudation, a volcanotectonic sketch can be outlined due based on its detailed geological mapping (Gyarmati et al., 1976) and the interpretation of remote sensing data (Zelenka, 2000). Both the form and manifestation of the volcanic activity were determined by the Szamos and the Hernád Lineaments as well as volcanotectonic lines within the depression.

The main volcanotectonic lines run either parallel or perpendicular to these lineaments. Most of the eruption centers and subvolcanic bodies are located along these lines or close to them, and the most significant ones are situated at their intersections. Moreover, location of the centers of postvolcanic and hydrothermal activities seems to be also controlled by the structural pattern (Fig. 3).

3. PETROGRAPHY AND PETROCHEMISTRY

The Tokaj Mountains volcanic chain is the only one among Hungarian volcanic mountains where, due to differentiation and contamination (Gyarmati, 1977) as well as magma mixing (Rózsa, 1994) volcanic rocks ranging from andesite to rhyolite can be found in significant quantity. Data for the present analysis were selected from previous (Gyarmati, 1980) and more recent publications by multiple filtering. In the first step, following the recommendations of Le Maitre et al., (1989), samples of 48-85% silica content regarded petrographically andesite, dacite and rhyolite were selected. In this way, the petrogenetically intermediate but highly weathered samples or volcanic products of extreme differentiation were excluded. In the next step of selection, samples of H_2O>10% and/or LOI>10% were rejected. The remained 572 samples dominantly plot into the calc-alkaline field after in Irvine and Baragar's (1971) AFM triangle; similarly, according to the K_2O vs SiO_2 diagram the samples show medium and high-K character, i.e. they represent calc-alkaline–high-K-calc-alkaline series (Rickwood, 1989), from andesite to rhyolite. Despite the petrographically continuous series, however, an obvious bimodal distribution can be observed, and the sample points can be cut apart at about SiO_2=70% dividing them into a so-called Tokaj1 (dominantly andesitic-dacitic) and Tokaj2 (dominantly rhyolitic) groups, respectively (Ó. Kovács & Kovács, 2001).

Andesite represents the dominant volcanic rocks in the mountains. They can be divided into two main rock types. The basic one (101 samples) has been mapped as andesite although it could be classified as basaltic andesite according to the TAS-diagram (Le Maitre et al., 1989) (Fig. 4). Forsteritic olivine may occur in this andesite type indicating basaltic andesitic character. The more acidic variety of the andesite (115 samples) is the most abundant rock type of the mountains. Because of its high silica content (with an average of 62%) it is mentioned as "acidic" andesite in the Hungarian geological literature. In general, dacite varieties of the mountains (163 samples) contain pyroxene as a mafic constituent; pyroxene-hornblende dacite and hornblende dacite appear in much less quantity. Rhyolite extrusion and lava flows produced numerous rock varieties (173 samples), such as gray-banded fluidal rhyolite, spherulitic rhyolite, perlitic rhyolite, perlite, etc. Characteristic feature of the volcanism of the Tokaj Mountains is the intense and widespread alkali metasomatism (Széky-Fux, 1970; Molnár & Pécskay, 2000). As a result of K-metasomatism of various degrees a continuous transition series from andesite to trachyte can be observed. Classification of this series is arbitrary: rocks with potassium content higher than 8% are classified as pseudotrachyte (20 samples).

To outline the geochemical trend of the volcanic rock series of the Tokaj Mountains the traditional Harker diagrams were used. As figure 5 shows TiO_2, Al_2O_3, FeO, FeO^{total}, MgO, CaO, and P_2O_5 are in strong negative correlation with SiO_2 content. Points of TiO_2, FeO, MgO, and are quite scattered, particularly in the andesitic and dacitic (SiO_2 less than 70%) range. Parallel to the increasing silica content, Fe_2O_3 and MnO values also decrease definitely, however, due to the various degrees of alteration, their points are extremely scattered. K_2O values show strong positive correlation with SiO_2; the anomalously high K_2O values in the 60-70% SiO_2 range can be attributed to K-metasomatism; some anomalously low CaO values in this SiO_2 interval were also resulted by this alteration. Points of Na_2O show definite bimodal distribution with some positive correlation to SiO_2. Their highly scattered pattern can be attributed partly to the various degrees of alteration and weathering; the extremely low Na_2O values in the 60-70% SiO_2 range are related to K-metasomatism. Distribution of sample points for H_2O^+ in the Harker diagram can be the result of several factors.

In some cases higher values can be attributed to the amphibole and/or biotite content, however, the highly scattered pattern for andesitic and dacitic rocks is controlled primarily by weathering processes of various degrees. Distribution of the points of the rhyolitic samples shows spectacular bimodality due to the low and high water content of the rhyolite and perlite samples, respectively.

While significant geochemical difference between rhyolites and diverse intermedier rock types is unambiguous, discrimination among subtypes of the latter set is more problematic. The most essential questions arise are the following:

- what are the most important magmatic and post-magmatic processes, one can define using the geochemical data;
- how well the existence of the petrographic classification scheme can be inferred using geochemical data;
- how is it possible interpret geochemical data based group structure of samples;
- is there any relationship between spatial distribution of known petrographic processes and those defining geochemical behavior of the samples studied?

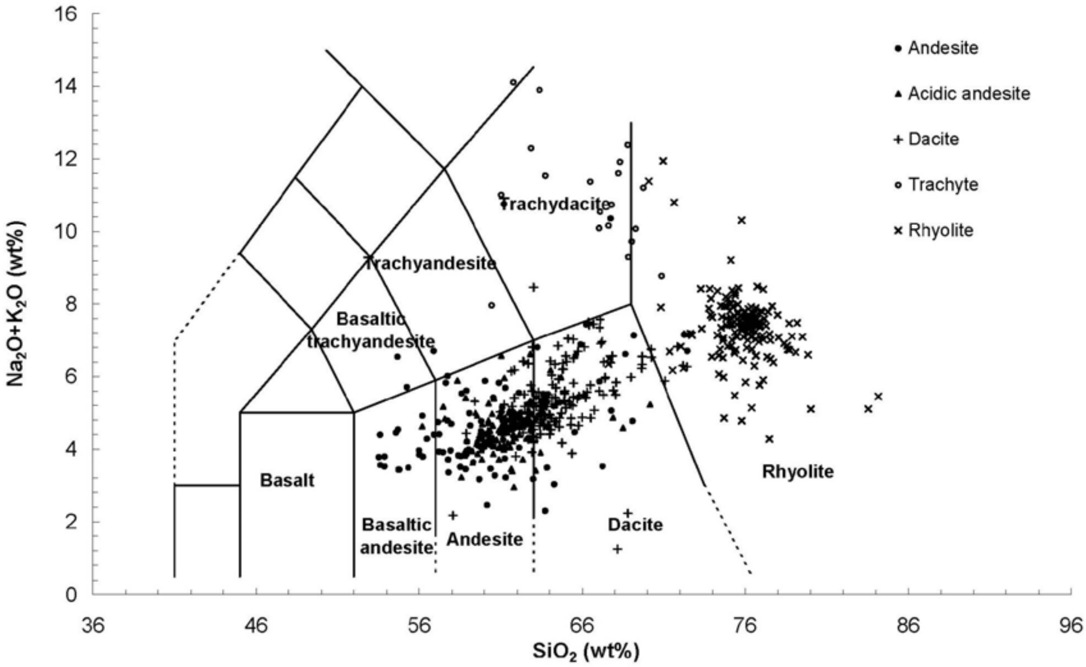

Figure 4. Position of the samples in the TAS diagram

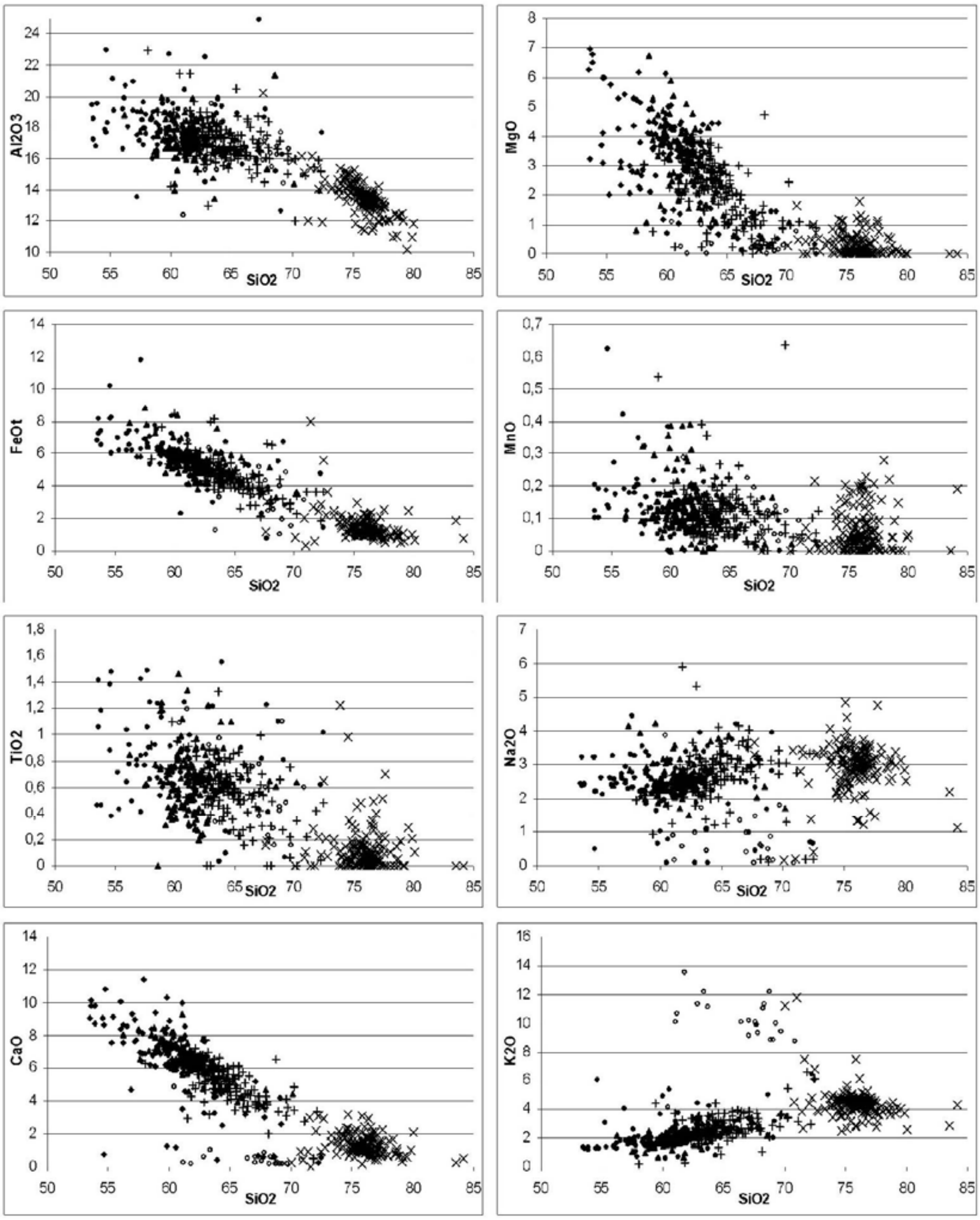

Figure 5. Position of the samples in the Harker diagrams (for symbols see figure 4).

4. GEOMATHEMATICAL ANALYSIS

4.1. Methods applied, flow chart of the evaluation

To answer the above questions, a sequence of standard mathematical procedures has been developed. The sequence according to the flow chart can be divided into three parts. In the course of the geomathematical process, first a simultaneous solution for a correlation and a factor analysis must be found. These two procedures allow establishing groups of variables. If the variable groups of the factor analysis are not explicable, it has to be repeated with new parameters and/or reduced. If the results of the two methods correspond to each other, the next step can be envisaged. After a cluster analysis, sample groups can be chosen. They are tested simultaneously by multidimensional scaling and discriminant function analysis. If the results do not correspond, a new sample group structure has to be chosen and tested again or a new cluster analysis with new conditions must be performed.

For analyzing the spatial distribution of selected variables ordinary kriging was applied with a linear variogram model. Detailed descriptions of the mathematical background of all the methods applied are given in several textbooks (e.g., Miller & Kahn, 1965, Anderberg, 1973, LeMaitre, 1982).

4.2. Results of the geomathematical treatment

4.2.1. Variable groups

According to the univariate statistics, every variable shows unimodal distribution. Al_2O_3, CaO FeO^{tot}, MgO, MnO, Na_2O, SiO_2 és TiO_2 represent normal, while CO_2, Fe_2O_3, H_2O^-, H_2O^+, K_2O, MnO, P_2O_5 show lognormal one. Since normal distribution of the variables is necessary for applying correlation and factor analysis, variables that can be used are as it follows: SiO_2, TiO_2, Al_2O_3, $\ln Fe_2O_3$, lnFeO, MnO, MgO, CaO, Na_2O, $\ln K_2O$, P_2O_5, $\ln CO_2$, $\ln H_2O^+$, $\ln H_2O^-$.

Linear correlation between the variables is illustrated in correlation profiles (Fig. 6). In this graph significantly related variables are connected. In this way, groups of elements having similar characters and changing together can be identified. A total correlation system is formed by MgO, CaO, FeO, -SiO_2, -K_2O, i.e. each element correlates to the others at $\rho > 0.5$. This close correlation system of the variables indicates that magmatic differentiation played an eminent role in creating the geochemical pattern.

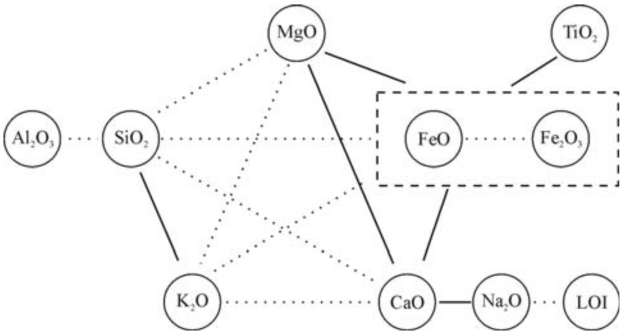

Figure 6. Correlation profile demonstrates grouping tendencies of major elements (solid line: positive, dashed line: negative correlation coefficient).

Other connections, such as FeO–(-Fe_2O_3), K_2O–(-Na_2O), and SiO_2–(-Al_2O_3), refer to the importance of post-magmatic processes. Beside the evaluation of the correlations between variable pairs, factor analysis can be applied for understanding group structures of the variables (Table 1). Five new factors can be chosen with eigen value >1, which together represent almost 80% of the total variance. On the basis of the major elements that determine the new factors keeping also petrographic observations in mind, it is possible to identify the background variable that causes the given multi-dimensional geochemical pattern. In the case of factor 1 (F1), decrease in Fe, Mg, Ca parallel to the increase in Si and K obviously refers to magmatic differentiation. (It must be noted, however, that products of mixing of differentiated magmas cannot be distinguished from that of magmatic differentiation. In the factor analysis of volcanic series, the component of the maximum eigen value can be generally identified as igneous differentiation (Owen, 1989). Increase in K parallel to decrease in Ca and Na, as well as the simultaneously increasing H_2O may suggest K-enrichment or K-metasomatism, and, in this way, secondary adularitization-sericitization of plagioclase (F2) and/or alunitization. Opposite behavior of Fe^{2+} and Fe^{3+} shows oxidation processes (F3). The fourth most significant factor refers to simultaneous variation of FeO, TiO_2 and P_2O_5. Petrologic interpretation of this factor is not unambiguous.

It may show the compatibility of these three elements, i.e. crystallization or, perhaps, accumulation of apatite and Fe-Ti phases; however, as Ti and P are essentially immobile elements, their coupled increase may indicate residual enrichment due to weathering. The last factor (F5: -SiO_2, Al_2O_3, H_2O, -K_2O) refers to the role of argilitization processes of feldspars.

As a whole, in the sample population of approximately 400 analyses, 78% of the total variance of the major elements can be described as the result of magmatic and/or post-magmatic processes. Increase of F1 suggests more-and-more differentiated rock; decrease of F2 and decrease of F5 indicate fresher rock; increasing F3 represents more oxidized samples.

4.2.2. Sample arrangement on the geochemical space

Having the most essential geochemical processes, three main questions arise concerning the evolution of the igneous rock samples.

Table 1. Results of the factor analysis.

Factor	Major element groups	Petrological process	Total variance %
F1	SiO_2, -FeO, -MgO, -CaO, K_2O	Igneous differentiation	33.5
F2	-CaO, -Na_2O, K_2O, H_2O	K-metasomatism, alunitization	47.2
F3	-FeO, Fe_2O_3	Oxidation	59.3
F4	TiO_2, FeO, P_2O_5	Accumulation of Fe-Ti, P phases	69.6
F5	-SiO_2, Al_2O_3, -K_2O, H_2O	Argilitization	78.1

The first problem is to understand the geochemical difference between the main petrographic sample groups in the factor space. Such dissimilarity is calculated using discriminant function analysis. The second question is weather or not one can infer existence of the diverse petrographic groups using geochemical data; how well petrographic and geochemical group structure of the individual samples fit. Finally, we calculate natural group structure of the samples in the 5-dimensional space of the geochemical processes.

Regarding the magmatic and post-magmatic processes forming the intermediate rocks of the Tokaj Mountains, it is possible to analyze the foundation of the lithologic classification of the intermediate volcanic samples. First, accepting the correctness of the classification, distinctiveness of the main rock types (0: andesite, 1: dacite, 2: acidic andesite) was analyzed in the space of the five factors (F1-F5) by using discriminant function analysis, while trachyte samples form the ungrouped set. The computed discriminant functions are as it follows:

(1) D1: $-0.9*F1 + 0.2*F2 + 0.4*F4 + 0.4*F5$

(2) D2: $-0.6*F1 - 0.8*F2 – 0.3*F4 – 0.4*F5$

In the case of function D1 magmatic differentiation (F1) is the most important, i.e. differences in the geochemical character of the three rock types are basically the result of magmatic processes corresponding to the petrographic observations. On the other hand, however, the signs of the two certainly post-magmatic factors (F2 and F5) unambiguously suggest that the higher magmatic differentiation (i.e. lower mafic mineral content) may be related to the less weathered state of rock samples. The F4 variable varies together with the degree of alteration, which may suggest that simultaneous increase in Fe, Ti and P can be regarded as a result of residual enrichment of immobile elements rather than a consequence of magmatic processes. The discriminant function D2 is most significantly determined by factors suggesting metasomatism. Their effects strengthen each other, i.e. degrees of metasomatism and argilitization increase simultaneously, while the amount of incompatible elements also increases relatively. Among post-magmatic processes, the role of K-metasomatism is dominant (Fig. 7). The trachyte samples form a closed cloud in the space of the samples; nevertheless this set does not differ basically from the other samples in the degree of magmatic differentiation. This corresponds to former interpretations (Széky-Fux, 1970; Gyarmati, 1977; Molnár & Pécskay, 2000) stating that their peculiar geochemical character cannot be regarded as an original magmatic signal, but they are formed by K-metasomatism (and other alterations) of dacitic and andesitic rocks.

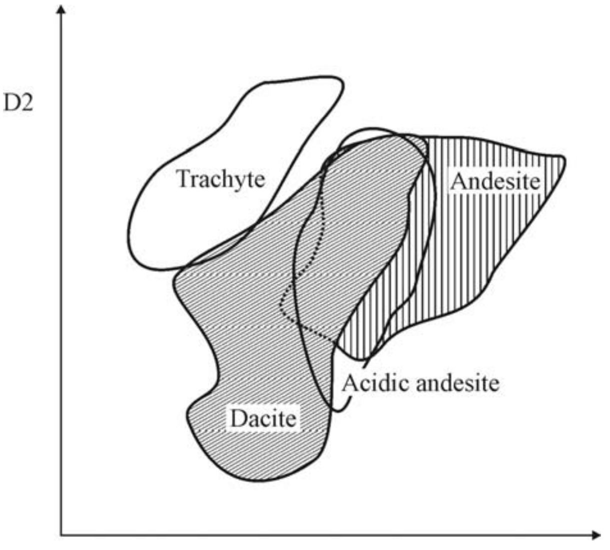

Figure 7. Discriminant functions D1 and D2 separate basic rock types with significant overlap. While along the D1 axis igneous differentiation is the main process, D2 is more responsible for post-magmatic alterations. Note that trachytes do not follow the differentiation trend.

Although effects of metasomatism and argilitization strengthen each other, as the discriminant functions also show, the third alteration process, oxidization (F3), is present in none of the above functions. Oxidization is a general effect, independent from the above mentioned group structure; therefore it cannot be used for distinction of the original lithologic types. Analysis of the two main petrographic andesite types (andesites and acidic andesites) by discriminant analysis produces the following function:

(3) $D3 = 0.7*F2 + 0.5*F4 + 0,5*F5$

It suggests the variable F1, i.e. magmatic differentiation, does not discriminate for the andesite types; in fact there is no significant difference between the andesite types concerning mean F1 values (degree of igneous differentiation). Therefore, the difference between them should be basically attributed to other processes. The main discriminant factors are K-enrichment, argilitization and, as a consequence, relative enrichment of immobile elements. The coinciding F1-F2 and F1-F5 plots (Fig. 8) suggest that the acidic andesite samples form a closed group inside the andesite field. This pattern might suggest that acidic andesite is a weathered variety of normal andesites. However, petrographic evidence clearly shows that it should not be the case. According to the suggestions of Gyarmati (1977) potassium and water enrichment may rather be resulted by crustal assimilation, which process is regarded to play the main role in formation of acidic andesites.

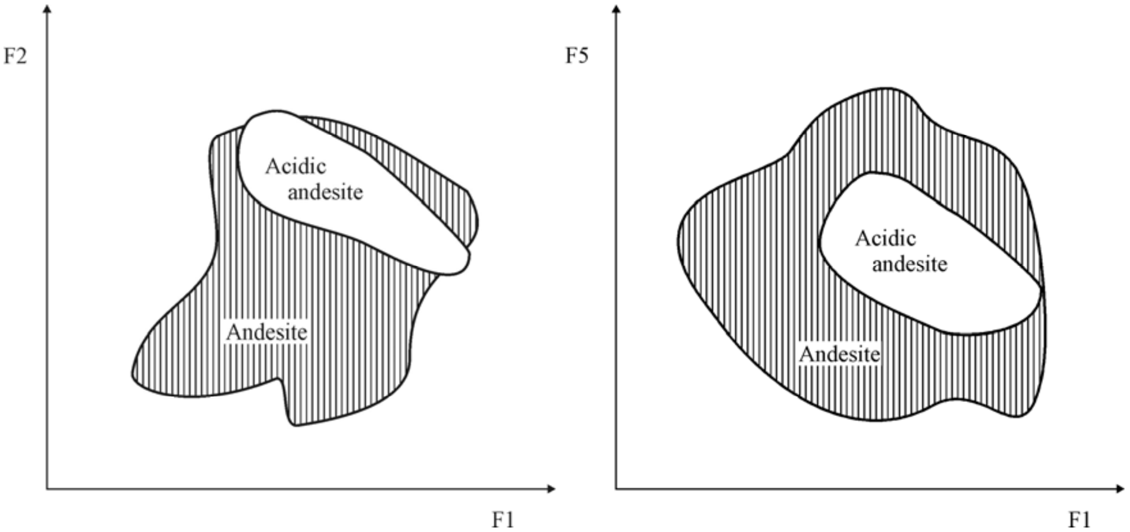

Figure 8. Acidic andesite samples form a closed group inside the andesite field both on F1-F2 (left) and on F1-F5 (right) plots suggesting an independent evolution.

Moreover, assimilation is regarded one of the major petrogenetic processes in other volcanic areas of the Inner Carpathian Volcanic Belt, too (Mason et al., 1996). It nevertheless seems that type and intensity of post-magmatic alteration depends on the composition of the original andesite. While more differentiated samples tend to alter due to argilitization, more primitive ones are K-metasomatised. In the geochemical space studied, no significant difference between the Upper Badenian andesite subgroup and the other andesites can be detected. On the other hand, the Upper Badenian dacites form a tight group of less differentiated and more altered samples inside the dacite field.

Using the above D1 and D2 discriminant functions, the geochemical character of the samples is in weak connection with the original petrographic classification; only 56% of samples classified as andesite can be qualified as andesite on the basis of the discriminant function analysis (16 and 28% of them can be regarded as dacite and acidic andesite, respectively). Similarly, based on their geochemical character, 68% of the dacite samples can be qualified as dacite (15% andesite, 17% acidic andesite), while 18 and 13% of the acidic andesite samples can be classified as andesite and dacite, respectively. As a whole, petrographic classification of approximately 65% of the studied samples can be supported by the analysis of their geochemical character.

After the evaluation of the petrographic classification, the natural group structure of the samples was identified in the factor space of the five main petrologic processes. During the cluster analysis applied for this aim, the Euclidean distance (orthogonal system) and complete linkage method was followed. In the hierarchical structure of sample groups, nine clusters can be clearly distinguished based also on discriminant function analysis of group pairs (G1 to G9; Fig. 9; Table 2).

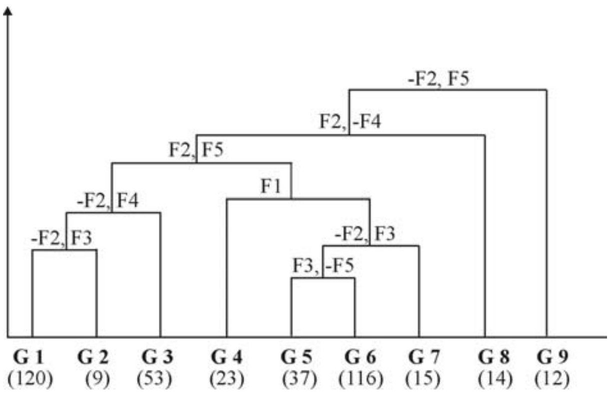

Figure 9. Simplified hierarchical structure (dendrogram) of the studied intermediate volcanics computed by cluster analysis using F1-F5 factors as grouping variables. G1-G9 denote sample groups, while numbers in brackets are for number of samples in each group. At the junctions of the dendrogram variables responsible for classification are highlighted. For details see text.

Samples of group G8 and G9 are highly altered and can be distinguished from all others by significance of F2 (K-metasomatism) and F5 (argilitization). About half of the trachyte samples fall into group G8 confirming the post-magmatic origin of this lithology. The main lithologies cannot be essentially distinguished in the geochemical space studied. Although, groups G1-G3 contain more primitive samples (SiO_2: 59.0 ± 3.6; K_2O: 2.1 ± 0.8; Al_2O_3: 17.1 ± 1.4), while groups G4-G7 are more differentiated (SiO_2: 62.5 ± 2.9; K_2O: 2.7 ± 1.0; Al_2O_3: 16.5 ± 1.5), original andesites and dacites do not exhibit any clear tendency to assemble. Between these two big classes rather basic alteration processes (F2, F5) are the reliable discriminating variables than igneous differentiation (F1) (Table 2). Further subdivision becomes possible using oxidation (F3) and immobile element accumulation (F4), but these subgroups do not fit with any of the previous classes of samples defined petrographically. The only subgroup for which igneous differentiation (F1) is the most important discriminating variable is G4 that contains the most differentiated dacite and about the half of the trachyte samples. Acidic andesites do not appear as an independent group in the cluster structure studied.

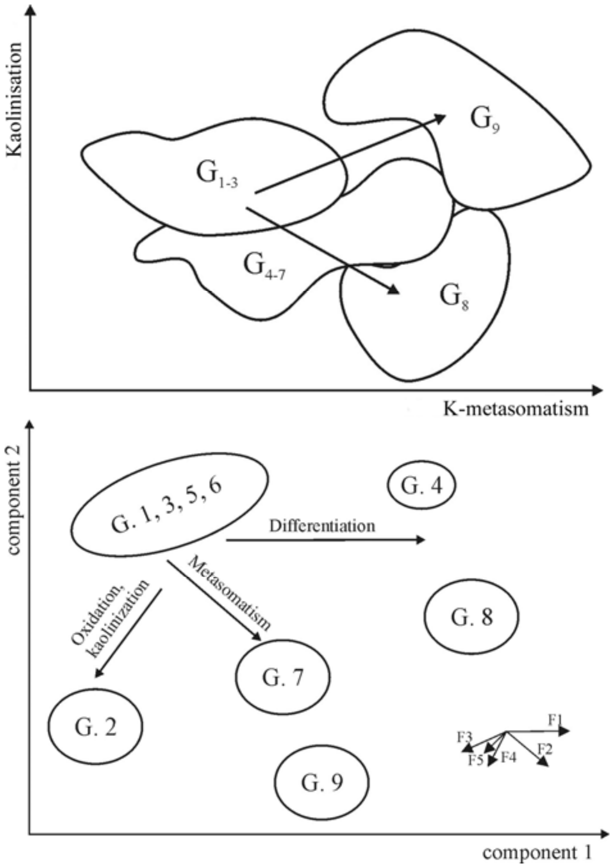

Figure 10. Selected plots exhibit the role of the main alteration processes. Samples of G1-G3 as well as G4-G7 are significantly mixed on the F2-F5 plot, while G8 and G9 represent highly altered samples. Note that andesites (G1-G3) are more kaolinized, whereas dacites (G4-G7) are K-metasomatized (upper diagram). On the multidimensional scaling map relative positions of all sample groups in the 5-dimensional variable space become visible. The inset shows directions of the 5 factor axes following projection (lower diagram).

Taking only the most important alteration processes (K-metasomatism, argilitization) into account, on the F2 vs. F5 plot a clear evolutionary trend from the unaltered towards altered magmatites exhibits. The complex effect of all magmatic and post-magmatic processes as well as the relative position of the above 9 groups in the 5-dimensional (F1 to F5) geochemical space can be followed simultaneously on a multidimensional scaling map (Fig 10). Here, groups G1, G3, G5 and G6 overlap significantly representing the original, unaltered igneous rocks. G1 is rather acidic (almost 60% of the samples classified into this group are dacite; andesite represent less than 13%); G3 is more andesitic (almost 40% of the samples are andesites, dacite represent about 25%); while groups G5 and G6 are slightly dominated by dacite and acidic andesite (37-37%) compared to andesite (25%). Samples of group G7 and G9 are highly altered andesite and dacite, while those belong to G2 are highly oxidized samples (Fe_2O_3: 5.61±1.1). G4 samples are deviant along -F1 direction and represent trachyte and high-K dacite (K_2O: 3.75 ±1.25) samples. Rocks in G8 are dominantly trachytes possibly evolved by complex post-magmatic processes. As a consequence, corresponding well to the previous interpretation of Széky-Fux (1970), Gyarmati (1977) and Molnár and Pécskay (2000) these rocks are not original magmatites but are rather pseudotrachytes.

4.2.3. Spatial arrangement

Spatial distribution of F1 (igneous differentiation; Fig. 11) follows reliably the known pattern of andesite and dacite dominated areas of the mountains (c.f. Fig. 2). The most differentiated localities coincide well with the dacitic volcanic and/or subvolcanic centers suggested by Gyarmati (1977). The most exhaustive centers of K-metasomatism (Fig. 13) also suggest a well-defined spatial pattern that seems to follow the distribution of the main volcanic and subvolcanic centers, at least in the central and northern parts of the mountains. Indeed, K-metasomatism was the most intense in these regions (Telkibánya, Regéc and Rudabányácska areas), where pseudotrachyte appears confirming the previous statement considering the post-magmatic origin of this rock type (c.f. Fig. 2).

In the southern and north-eastern parts of the area dacitic volcanic activity and post-magmatic metasomatism do not seem correlating spatially. A possible reason for this may be that these areas are younger and less eroded (Molnár & Pécskay, 2000). Since post-magmatic activity in the mountains is frequently associated with volcanic or subvolcanic centers (Molnár & Pécskay, 2000), some volcanic centers not signed on the volcanotectonic map of Gyarmati (1977) can be outlined as suggested on figure 12 by arrows.

Their existence was also supposed by the interpretation of remote sensing data, previously (Zelenka, 2000). Spatial distribution of argilitization (F5; Fig. 13) follows F1 as well, even if spatial correlation is not as clear as it is for F2. The spatial behavior of F4 (immobile element; Fig. 14) is more complex and its interpretation is not as straightforward as other processes. In the northern part of the mountains eruption centers with intense alteration (F2, F5) can be characterized by elevated F4 values resulted from relative accumulation of immobile elements.

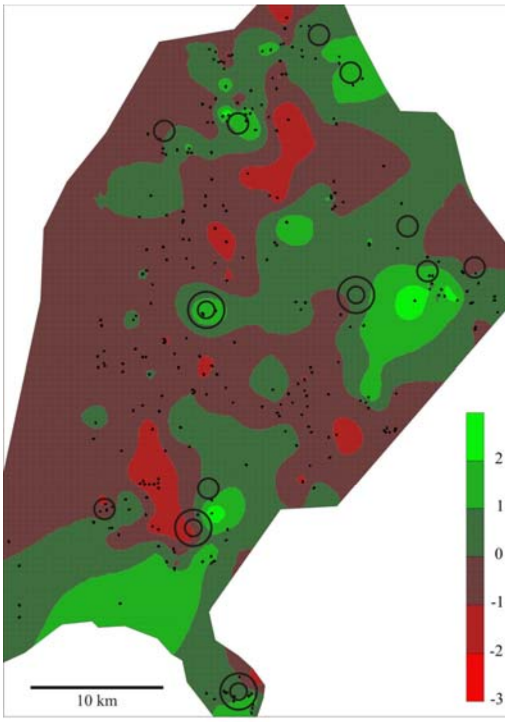

Figure 11. Isoline map of the igneous differentiation factor (F1) mimics dacite and andesite dominated domains of the study area. Spots with highest F1 values coincide well with known dacitic eruption centers (cf. fig. 3.)

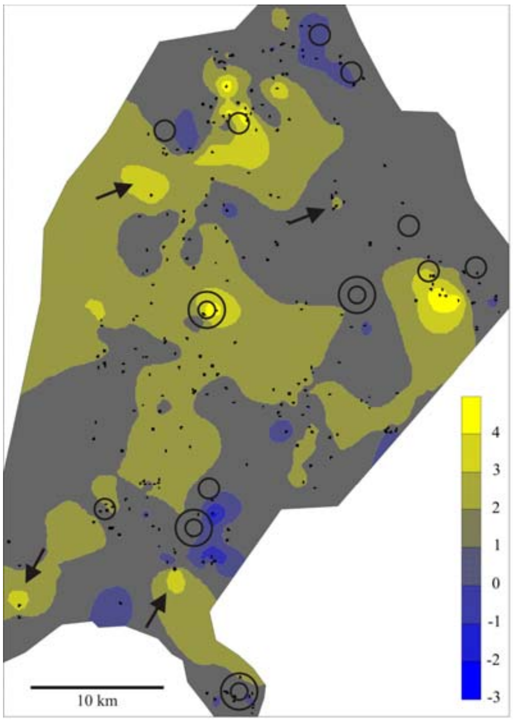

Figure 12. Isoline maps of the basic alteration processes: K-metasomatism. The known dacitic volcanic and subvolcanic centers appear on the map with high values suggesting the significant role of post-magmatic activity. Arrows show volcanic centers suggested by Zelenka, 2000).

On the other hand, all around the study area, spatial pattern of F4 mimics that of F1 suggesting a simple explanation of higher Fe, Ti and P concentration in andesites related to dacites. High F4 values in the south seem to indicate an original feature of the major element composition.

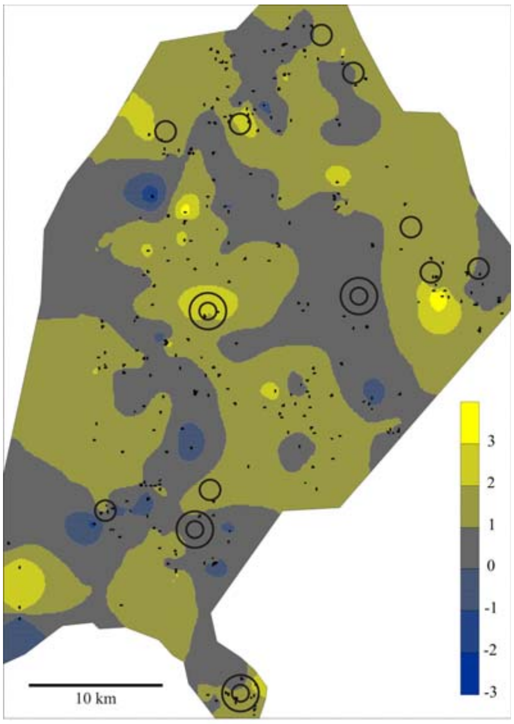

Figure 13. Isoline maps of the basic alteration processes: argilitization (F5). The known dacitic volcanic and subvolcanic centers appear on the map with high values suggesting the significant role of post-magmatic activity.

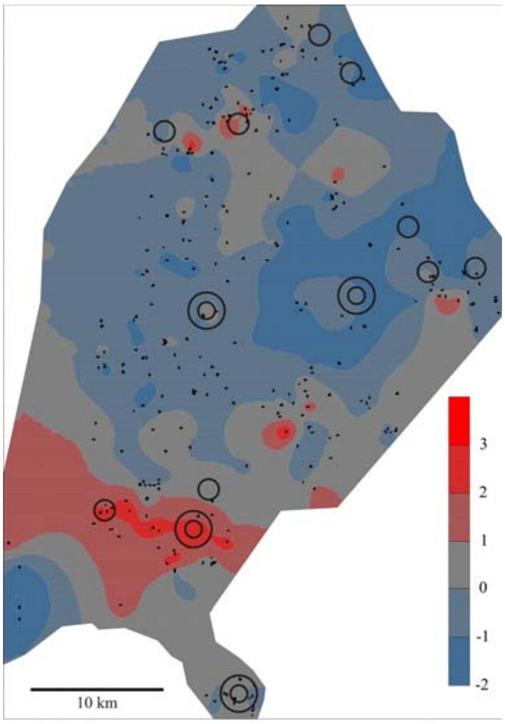

Figure 14. Isoline map of the immobile element enrichment processes (F4). Anomalies can be interpreted by different way there in the NW and in the S (see text).

Table 2. Results of the discriminant function analysis

Group pairs	F1 - igneous differentiation	F2 - K-metasomatism	F3 - oxidation	F4 - immobile elements	F5 - argilitization
1-8, 9	-	-0.70	-	-	0.90
1-7, 8	0.49	0.77	-	-0.49	-
1-3, 4-7	-0.25	0.68	-	-	0.78
1-2, 3	-	-0.66	-	1.07	-
4, 5-7	0.94	0.25	-	-	0.32
5-6, 7	-0.32	-0.78	0.63	-	0.60
1,2	-	-0.41	0.92	-	-
5,6	-	-	0.87	-	-0.50

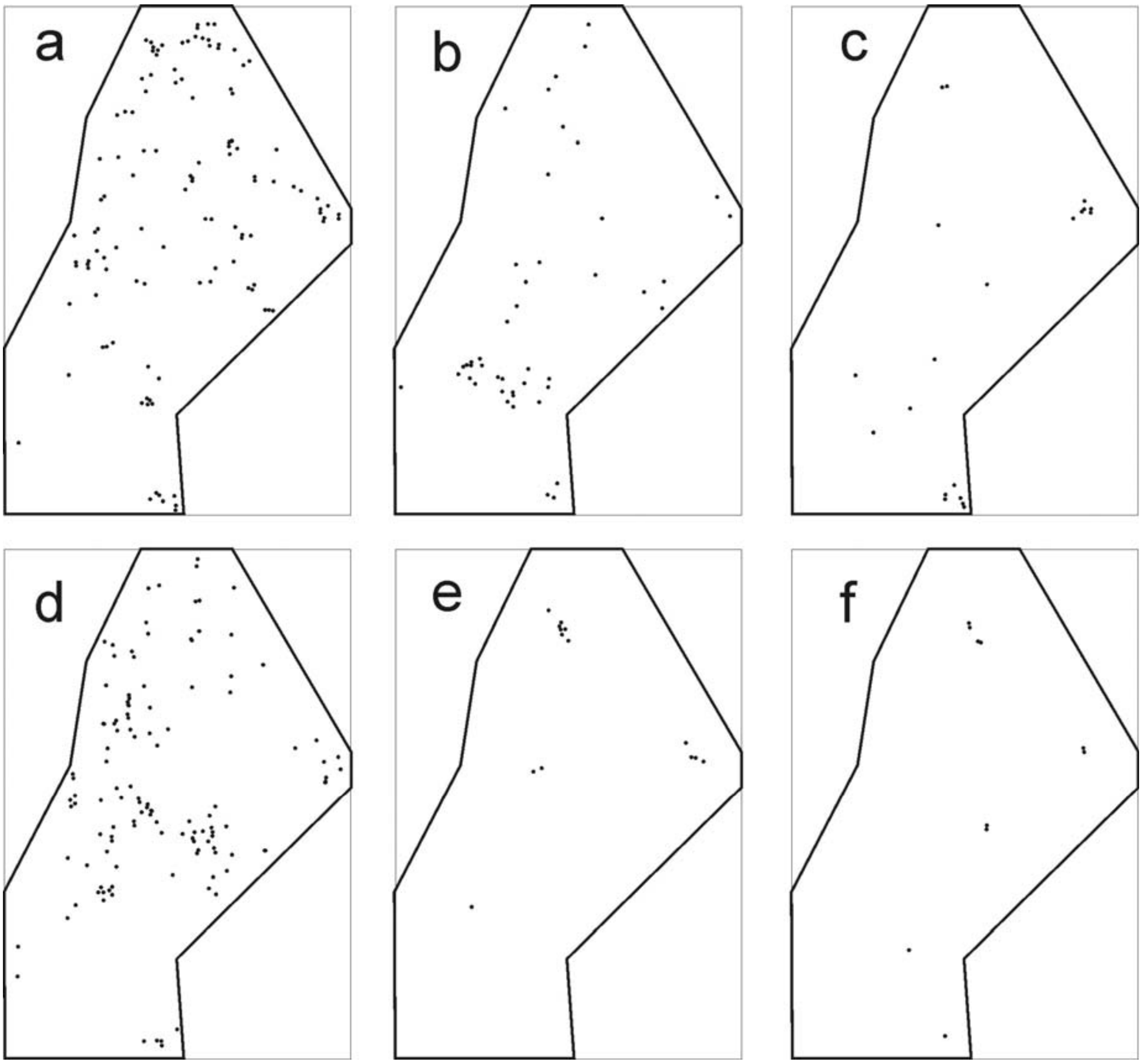

Figure 15. A series of point maps for the natural sample groups generated by cluster analysis. For details see text. a) G1, b) G3, c) G4, d) G5 and G6, e) G8, f) G9

Comparing to other andesites in the mountains, the southernmost andesite and acidic andesite can be characterized by relatively high iron and titanium content (Saad & Rózsa, 1992).Spatial arrangement of F3 (oxidation) does not exhibit any regular pattern suggesting that post-magmatic oxidation was independent of igneous activity.

Regarding the spatial arrangement of groups G1, G3, G5 and G6 (Fig. 15) representing the original, more-or-less unaltered intermediate rocks overlap all the area built in andesite, acidic andesite and dacite. Local concentration of the samples, however, can be observed in the case of group G3, i.e. most of these samples concentrate in the southern part of the mountains. This phenomenon corresponds to high F4 values in the south, and, as it was mentioned above, overlaps the area of the high-Fe-Ti andesite and acidic andesite. Samples belonging to G8 concentrated on the three areas of the deeply eroded hydrothermal systems (Telkibánya, Regéc and Rudabányácska).

5. CONCLUSIONS

According to the factor analysis of the major element data of the intermediate lava rocks of the Tokaj Mountains five factors can be chosen with eigen value >1, which together represent almost 80% of the total variance. The most important factor, F1 – decrease in Fe, Mg, Ca parallel to the increase in Si and K – refers to magmatic differentiation; F2 – increase in K and H_2O parallel to decrease in Ca and Na – may suggest K-metasomatism and/or alunitization; F3 – opposite behavior of Fe^{2+} and Fe^{3+} – reflects oxidation processes; F4 – simultaneous variation of FeO, TiO_2 and P_2O_5 – shows accumulation of apatite and Fe-Ti phases during crystallization or may indicate residual enrichment due to weathering. Finally, F5 – decrease in SiO_2 and K_2O with simultaneous increase in Al_2O_3 and H_2O – refers to the role of argilitization processes of feldspars.

Disrcriminant function analysis of the main petrographic sample groups (andesite, dacite, acidic andesite) suggests that differences in the geochemical character of the three rock types are basically the result of igneous differentiation (F1) (D1 = -0.9*F1 + 0.2*F2 + 0.4*F4 + 0.4*F5). The signs of the two certainly post-magmatic factors (F2 and F5) indicate, however, that higher magmatic differentiation is related to less weathered state of rock samples. Simultaneous variation of F4 with F2 and F5 suggests that increase in Fe, Ti and P may be a result of residual enrichment of immobile elements.

Discriminant function D2 (D2 = -0.6*F1 - 0.8*F2 – 0.3*F4 – 0.4*F5) is basically determined by metasomatism. The trachyte samples do not differ from other samples in the degree of differentiation; however, form a closed cloud in the sample space. This pattern corresponds to the former interpretation on their origin, i.e. they form by K-metasomatism of andesite and dacite (Széky-Fux, 1970; Gyarmati, 1977; Molnár & Pécskay, 2000). Using the above D1 and D2 discriminant functions, the geochemical character of the samples is in weak connection with the original petrographic classification; as a whole, petrographic classification of approximately 65% of the studied samples can be supported by the analysis of their geochemical character (56% of andesite, 68% of the dacite and 69% of the acidic andesite samples).

D3 discriminant function (D3 = 0.7*F2 + 0.5*F4 + 0.5*F5) used for the analysis of the two main petrographic andesite types (andesites and acidic andesites) suggests that magmatic differentiation (F1) does not discriminate for the andesite types. Their position on the F1-F2 and F1-F5 plots might suggest that acidic andesite is a weathered variety of normal andesites. Based on petrographic evidence, however, it is more likely that potassium and water enrichment in acidic andesite may rather be the result of crustal assimilation as suggested by Gyarmati (1977). Moreover, it also seems that more differentiated samples tend to alter due to argilitization, while more primitive ones are K-metasomatised. In the geochemical space studied, there is no significant difference between the Upper Badenian andesite subgroup and the other andesites. The Upper Badenian dacites, however, form a tight group of less differentiated and more altered samples inside the dacite field.

The natural group structure of the samples was identified in the factor space of the five main petrologic processes. Based on discriminant function analysis of group pairs, nine clusters can be clearly distinguished. Samples of group G8 and G9 are highly altered and can be distinguished from all others by significance of F2 (K-metasomatism) and F5 (argilitization). About half of the trachyte samples fall into group G8 confirming their post-magmatic origin. Most of the andesite and dacite samples fall into groups G1-G3 and G4-G7, but they do not form clear clusters, rather appear mixed. G1 is rather dacitic, G3 is more andesitic, while groups G5 and G6 are slightly dominated by dacite and acidic andesite. On the multidimensional scaling map these four groups (G1, G3, G5 and G6) overlap significantly representing the original, unaltered igneous rocks. Group G7 and G9 include highly altered andesites and dacites, while samples belonging to G2 are highly oxidized samples. Samples of G4 are dominated by high-K dacites and trachytes, while most G8 samples are trachytes.

Spatial distribution of F1 (igneous differentiation) follows andesite and dacite dominated areas of the mountains, and the most differentiated localities coincide well with the dacitic volcanic and/or subvolcanic centers suggested by Gyarmati (1977). The most exhaustive centers of K-metasomatism also follow well the distribution of the main volcanic and subvolcanic centers in the central and northern part of the mountains. Lack of spatial correlation between dacitic volcanic activity and post-magmatic metasomatism in the southern and north-eastern parts of the area can be explained by their younger age and less eroded surface (Molnár & Pécskay, 2000). Higher F4 values in the northern part of the mountains around eruption centers with simultaneously intense alteration (F2, F5) can be caused by relative accumulation of immobile elements. On the other hand, high F4 values in the south seem to indicate original feature of the major element composition. On the basis of spatial distribution of post-magmatic activity some volcanic centers not indicated on the volcanotectonic map of Gyarmati (1977) can be identified confirming the last volcanotectonic interpretation of remote sensing data (Zelenka, 2000).

ACKNOWLEDGEMENT

The authors thank Pál Gyarmati for providing his major element data collection and Tibor Zelenka for his helpful comments. Richard W. McIntosh is acknowledged for thoroughly cleaning the English.

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Received at: 29. 06. 2012
Revised at: 12. 09. 2012
Accepted for publication at: 22. 09. 2012