STUDIA UBB AMBIENTUM, LVIII, 1-2, 2013, pp. 55-63
(RECOMMENDED CITATION)

A STATISTICAL APPROACH TO THE MINERAL WATERS OF TRANSYLVANIAN BASIN-EASTERN CARPATHIANS BOUNDARY

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ABSTRACT. In Romania important resources of sparkling mineral waters are related to the Neogene magmatic activity in the Eastern Carpathians. These mineral water springs are located on the eastern and western slopes of the Neogene to Quaternary volcanic chain. Based on a survey carried out in the Rodna-Bârgăului, Călimani-Gurghiu-Harghita Mountains, and on the Transylvanian Basin boundary, we have investigated 63 CO_2-rich mineral water springs, including four physical (T, pH, redox potential, electrical conductivity) and 15 chemical parameters (CO_2 , HCO_3^-, Cl^-, SO_4^{2-}, Li^+, Rb^+, Na^+, K^+, Ca^{2+} and Mg^{2+}, Fe^{3+}, Zn^{2+}, Cd^{2+}, Pb^{2+}, Cu^{2+} content) were determined. The mineral waters are of Ca-Mg-HCO_3 and Na-K-HCO_3 type, used both for drinking purposes and for local spas. We have analysed the chemical composition of the mineral water springs from a statistical point of view. Using the cluster analysis the waters were separated into several groups, according to similarities in their chemical composition. These groups confirm the mixing trend of the mineral water types demonstrated also by geochemical tools. As a result of their geographical position, being at the boundary of two major geological units, the Transylvanian Basin and the Eastern Carpathians, the chemistry of mineral waters is highly influenced both by volcaniclastic and sedimentary rocks.

Key words: *Eastern Carpathians, Transylvanian Basin, mineral waters, statistics*

INTRODUCTION

In Romania, the Neogene to Quaternary volcanic chain (Eastern Carpathians) is one of the most important areas from the point of view of CO_2-rich mineral waters. These mineral water springs are associated with other post-volcanic phenomena like dry CO_2 emissions, mofettes, bubbling pools and H_2S gas emissions.

In the study area, the western slope of the volcanic chain at the Transylvanian Basin boundary, mineral waters are used by people for drinking and for local spas. These mineral waters are located at the northern and southern part of the chain, starting from the Rodna-Bârgăului Mountains to the Călimani – Gurghiu-Harghita chain. The investigated locations are Rodna, Valea Vinului, Anieș, Sângeorz Băi, Bistrița, Parva in the first mentioned mountains unit, and Corund, Odorheiu Secuiesc, Băile Homorod, Vlăhița, Lueta and Băile Chirui in the second one. The aim of the study is to evaluate 63 mineral water springs from a statistical point of view and to compare with previous geochemical analysis.

GEOLOGY

The calc-alkaline magmatism in the Eastern Carpathians started around 21 Ma, and it developed in the Rodna-Bârgăului Mountains between 11.9-8.3 Ma and in the Călimani-Gurghiu-Harghita segment around 10 to 0.03 Ma respectively (Pécskay et al., 2006; Rădulescu and Săndulescu, 1973; Seghedi et al., 1995).

The Rodna-Bârgăului Mountains are characterized by intrusive magmatism. The magmatic bodies, laccolites, dykes and sills intruded in metamorphic and Paleogene sedimentary host rocks (Nițoi et al., 1995, 2000; Rădulescu and Dumitrescu, 1982; Ureche 1999). The Călimani-Gurghiu-Harghita (CGH) is the southernmost and the longest (160 km) continuous volcanic chain, consisting of a row of composite volcanoes and their volcaniclastic deposits. Volcanic products are calc-alcaline rocks, andesites, dacites and in the southern part of the chain shoshonitic rocks (Seghedi et al., 1998; Szakács and Seghedi, 1995; Seghedi et al., 2004).

Below the volcaniclastics the Paleogene and Neogene sedimentary deposits of the Transylvanian Basin are present, made up of alternations of marls, silty clays and sandstones, volcanic tuff and important evaporitic deposits (salt) (Krézsek and Filipescu, 2005; Krézsek and Bally, 2006; Paucă, 1967).

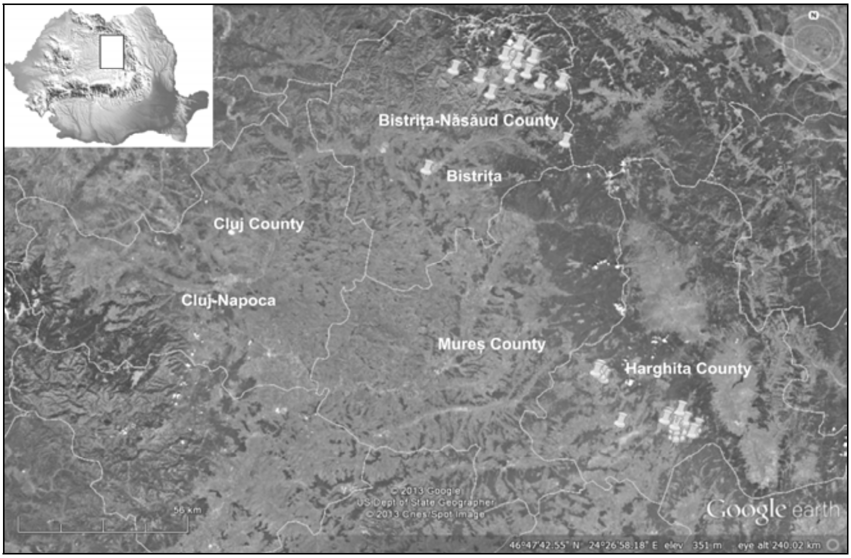

Fig. 1. *Localization of the investigated mineral waters on Google Earth map. The CO_2-rich springs are plotted in the north and the south of the volcanic chain at the Transylvanian Basin boundary.*

The proximity of the volcanic range is characterized by active post-volcanic phenomena, such as CO_2 degassing and mineral sparkling waters. Carbon dioxide appears as "dry" emanations (mofettes) or as dissolved gas in groundwater, conditioning the occurrence of CO_2-rich mineral waters. The circulation of fluids on the study area is facilitated by the presence of fractures. More than 2000 mineral water springs are estimated according to Bányai (1934) and Pricăjan (1972), of which we have analysed 62, following the Eastern Carpathians volcanic chain from north to south (figure 1).

MATERIALS AND METHODS

Four physical parameters (T, pH, redox potential (Eh), and electrical conductivity (EC)) and 15 chemical parameters (CO_2 , HCO_3^-, Cl^-, SO_4^{2-}, Li^+, Rb^+, Na^+, K^+, Ca^{2+}, Mg^{2+}, Fe^{3+}, Zn^{2+}, Cd^{2+}, Pb^{2+}, Cu^{2+} contents) were measured in 63 mineral sparkling water springs following the chain from north to south.

Sampling and sample handling

Waters of 63 springs and spas were collected according to the EPA prescriptions: collected in 500 ml PET bottles, conserved on spot with 1 ml of conc. HNO_3 and kept at 4ºC.

Instrumentation and procedure

The temperature, pH, Eh and EC values were determined by using a multi-parameter device (Multi 350i, Weilheim, Germany). The quantification of the alkaline metals was carried out with a Perkin Elmer 373 (Waltham, MA, USA) flame atomic absorption spectrophotometer. The Cl--ion content was determined by argentometric potentiometric titration (670 Titroprocessor, Mettler, Herisau, Swiss); the quantification of SO_4^{2-} and Fe^{3+} ions were performed in molecular absorption mode at λ = 490 nm using a double beam UV-Vis spectrophotometer (T70+, PG Instruments Ltd., UK). The heavy metals Zn^{2+}, Pb^{2+}, Cd^{2+}, and Cu^{2+} were analysed by stripping voltammetry using Va 797 Computrace Metrohm (USA) and Fe^{3+} with UV-Vis spectrophotometer.

A set of measurements were performed in the field: water temperature, electrical conductivity, pH and redox-potential. Quantification of the dissolved CO_2 and HCO_3^- content were also performed by acid-base titration with 1N HCl. The other components were measured in the laboratory.

The experimental data were processed and interpreted statistically and chemometrically by using Aquachem 3.7 (Schlumberger Water Services), and Statistica software, version 7 (StatSoft.Inc., OK, USA).

RESULTS AND DISCUSSION

In order to define the main mineral water types, the most commonly used tool in evaluating the water type, the Piper diagram was plotted both for the northern and for the southern part of the study area. The Piper diagrams take into account the major ions: Na^+, K^+, Ca^{2+}, Mg^{2+} (cations) and HCO_3^-, Cl^- and SO_4^{2-} (anions) calculated and expressed in meq/l (Fig. 2 and 3).

From the point of view of cations, the chemical composition of the mineral waters in the northern area (figure 2) is dominated by Na^+, with few exceptions when Ca^{2+} occurs in higher amounts, and in some cases there is no dominant cation. A transition from the Na corner to the centre of the triangle can be noticed, suggesting a mixing trend between different kinds of waters. Regarding the anions, most of the samples lie between the HCO_3 and the Cl^- end-members.

In the southern area (figure 3) the mixing trend is well defined for both cations and anions. Most of the springs show a Na-dominant composition, following a trend towards the centre of the triangle, with no dominant cation. Some springs from Vlăhița and Corund are located closer to the Ca vertex.

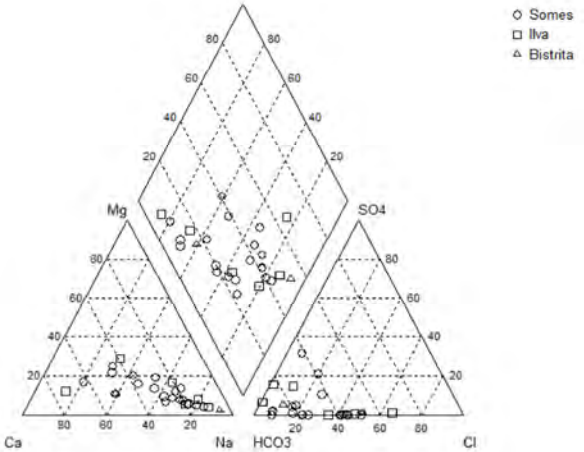

Fig. 2. *Chemical composition (major ions) of the mineral waters from the northern area – Piper plot.*

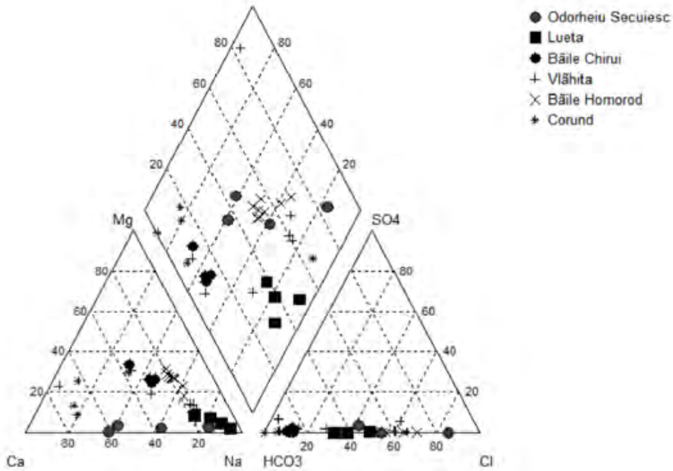

Fig. 3. *Chemical composition (major ions) of the mineral waters from the southern area – Piper plot.*

According to the two Piper plots the main water types are Na-HCO_3, Ca-HCO_3 and Na-Cl. Since the springs are located at a boundary area between the Transylvanian Basin and the volcanic area of the Eastern Carpathians it is likely that both igneous and sedimentary rocks had a great influence on the chemical parameters of the mineral waters. Sedimentary rocks are located under relatively thick volcaniclastic layers (Schreiber, 1980), which are highly fragmented, facilitating the leaching of both geological formations.

Cluster analysis of all the physical and chemical parameters was used to define the main influencing factors (figure 4). These analyses were performed according to all the measured ionic components, physical and chemical parameters, using Euclidean distances reflecting the similarity between the mineral waters in chemical composition.

In Figure 4, the cluster analysis of 19 physical and chemical parameters reveals two main groups. The first group is formed only by the CO_2 and Eh, the second group consists of all the ions and physical parameters. The separate CO_2-Eh suggests the relationship between CO_2, which has an influence on the pH and through it also on the redox conditions of the water. The second group consists of two subgroups which divides the main ions and the heavy metals. The highest influence on the composition of mineral waters has the Na^+ and the Cl^-, together with the electrical conductivity, because they show the shortest distance within one group.

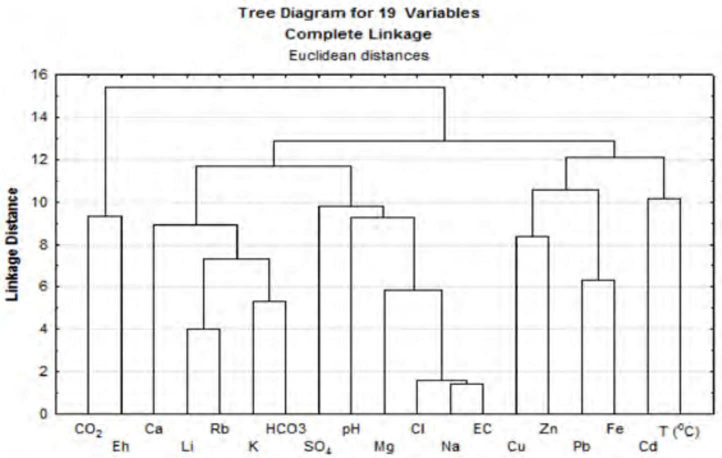

Fig. 4. *Cluster analysis of all the 19 physical and chemical parameters measured in the mineral waters.*

For a more detailed analysis, the correlation matrix between all the 19 parameters was produced (figure 5). Electrical conductivity best fits with Cl, HCO_3, Na, K and Mg with values of 0.97, 0.69, 0.98, 0.69 and 0.78 respectively suggesting that electrical conductivity of waters mainly depends on the main dissolved ions in the water. Similarly HCO_3 and Cl have strong positive correlations, around 0.60-0.80 with the alkali and alkali earth metals, forming together the main dissolved salts in the mineral waters.

The strong negative correlation (-0.91) between pH and redox potential highlights the fact that in aqueous systems usually Eh is governed by the stability of water, which is a function of pH (Railsback, 2006). Consequently mineral waters with negative redox potential suggest redox conditions.

	T °C	EC	pH	Eh	CO_2	Cl	SO_4	HCO_3	Na	K	Mg	Ca	Rb	Li	Fe	Zn	Cd
T °C	1																
EC	-0.11136539	1															
pH	-0.04133705	0.31445316	1														
Eh	0.094548846	-0.27856705	-0.9169	1													
CO_2	-0.35311859	-0.16967626	-0.362358	0.30241	1												
Cl	-0.07599441	0.87980098	0.3096407	-0.268658	-0.287931	1											
SO_4	-0.15795787	0.4571993	0.1873669	-0.178686	-0.234272	0.5198019	1										
HCO_3	-0.23043706	0.69445616	0.3297666	-0.309559	0.1852477	0.5563229	0.0738785	1									
Na	-0.08317137	0.98327313	0.3400106	-0.299683	-0.260679	0.9806922	0.4755462	0.6630524	1								
K	-0.09487999	0.69302662	0.2240808	-0.209867	0.1206058	0.600143	0.1007862	0.7746179	0.6392467	1							
Mg	-0.09627582	0.78218482	0.3281119	-0.271651	-0.030173	0.7225411	0.2335229	0.6720167	0.7363015	0.6326499	1						
Ca	-0.27139284	0.22209795	0.2353002	-0.245366	0.2468802	0.079833	-0.146697	0.6591647	0.1589359	0.3604251	0.1949295	1					
Rb	-0.269491	0.19900252	0.1568904	-0.149008	0.3074093	0.0863799	-0.138344	0.5645904	0.1409389	0.7128264	0.1955628	0.5130907	1				
Li	-0.21177763	0.39026397	0.1123309	-0.124219	0.2683986	0.2682783	-0.092762	0.8953951	0.3298655	0.8316648	0.2889694	0.4742782	0.8078716	1			
Fe	0.193711688	-0.15955429	-0.340378	0.3810822	0.1192629	-0.130907	-0.232675	-0.223073	-0.148532	-0.252174	-0.134195	-0.202244	-0.240751	-0.182391	1		
Zn	0.091328293	0.06060892	-0.022315	0.0637119	-0.165784	0.0822665	-0.070536	-0.073049	0.047608	-0.106616	-0.110152	0.1100144	-0.130312	-0.081562	0.1476451	1	
Cd	0.166786298	0.05677059	-0.153283	0.2110523	0.1371116	0.0507944	-0.047073	-0.05895	0.0588074	-0.168365	-0.122706	0.1707423	-0.208978	-0.141542	0.1425753	0.2985544	1
Pb	0.12324862	-0.09965654	-0.191128	0.1725705	-0.046903	-0.089543	-0.153171	-0.071586	-0.10008	-0.096278	-0.14049	-0.024682	-0.060379	-0.049382	0.6808252	0.4100615	-0.170504
Cu	0.024940551	0.32917698	0.035956	-0.026712	-0.194366	0.3509862	0.2014468	0.1642084	0.3615727	0.1990364	0.1005012	0.0569543	0.1099056	0.1911905	0.3234198	0.431508	0.0440392

Fig. 5. *Correlation matrix of the 19 physical and chemical parameters. Temperature expressed in ºC, electrical conductivity in mS cm*$^{-1}$*, Eh in mV, dissolved* CO_2 *and all the chemical parameters in mg/l.*

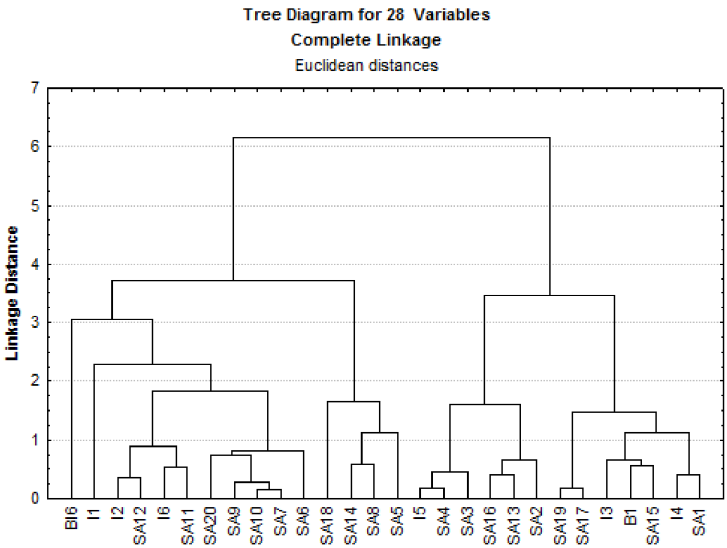

Fig. 6. *Cluster analysis of the 28 mineral waters from northern area.*

The cluster analysis of the 63 springs was made separately for the northern and the southern part of the study area (Figs. 6 and 7.).

The cluster analysis for mineral waters from the northern area (Fig.6.) plots the 28 samples into two well defined groups. The two groups are divided according to physical and chemical similarities. Starting from the left of the graph, in the first group, the mineral waters with higher salinity are plotted, like those from Sângerorz-Băi, Parva, the upper part of Ilva valley and some springs from Anieș, where the contribution of Paleogene sedimentary deposits to the chemistry of mineral waters has been already mentioned by Chintăuan (1998). These mineral waters are of Na-HCO_3 type showing a trend towards Na-Cl, leached from sedimentary deposits. The second group is formed by lower salinity waters, located in the upper part of the rivers, at Colibița, Valea Vinului, Șanț, Rodna, Măgura Ilvei and some springs from Ilva Mare, leaching mainly volcaniclastic deposits, having high dissolved CO_2 and HCO_3 content around 3000 mg/l. These mineral waters are relatively balanced from the point of view of cations or have a trend towards the Ca vertex shown on the Piper diagram. Their anion content is dominated by HCO_3.

In the southern part of the study area, the 35 samples show similar but less obvious division of the Na-HCO_3, high salinity, and Ca-Mg-HCO_3, low salinity waters. The mineral waters are plotted into two main groups, the right one having secondary divisions. In the first (Fig. 7, similarly starting from the left of the graph) group, the Na-Cl waters from Corund, Lueta and Odorheiu Secuiesc can be found which are highly influenced by the leaching of Miocene halite outcrops (Bányai, 1934). At the right of the graph, the rest of the samples from Corund, Odorheiu Secuiesc, Băile Homorod, Vlăhița and Băile Chirui which are typically of Na-K-HCO_3 and Ca-Mg-HCO_3, type according to the Piper plot. Most of the springs lay in subgroups according to compositional similarities, suggesting also a mixing, consistent also with the statements affirmed according to the Piper plot.

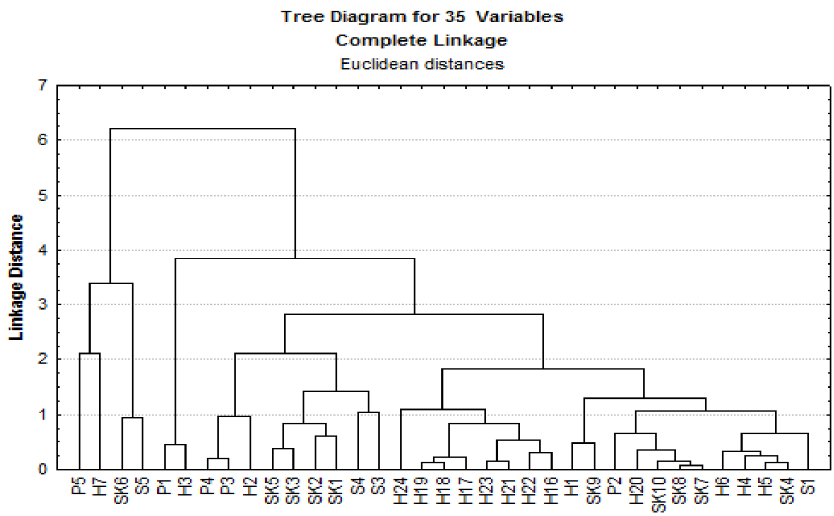

Fig. 7. *Cluster analysis of the 35 mineral waters from South*

CONCLUSIONS

The composition of mineral waters in the border area between the Transylvanian Basin and the Eastern Carpathians is relatively balanced between the major cations Na^+, Ca^{2+}, and Mg^{2+}, with particular cases of shifts towards an increase in Na^+. From the point of view of anions, the mineral waters are mostly of HCO_3^- type due to the high CO_2 dissolved in the water. Both the geochemical classification results shown on the Piper diagram and cluster analysis highlight the mixing between Ca-Mg-HCO_3 and Na-HCO_3 types and the influence of sedimentary deposits on the chemical composition of mineral waters. These phenomena are more evidenced in the southern part of the study area.

Acknowledgements

The present work was financially supported by POSDRU CUANTUMDOC "Doctoral studies for european performances in research and inovation" ID79407 project funded by the European Social Found and Romanian Government, the Sectoral Operational Programme for Human Resources Development 2007-2013, and co-financed by the Romanian National Research Council, Project PN-II-ID-PCE-2011-3-0537.

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