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STATISTICAL REVIEW OF MAJOR ELEMENT DATA FROM THE MIocene TUFFS IN HUNGARY

Lajos Ó. KOVÁCS ¹ & Gábor P. KOVÁCS ²

Hungarian Geological Survey, H-1440 Budapest, P.O. Box 17, Hungary
¹E-mail: Lajos.O.Kovacs@mgsz.hu   ²E-mail: Gabor.Kovacs@mgsz.hu

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Abstract: The Miocene volcanic activity in Hungary, the central part of the Carpatho-Pannonian Region, was remarkably heterogeneous in terms of eruption characteristics, structure, texture, mineral and chemical compositions of rock products, etc. Often, the corresponding complexes are classified as belonging to either an acidic, or a calc-alkaline type of volcanism, although the numerous spatial overlaps of the volcanic formations together with the published radiometric age and isotope data introduce uncertainties into any simple typification. In the given study, treated together all available, summing up to several hundred, major element chemical composition data determined in Miocene tuffs are analyzed with simple statistical methods. The major element composition of these tuffs reveals an essential univariate, bivariate and multivariate unimodality, as opposed to the statistical behavior of the corresponding effusives that have a well-known bimodal character. The tuffs have a significantly higher content of compositional water than the lavas. Part of the water in tuffs is of magmatic origin, part of it is due to hydration related to conditions after and/or during eruption. The distribution of Na is similar in both rock types, although a generally more intense surface weathering, leading to Na leaching, in tuffs is suggested. There is a discrepancy also in the potassium distributions which may incorporate a primary (i.e. related to the magmatic stage) difference, and traces of a potassium metasomatism having been able to better develop in some lavas. The bivariate distribution of Fe₂O₃ and FeO provides an estimate (being about 10%) for the maximum of total iron occurring in the primordial magmas of these rocks. The compositional unimodality of tuffs produced by the represented volcanisms (no matter how many types of them are assumed) suggests significant genetic relations.

Key words: Tuff, Major oxides, Statistics, Petrochemistry, Miocene, Hungary, Carpatho-Pannonian Region

1 Introduction

Huge and wide-spread masses of the Neogene andesitic to rhyolitic complexes in Hungary have drawn the attention of geologists with different specialties, like mapping, structural geology, petrography, geochemistry, petrology, etc., for decades. Many earlier and some more recent studies concentrate on separate geologic-geographic areas and treat the occurring volcanisms (or types, forms, stages, etc. of a volcanism) embedding them into the history of each particular area, e.g. Varga et al. (1975) – Mátra Mts., Balla & Korpás (1980), Karátson (1995) – Bőrzsöny Mts., Balogh (1964), Cappaccioni et al. (1995) – Bükkalja region, Gyarmati (1977) – Tokaj Mts., Szék氟-Fux & Kozák (1984) – Nyírség area, Radócz (1975) – Ózd basin, just to mention a few. More recent studies, based on advances in understanding the petrologic/physical background of volcanic processes in general and also in resolving the Cenozoic tectonic history of the Carpatho-Pannonian Region, frequently deal with several volcanisms separated in some way or other and regarded as systems of correlatable volcanic phenomena within the entire Carpathian Basin (e.g. Póka, 1988; Szabó et al., 1992; Downes et al., 1995; Harangi, 2001). Practically all relevant studies point out to essential heterogeneities in terms of eruption characteristics, and/or structure, texture, mineral and chemical compositions of rocks, etc. occurring within any particular volcanism. Most of the complexes include a considerable or, some of them, predominant amount and a great variety of pyroclastics.

Most of the studies from the past 15-20 years have found that structural, petrographic, chemical, etc. features of these Neogene volcanites fit the subduction-related volcano-magmatic models applicable to the Paleogene to Quaternary megatectonic position of the Carpatho-Pannonian Region discussed for example by Csontos (1995), Tari et al. (1999) and Bada & Horváth (2001). More recent considerations (for a review see Harangi, 2001) attempt to incorporate factors of decompression melting,
and/or asthenosphere upwelling in extensional regime, and/or interaction of mantle-derived magmas with subduction-related fluids or crustal material. Although some of the details of petrogenesis of these formations related to the source region of primary magma(s), magma mixing, crustal contamination, etc., are a subject of debate, presented isotope data (e.g. in Salters et al., 1988; Downes et al., 1995; Harangi, 2001) document important genetic similarities/relations among the complexes.

No clear pattern has been evidenced regarding the spatial and temporal distribution and especially the time-space relationship of these complexes. This is considerably due to frequent spatial overlaps among these formations, to a (probably inevitable) scatter of radiometric age data, and to the different data-weighting ways of reasoning followed by the researchers (e.g. Póka, 1988; Pécskay et al., 1995; Márton & Pécskay, 1998; Balogh & Pécskay, 2001; Haas et al., 2001; Hámor et al., 2001) which led to various in length and central tendency age intervals attributed to particular complexes. Given the temporal and spatial overlaps, despite the applied (but not totally unambiguous) subdivisions, like acidic and andesitic, or silicic and calc-alkaline, etc., one may want to consider the figuring formations together.

With regard to the common conditions affecting the birth and evolution of magmas parental to these Neogene volcanites, a joint analysis of a statistical amount of data from them may reveal/document important similarities and dissimilarities among them. As in most of the cited references the Miocene volcanic events belong to a more or less separable stage of tectono-magmatic evolution of terrains composing Hungary, the given study focuses on these formations. Relatively little has been said in the literature about the chemical properties of the pyroclastics of these complexes. Hence, the aim of the given study is to provide a basic major-element statistical image of the Miocene pyroclastics in Hungary.

2 Data

Major element data from pyroclastics are relatively rare, compared to those from effusives, in the literature on the volcanites of Hungary. The most probable cause of this is that many types of pyroclastics – due to an easier weathering, a sorted or sometimes, on the contrary, an extremely unsorted character, uncertainties with the origin of water contained, etc. – are thought to be less, or less unambiguously, informative about the magma origin what is usually a major concern of petrologists.

Fig. 1. Map of distribution of the Neogene-Quaternary acidic to intermediate volcanic formations in the Carpatho-Pannonian Region (modified after Pécskay et al. 1995). 1: Alpine-Carpathian flysch belt, 2: Outcrops of pre-Tertiary basement, 3: Neogene-Quaternary sedimentary infill of the Pannonian Basin, 4: Outcropping intermediate volcanic rocks, 5: Buried intermediate volcanic rocks, 6: Outcropping acidic volcanic rocks, 7: Buried acidic volcanic rocks, 8: State border of Hungary.
Nevertheless, altogether several hundreds of chemical analyses have been produced and presented in publications and technical reports. Fisher & Schmincke (1984) emphasize that petrogenetic implications of this kind of data should not be neglected.

2.1 Database

For the given study, major oxide data were selected from the collective petrochemical database of Cenozoic volcanites of Hungary a detailed description of which is given in Ó.Kovács & Kovács (2001). In this database are registered a complete reference of all data sources, the most possible exact location of each sample, ages and lithostratigraphic units of the rocks analyzed, original major element and related chemical data, component values recalculated on a common basis, and some relevant background information. Although in the database the great variety of pyroclastics mentioned above is represented unevenly, the significant number of data is expected to ensure a basic degree of stratigraphic/geologic representativeness.

In principle, comparison of any type/group of pyroclastics with other volcanites might be of interest, hence, selecting even the total set of pyroclastics could be an option. Considering however that rocks described as agglomerates (not necessarily tuff-agglomerates but possibly lava-agglomerates) often contain larger lithic fragments causing some ambiguity when sampled, and that even smaller fragments are usually not defined whether they are juvenile, cognate or accidental relative to the given volcanic eruption, agglomerates were not included in the study set of samples here. Generally speaking, rocks named as tuff, welded tuff, ignimbrite and similar were selected, and they are referred to as tuffs in this paper. A rough areal distribution of the volcanic formations containing these tuffs is given in Fig.1. In terms of lithostratigraphic units (see Császár, 1997 and Ó.Kovács & Kovács, 2001) the Börzsöny, Cserehát, Felsenyárád, Galgavölgy, Gyulakeszi, Hasznos, Mátra, Nyírség, Sajóvölgy, Tar and Tokaj Formations, and some unassigned Miocene volcanites (from the Danube-Tisza Interfluve) are concerned.

Furthermore, as waters (H$_2$O- and H$_2$O+) determined in samples are important when characterizing tuffs, and tuffs often contain a considerable amount of dampness (H$_2$O-), only those samples were accepted for which waters are given. Another selection criterion was the sum of component values which was accepted only if it falls between 98% and 102%. This is expected to confirm a relatively good quality of the chemical analysis.

2.2 Recalculation on a H$_2$O-free basis

Although the laboratory conditions for determination of H$_2$O are not standardized, it might be a useful component when certain physical properties of rocks are investigated or character-
ized. However, when attempting to relate the chemical composition of rock samples with the volcanic and postvolcanic conditions and processes, it is necessary to work with a petrology-related component set, especially when H$_2$O$^+$ has relatively high values (here up to 14%). Therefore, the major components were recalculated to the same 100% on a H$_2$O--free basis. Although CO$_2$ and H$_2$O$^+$ are not popular amongst petrologists – obviously because of their possible secondary provenance –, they were kept in the component set here in order to fully characterize the compositional variations.

As the database has been composed of data taken from sources different in purpose and/or character, in a number of samples one or two major components have not been determined, or just are not given in the source. Luckily, these are components with very low concentrations in those samples which means that the criterion 98%<sum<102% can still be applied and that correction for the withdrawal of H$_2$O$^+$ preserves the comparability of the figuring components across samples.

### 2.3 Separating atypical samples

Statistical behavior of data even in the simplest methods might be biased due to atypical values (often called outliers, anomalies, extremes, outside values, etc.) in the data set. Although definition of atypicality is not obvious and for different purposes different atypicality conditions might reasonably be defined within the same data set, a trimming of data based on the visual analysis of the lower and higher percentiles usually performs well, despite it may be subjective. In Table 1 for each component the most remarkable change(s) in the series of percentiles were searched for. Also verified by general petrochemical experience, the corresponding percentile values were accepted as atypicality thresholds. For SiO$_2$ both lower and upper thresholds were chosen. In case of MnO, Na$_2$O and P$_2$O$_5$ no threshold seemed to be necessarily defined.

All selected samples were checked for atypicality and those having a value outside the threshold at any component were omitted from the work dataset. As a result, 382 tuff and 1259 lava samples were kept for analysis.

### 3 Data analysis

#### 3.1 Univariate similarities of the tuffs

Regarding the important differences in character of the birth-giving eruption (pyroclastic or hydroclastic), conditions of accumulation (fallout, pyroclastic flow or other), structure, texture, fabric, etc. of the given pyroclastics (see references in Introduction), and the chemical variations within the Miocene volcanites (e.g. Póka, 1988; Ó.Kovács & Kovács, 2001), one would expect a significant chemical variability within the tuffs as well. That would mean considerable differences in the robust statistics of tuff sets belonging to different lithostratigraphic units, multimodality in the frequency distributions of component values, sample clusters in the multivariate sense, etc.

In this section, the 5 most numerous tuff sample sets, designated by the names of the comprising lithostratigraphic formations, are compared in terms of their main univariate robust statistics (observations related to frequency distributions, bivariate patterns and multivariate scatter are given below). The grouped box-and-whiskers plots given in Fig.2 show a fairly striking picture: all 5 lithostratigraphic units are very similar in terms of the general statistical features of almost all components. No matter if one compares the central tendencies (medians) or the bulk of values (boxes) of the formations, they are very close except for only a few cases. Among the latter, FeO of Nyírség compared to Galgavölgy, MgO of Tar compared to Gyulakeszi, Na$_2$O of Nyírség compared to the other 4, H$_2$O$^+$ of Nyírség compared to Galgavölgy and Tokaj, CO$_2$ of Galgavölgy and Gyulakeszi compared to the other 3, and total alkali of Nyírség compared to Gyulakeszi can be named, admitting some subjectivity. Considering also the characteristic ranges of values (whiskers) one would get the same feeling: the formations are much more similar than expected.

The most remarkable discrepancies are probably the relatively high Na and low H$_2$O$^+$ values in Nyírség. The higher Na content might be a consequence of the buried (below 500-2000m of Pliocene sediments) position of the Nyírség volcanites which could prevent them from a more intense weathering and Na-leaching; although an originally higher Na-content cannot be excluded either. A weaker weathering might explain also the lower H$_2$O$^+$ concentration but for the latter other causes are also possible (e.g. a more intense degassing in the volcanic phase).

In all, based on the suggested by these observations uniformity of the given pyroclastics, in the next two sections their whole combined set (all 382 samples) is compared with the effusive members (all 1259 samples) of the same complexes.

#### 3.2 Univariate differences between the tuffs and lavas

The investigated formations possess a fundamental heterogeneity: among their rocks there are predominantly rhyolitic ones (e.g. the acidic series of the Tokaj Volcanite Formation), and there are predominantly andesitic ones (e.g. the bulk of the Mátra Andesite Formation). Hence, a statistical comparison of the pyroclastics with the associated effusives can conveniently and appropriately be done through their frequency distributions (Fig.3). The following observations can be made. The histograms of the lava rocks clearly display the mentioned bimodality with a quantitative dominance of intermediate rocks. Although this dominance is understood in terms of the number of analyses available from these rocks, there is no reason to suppose that the proportion of volumes of these rocktypes is some-
thing completely different. In any case, SiO$_2$, TiO$_2$, Al$_2$O$_3$, FeO, Fe$_2$O$_3$$^{total}$, MgO, CaO and, possibly, K$_2$O reveal bimodality. At the same time, bimodality is far less characteristic of the tuffs: It is only the histogram of SiO$_2$ that suggests the presence of a second mode. It obviously corresponds to the andesitic tuffs and mainly represents formations with typically intermediate compositions (like Hasznos, Börzsöny, etc.). Nevertheless, regarding also the other histograms, the set of tuffs is statistically more homogeneous, and no doubt its bulk is typically acidic.

It should also be noticed that among those components that
reveal unimodal frequency distributions for both the tuffs and lavas Fe$_2$O$_3$, P$_2$O$_5$ and, especially, H$_2$O$^+$ have significantly different distribution parameters. The statistically higher values of H$_2$O$^+$ may evidently be related to one of the basic conditions of generating pyroclasts: the significant role of water acting in the volcanic process either as a volatile in melt or as a fragmenting (and partly assimilated) agent in hydroclastic conditions. Part of H$_2$O$^+$ may also be due to secondary/surficial alterations enabled by the typically high porosity/permeability of pyroclastics. Such alterations are expected to cause related changes in the distributions of Na$_2$O (weathering of plagioclase and leaching of Na), or CaO (calcitization), or Al$_2$O$_3$ (argillization), or similar, and they are easily disclosed by petrographic observations. And indeed, traces of numerous (local) alterations are described by Varga et al. (1975). Ilkey-
Fig. 3. Histograms of major components of the lavas and tuffs of the studied Miocene volcanites. For explanation see section ‘Univariate differences between the tuffs and lavas’.
Perlaky (1966) and Széky-Fux (1970) for instance, and some of them can be recognized on the histograms as well: the peak around 0.3% of Na$_2$O (degradation of plagioclase), or the high values of K$_2$O (potassic metasomatism). However, no uniformly spread alteration is known, and the Na-leaching might possibly be the only type having a statistical signature expressed as somewhat lowered and more scattered concentrations in the tuffs.

3.3 Bivariate comparison of the pyroclastics and effusives

Detailed analysis of the bivariate distributions of major oxides would be worth a separate study, especially if one would like to make petrologic conclusions from the numerical correlations of components, as interpretational difficulties with compositional data always generate exciting problems (see e.g. in Pawlowsky-Glahn, 1997). Here, a few selected bivariate scatter plots (Fig.4) are given in order to further demonstrate some dif-

Fig. 4. Selected bivariate plots of the studies Miocene volcanites. Horizontal strokes denote lavas, vertical ones represent tuffs. For explanation see section ‘Bivariate comparison of the pyroclastics and effusives’.
ferences between the tuffs and lavas, and also several other relationships. Probably the first observation one would make is that whereas lavas show bimodality (two clusters) in all plots, tuffs reveal gathering around one center and this gathering is close to the smaller cluster (that of acidic rocks) of lavas. Despite of this, the outlines of scatter for both sets are similar which may be an indication of their genetic relation.

Just as on the corresponding histograms (previous section), samples with traces of potassic metasomatism on the SiO₂-K₂O plot (upper half of the diagram) and samples with leached out Na on the SiO₂-Na₂O plot (lower domain of the diagram) can be recognized, expectedly. The SiO₂-H₂O⁺ plot shows a substantial, although not uniform, enrichment of tuffs in H₂O⁺. Plot FeO-Fe₂O₃ could be interpreted in different ways but no doubt irons are related in a general inverse manner expressed by the bounded scatter of points (that is total iron is maximized). This maxi-

Fig. 4. (continued)
mum (about 10%) may correspond to the iron content of primordial magma(s), while the rocks with lower total iron may represent derivatives from magmatic differentiation, or compositions modified during/after eruption.

3.4 Bivariate patterns within the tuffs

Observations suggesting a kind of homogeneity of the studied pyroclastics can be further analyzed on bivariate plots made for the set of tuffs alone. On most of such plots a pattern similar to that in Fig.5a can be seen. Probably, more would have the feeling that this point cloud represents a composition series comprising a relatively compact core and a tail, in which the further we are from the core, especially in terms of the SiO\textsubscript{2} content, the more variable the cloud becomes (in terms of the other component). Graphically this can be better visualized if different symbols are used for different parts of the point cloud. In Fig.5b samples are (arbitrarily) divided into three categories: those with SiO\textsubscript{2} ≥ 67% (crosses) corresponding to the core, those with SiO\textsubscript{2} < 60% (triangles), and the rest (rectangles). They demonstrate a decreasing variability towards the higher SiO\textsubscript{2} contents. The same sample groups are plotted with the same symbols in Fig.6. And they provide the same comet-like pattern consisting of a denser core and a sparser tail.

Spectacularly different patterns are shown by the total alkali-SiO\textsubscript{2} and the H\textsubscript{2}O--SiO\textsubscript{2} plots (Fig.7). Based on the plot with the alkalis, there are samples from which alkalis had been almost entirely leached out, and there are samples with relatively very high contents of total alkali. Even if one ignores these samples and considers only the bulk the pattern is different from the one seen in Fig.5a. There, the acidic varieties formed a more compact group (the core), here the trend seems even inverse: the variance increases towards the more acidic compositions. On the plot with water no trend can be noticed: enrichment in water relative to the lavas (recall Fig.3) is characteristic of tuffs in all ranges of silica content. All this may indicate that the alkalis and water had been affected by at least partly different petrologic factors than the other components.

3.5 Multivariate homogeneity of the tuffs

A natural sample assemblage is never expected to be completely homogeneous in the multidimensional space of components. It would not be easy to prove any kind of natural homogeneity either. However, the rather continuous character and fair unimodality of distributions observed in one and two D might be considerable indications of a multidimensional homogeneity. It is obvious that a homogeneity can only be relative as within a heterogeneous set (e.g. all types of volcanites) a subset (e.g. those with acidic compositions) may seem to be homogeneous and, at the same time, have further subsets (e.g. alkaline and subalkaline types).

Considering all this, here the suggested by the above sections relative homogeneity of the tuffs compared to that of lavas is attempted to be elucidated in multivariate space, i.e. considering the major components together. As some of the major oxides are not given for a number of analyses, 324 tuff samples having SiO\textsubscript{2}, TiO\textsubscript{2}, Al\textsubscript{2}O\textsubscript{3}, Fe\textsubscript{2}O\textsubscript{3}, FeO, MgO, CaO, Na\textsubscript{2}O, K\textsubscript{2}O and H\textsubscript{2}O determined were used for this purpose. A similarity measure (namely the Euclidean distance on standardized variables) was computed for all pairs of samples, and a histogram of all these values was made (Fig 8a). For a comparison, the same
similarities of 186 randomly selected lava samples from the Tokaj Formation were calculated and plotted on a histogram (Fig. 8b). The Tokaj Formation is known for its compositional bimodality (see for example Gyarmati, 1977, or Ó.Kovács & Kovács, 2001). The difference between the two frequency distributions is evident: that of the tuffs is essentially unimodal while that of the lavas is bimodal which is a rather straightforward demonstration of the more homogeneous (in a sense) character of tuffs, and also that they have a single concise subset (referred to as core above) in multidimensional space.

4 Discussion

It is clear that the Miocene volcanism in Hungary was so multicolored, yielded so many different types of rock products that any generalization can only help to understand one or several particular aspects of this complex phenomenon. Furthermore, the database used here is only a more or less comprehensive collection of the available chemical data and one can only assume that the samples are roughly representative of the relevant processes and their products. In any case, the above observations are statistical and considered to be substantial, and they have proved to be essentially the same when components recalculated on a H$_2$O$^+$-free (or fully volatile-free) basis have been used. Therefore, a short genetic discussion is presented below.

The given Miocene tuffs and effusives are products of the same series of tectono-magmatically related volcanisms. The statistical behavior of their components, however, are different. Some of the differences can directly be related to the differences in the volcanic and/or postvolcanic and surficial processes that produced and then affected these rocks. In general, the often higher water content of tuffs is related either to the higher volatile content of magmas prone to explosive (pyroclastic) eruptions, or to assimilating water during eruption, diagenesis and weathering. In magmas the two most abundant volatiles are
water and CO$_2$, and they often, although not always, correlate. As in the given tuffs and lavas the CO$_2$-distribution is essentially the same, the higher water content in tuffs, at least part of it, is probably related to the post-magmatic (that is eruptive or later) stage of their history. Also, as was pointed out above, the statistical distribution of alkalis had been affected by postvolcanic (potassium metasomatism) and surficial (weathering) processes, and the intensity of these processes might have been different (a more expressed Na-leaching in the tuffs, and a stronger potassium metasomatism in some lavas).

Genetic interpretation of a set of presumably related differences, however, would require extension of the database. These are the more acidic and more homogeneous (in terms of a number of components alone, or considered together) character of the tuffs, and the impression that the more acidic the more homogeneous they are. Considering that these rocks spread over a large area and they represent a number of eruptions (in terms of time and eruption centers, even if the latter are not always known), such general effects can only be conceived as shared outcomes of these volcanisms. To investigate whether these effects reflect the general tectono-magmatic situation in the region, or they are due to certain corresponding events of individual volcanisms (e.g. magma chamber processes or other features of magma evolution), trace element and isotope data from...
all studied formations should also be acquired and analyzed (see e.g. Rollinson, 1993; Faure, 2001). In any case, the observed homogeneity of tuffs at the level of major elements suggests significant genetic relations.

One might feel that considering these volcanism together from this aspect is somewhat labored, and suggest conducting a similar investigation within a more coherent volcanic complex. A relatively limited, compositionally variable and the most densely sampled region is the Tokaj Mts. Interestingly but not surprisingly, calculating and analyzing the statistics used above, essentially the same results can be gained for this region alone. Based on the entire database however, an attempt to extrapolate the conclusions to the whole set of Miocene tuffs seems to be more challenging.

5 Conclusions

The major element composition of the Miocene tuffs in Hungary reveals an essential univariate, bivariate and multivariate unimodality, as opposed to the statistical behavior of the corresponding effusives that have a well-known bimodal character.

The tuffs have a significantly higher content of compositional water than the lavas, and a uniformly wide range in the H2O+ concentration irrespective of the SiO2 value. Part of the water in tuffs is of magmatic origin, part of it is due to hydration related to conditions after (and possibly during) eruption.

The distribution of Na is similar in both rocktypes. Its histograms reveal a small group of samples from which Na had been diluted out. The only difference between the distributions is that the tuffs have statistically lower (by about 1%) and more scattered values which may be an indication of a generally more intense surface weathering (including plagioclase degradation), possibly due to their higher permeability.

There is a slight discrepancy in the potassium distributions which may incorporate a primary (i.e. related to the magmatic stage) difference, and traces of a potassium metasomatism having been able to better develop in some lavas.

The bivariate distribution of Fe2O3 and FeO provides an unimodal, as opposed to the statistical behavior of the corresponding effusives that have a well-known bimodal character. 

Compositional unimodality of the tuffs produced by the represented Miocene volcanisms (no matter how many types of them are assumed) suggests important genetic relations between the formations studied.

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