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Hydrogeochemical features of some mineral waters at the contact between Harghita Mts. (Eastern Carpathians) and the Transylvanian Basin

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Abstract

The study area, located at the contact zone between the Harghita Mountains and the Transylvanian Basin is well known for the abundance and diversity of mineral water springs. These mineral waters are used by the local people for drinking and also as Spas. This paper focuses on the mineral waters of some traditional Spas from this area, Odorhei Secuiesc (Seiche Spa, Kápolnás Spa or Solymossy Spa), Upper Vârghiș Valley (Selters Spa and Nádasszék Spa) and Chirui Spa. The aim of the present work is to characterize the mineral waters based on the quantification of chemical content and also to establish correlations between the geological structure and the water's chemical composition. The geological setting and tectonics have a large influence on the chemical composition of mineral waters. Two main water types can be described, mineral waters of Na+ – Cl- type, present at Odorhei Secuiesc, Kápolnás Spa and of HCO3- type with no dominant cation at Chirui Spa. The mineral waters located on a fault at Odorhei Seiche Spa have high CO2 values. Possible mixing zones might be identified between the two types which are present in the Upper Vârghiș Valley where mineral waters of Na+ – HCO3– Cl- type are present except one source, which is of Na+ – Cl- type. The mixing is reflected not only by the chemical composition, but also by the quantity of dissolved CO2. The present paper deals with all the existing mineral water springs in the area providing information in a high resolution about the local hydromineral system.

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Keywords: mineral water; hydrogeochemical features; Eastern Carpathians; Odorhei Secuiesc; Spa

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1. Introduction

The chemical content of mineral waters mainly depends on the geological background, in terms of structure and lithology. The chemical composition of the water provides important information on the functioning of the hydro-mineral system.

The volcanic chain of the Eastern Carpathians is one of the most important European areas from the point of view of mineral water resources especially sparkling mineral waters.

The mineral waters have been studied from the perspective of chemical composition and some correlations were made with the geological background. The most important contributions were performed by Bányai [1], Pricăjan et al. [2] who also established the main mineral water types of the region.

Significant studies on the origin of mineral waters in the area of Harghita Mountains using stable isotopic methods were performed by Papp et al. [3], in the region of Băile Tușnad, by Crăciun et al. [4] and Vaselli et al. [5] giving a general geochemical overview on the functioning of the geothermal and mineral water system in the Carpathian region.

The aim of our work is to characterize the mineral waters based on the quantification of chemical content and also to establish the existing correlations between the geological background and the water’s chemical composition.

According to Bányai [1] there are about 2000 springs in this region, which are divided into three main groups: mineral waters from the Post-Volcanic Manifestations Area (term used by Airinei [6]), mineral waters from the Carpathian flysch area, and mineral waters from the Transylvanian Basin which are related to salt deposits and hydrocarbons.

The early studies on the chemical composition of the mineral waters from the study area date back from the beginning of the 18th Century, assessing the medical effects of the mineral waters by Crantz in 1733. Detailed chemical analyses were performed by Kibédi, who published his results in 1787. Wagner (1773) has published a complex monography of the medical effects, chemistry and ways of exploitation of mineral waters. Later on, in the 19th and 20th Centuries, authors like Hankó, Bányai, Pricăjan, etc., have focused on the occurrence, chemical composition, and classification of mineral waters. They also made assumptions on the value, proper exploitation and use of the mineral waters [7].

The study area, located at the contact between the Harghita Mountains and the Transylvanian Basin is famous for the abundance of mineral water springs of different types. These mineral waters are used by the local people for drinking and also as spas.

We focused on the mineral waters of some traditional spas from the areas: Odorhei Secuiesc (Seiche Spa, Kápolnás Spa or Solymossy Spa), Upper Vârghiș Valley (Szeltersz Spa and Nádasszék Spa) and Chirui Spa. Seiche Spa, located in the northern part of Odorhei Secuiesc town, is known since 1766, and mentioned as a famous place for its mineral water springs. It became a spa during the 19th Century when Orbán Balázs, its owner, built a basin for Attila spring, the one with the highest discharge. [8]. Today at Seiche there is a Mineral Water Museum where one can find information about the mineral water springs of the region and see the first map of mineral waters, drawn by Bányai János. At the southern part of the town, the remains of Kápolnás Spa (or Solymossy Spa) can be observed. In 1872 the chemical composition of the springs was investigated by Solymossy János, who built a spa in that place [8]. Unfortunately, the area is completely ruined today. Along the Upper Vârghiș Valley several mineral water springs exist, which are often compared to the mineral waters from Germany (Selterswasser) because they are both fizzy and salty. Today Vârghiș Valley is famous for the traditional spa Nádasszék, and also for its mineral waters which are used by the local people [8]. The locality of Chirui, together with its mineral waters, was documented for the first time in a protocol of litigation as Keroly in 1623 [9]. The exploitation of the mineral water resources as spas began in the 18th Century.
A well was drilled at Lobogó in 1999, as part of a research project that focused on mineral and thermal water resources in Chirui, Vlăhița and Homorod Bâi area. Beside the Lobogó well, many mineral water springs also exist at Chirui Spa.

2. Geological background

As a consequence of the Neogene – Quaternary volcanic activity, numerous mineral springs and CO₂-dominated gas emissions currently occur in the area. From the point of view of our study the Eastern segment of the Neogene – Quaternary volcanic chain is the most important. This segment is located between the Carpathian thrust-and-fold arc and the Transylvanian Basin. Around the volcanic edifices a wide volcaniclastic plateau was developed, which extends into the basin. The surface of the plateau and the Middle Miocene successions of the Transylvanian Basin are tilted towards the chain axis suggesting a post-volcanic basement sagging. The Neogene salt-tectonics developed under a regional compressive stress field and the spreading of the volcanic edifices with the increasing heat flux have strongly influenced salt diapirism. [10]

The Eastern segment of the volcanic chain hosted the youngest, mostly intermediate calc-alkaline magmatic activity related to the Carpathian arc. The volcanic activity shows a progression from North to South. The most recent activity took place in the area Călimani – Southern Harghita between 11 and 0.3 Ma. [11, 12]

We analyzed the mineral waters from springs in the upper part of Vârghiș Valley and Chirui Spa which are closer to the volcanic chain and mineral waters from Odorheiu Secuiesc area, namely Seiche Spa and Kápolnás Spa, which are located in the Transylvanian Basin.

In Odorheiu Secuiesc area, the Middle-Upper Miocene deposits of the Transylvanian Basin occur. The Pannonian (Upper Miocene) consists of gravel, clays, silty clays and sand. The Sarmatian consists of silty clays, sand with lenticular conglomerate deposits, polymictic conglomerates and sandstones. Badenian marls alternating with sands and volcanic tuffs are also present, and in the depth there are salt deposits [13]. The main tectonic feature is the anticline Vasileni-Odorhei, which is fragmented by a NW-SE driven fault [13]. The fault has an important role in the presence of the sparkling mineral waters in the north-eastern part of Odorheiu Secuiesc, in Seiche Spa area. The Upper Vârghiș Valley and Chirui Spa are located on the volcanic plateau of the western slope of Harghita Mountains, part of the Eastern Carpathians. The plateau was formed as a result of several volcanic eruptions during the Pleistocene. The plateau pertaining to the Harghita Mountains consists of pyroclastites, epiclastites and andesitic lava, belonging to the Vlăhița-Chirui Volcaniclastic Formation. After the eruption, due to external, erosive effects, volcanic rock debris is formed. They are significantly present in every layer corresponding to an eruptive episode. The thickness of the volcanogenic sediments is 100 to 650 m [14]. The sedimentary deposits of the Transylvanian Basin are represented by Sarmatian (Upper Miocene) deposits of Merești Formation, consisting of conglomerates, sandstone, sand, silty clays. The Badenian (Middle Miocene) deposits consist of marls, silty clays, polymictic conglomerates. The area is fragmented by faults which have a strong influence on the circulation of volcanic gases (mainly carbon dioxide) and groundwater [15].

3. Mineral water springs

The study area is very diverse from the point of view of mineral water types and aquifers. There are two main areas of occurrence of the mineral water springs in Odorheiu Secuiesc, in the north-east of the town (Seiche Spa) and in the south (Kápolnás or Solymossy Spa). At Seiche Spa the mineral water
springs are fizzy with H$_2$S. A well brings to the surface salty mineral water with hydrocarbons content [16].

In the southern part, the main aquifers are located in the Sarmatian and Pliocene deposits [17]. Due to the presence of the Badenian salt in some wells, the mineralization of the groundwater is above 5.7 g/l (in a 100 m deep well), and 142.7 g/l (in a 370 m deep well). The presence of Br$^-$ and I$^-$ was noticed, suggesting the influence of old formation water. The mineral waters from Kápolnás Spa have dissolved salts around 81 g/l and also have Br$^-$ and I$^-$, and H$_2$S content. The main ions identified in the water were Cl$^-$, Ca$^{2+}$, Mg$^{2+}$, Br$^-$, I$^-$, HCO$_3^-$, SO$_4^{2-}$ [17].

The mineral water springs from Upper Vârghi Valley (also named Székely Szeltersz) are fizzy and ferrous but also with high NaCl content. Bányai [1] explains the presence of NaCl by the fact that although the water comes to the surface through volcanlastic deposits, it originates from deeper Miocene aquifers that contain salty clays. Bányai [1] notes that the mineral water springs from Vârghi Valley represent a transition from fizzy waters towards salty. On Vârghi Valley (Székely Szeltersz and Nádasszék Spa) the mineral water springs are fizzy and of Cl$^-$—Fe—HCO$_3^-$ type [16].

At Chirui Spa 5 mineral water sources occur, namely Festő spring, Lobogó well, Zsuzsa spring, Rebeka spring and the Main mineral water spring. Berszán et al. [18] include these waters in the HCO$_3^-$—Ca$^{2+}$—Mg$^{2+}$ and HCO$_3^-$—Cl$^-$—Ca$^{2+}$—Mg$^{2+}$—Na$^+$ types.

The Lobogó artesian well is 150 m deep, and has penetrated different rock types: pyroxene andesites, andesite agglomerates, grey marl, calcite sandstone and coherent clay marl on the base of the well [19]. The flow regime of Lobogó well is alternating between outbursting periods and inactive periods (without any water release) [14]. A periodicity of 38 hours of outbursting and 13 hours of inactivity has been observed. The water temperature of 16-17°C could be related to a high heat flux. The most important water yield is provided by the Lobogó well, of more than 20 000 l/day in average. The other springs have a mean discharge of 0.2 – 1 l/s [20].

Fig.1. Geological map of Odorhei Secuiesc (modified after [13])
4. Materials and methods

In July 2011, a total of 23 mineral water sources were sampled in Odorhei Secuiesc area: Seiche Spa, Kápolnás Spa, the Upper Vârghi Valley and Chirui Spa. The criteria on which the 23 water sources were chosen is the mineral water directive 80/777/CEE [21] which defines the natural mineral waters as having a TDS above 1000 mg/l. In the case of these 23 water sources the total dissolved solids value was above 1000 mg/l. The month of July was chosen because of the long-lasting dry season in the year of 2011. The measurements were made continuously in 2 days.

Water temperature, electrical conductivity, redox potential, dissolved oxygen, dissolved carbon dioxide and bicarbonate single measurements were performed in the field by using a multiparameter measuring device HI 9829, and titration with 1N HCl.

Water samples were treated with 1 mL of conc. HNO₃ for conservation. Major constituents (Cl⁻, SO₄²⁻, Ca²⁺, Mg²⁺, Na⁺, K⁺) were determined in laboratory by potentiometry using Titroprocessor 670 Metrohm, titrimetry, spectrophotometry by using spectrophotometer T+70 UV/VIS (PG Instruments Ltd.) and flame AES by using a Perkin-Elmer 373 spectrometer. The values obtained are the averages of 4-6 measurements/parameter.

The chemical data were processed and interpreted by using Aquachem 3.7 and Statistica 8.

5. Results

The results of chemical analyses performed onsite and in the laboratory are shown in the tables 1, 2, 3 and 4 respectively. The mineralization of mineral water springs varies in the four study areas.

At Seiche Spa (Table 1) the electrical conductivity of waters is above 2.7 mS/cm, with a relatively high value of 8.68 mS/cm at Attila spring (Sz5). In the case of Sz2 borehole, the electrical conductivity is
extremely high, denoting the presence of a brine. High CO₂ values were also recorded in this case (3520 mg/l). This source presents extreme values in all chemical components registered.

Table 1. Chemical data of mineral springs from Odorheiu Secuiesc-Seiche Spa

<table>
<thead>
<tr>
<th>Code</th>
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<th>T °C</th>
<th>EC mS/cm</th>
<th>pH</th>
<th>Eh (mV)</th>
<th>O₂</th>
<th>CO₂ mg/l</th>
<th>HCO₃</th>
<th>Cl-</th>
<th>SO₄</th>
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<td>207</td>
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The southern part of Odorheiu Secuiesc-Kápolnás Spa (Table 2) presents different hydrochemical features. The electrical conductivity values are between 8.17 and 125.3 mS/cm. The presence of CO₂ is significantly lower compared to the north-western part of the town, ranging between 0-440 mg/l.

Table 2. Chemical data of mineral springs from Odorheiu Secuiesc-Kápolnás Spa

<table>
<thead>
<tr>
<th>Code</th>
<th>Spring name</th>
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<th>pH</th>
<th>Eh (mV)</th>
<th>O₂</th>
<th>CO₂ mg/l</th>
<th>HCO₃</th>
<th>Cl-</th>
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</table>

Towards the Upper Vârghiş Valley (Table 3) the mineral waters are relatively similar to the ones sampled at Seiche, regarding electrical conductivity and CO₂ contents. Here are the highest CO₂ concentrations recorded in the study area, with an average of 2068 mg/l, except the Nádasszék Spa (SzK6), where due to the artificial warming of the water the CO₂ is fastly removed, and the concentration cannot be accurately measured.

The mineral waters from Chirui Spa have the lowest electrical conductivity and have similarities in composition with the mineral water springs from the Upper Vârghiş Valley (Table 4). Also high CO₂ contents were measured, ranging between 1672 and 2200 mg/l.
Table 3. Chemical data of mineral springs from the Upper Vârghiş Valley

<table>
<thead>
<tr>
<th>Code</th>
<th>Spring name</th>
<th>T (°C)</th>
<th>EC (mS/cm)</th>
<th>pH</th>
<th>Eh (mV)</th>
<th>O2</th>
<th>CO2</th>
<th>HCO3</th>
<th>Cl-</th>
<th>SO4</th>
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Table 4. Chemical data of mineral springs from Chirui Spa

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<th>Eh (mV)</th>
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<th>CO2</th>
<th>HCO3</th>
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</table>

6. Discussion

The results of the chemical analyses were plotted in the Piper diagram in order to distinguish the water types and to establish the potential mixing zones between the different water types (Fig.3). The mineral waters from the Upper Vârghiş Valley are dominantly of Na⁺ – HCO₃⁻ – Cl⁻ type except one source, SzK6, Nádasszéki Spa which is of Na⁺ – Cl⁻ type. At Chirui Spa the mineral waters are dominantly of HCO₃⁻ type without any dominant cation. The mineral waters of Seiche Spa are HCO₃⁻ – Cl⁻ – Ca²⁺ – Mg²⁺ type, excepting the water from the well Sz2 which is Na⁺ – Cl⁻ type. The mineral waters of Kápolnás Spa are dominantly of Na⁺ – Cl⁻ type.

Interpreting the Piper diagram we can delineate the potential mixing area between the Ca²⁺ – Mg²⁺ – HCO₃⁻ and the Na⁺ – Cl⁻ water types. These are mostly located on the Upper Vârghiş Valley and at Odorhei Seiche.

Some mineral water sources, namely Sz2 located at Odorhei Seiche and SzK6 at Upper Vârghiş Valley have extreme values in salinity even though they are located in an area where waters of Ca²⁺ – Mg²⁺ – HCO₃⁻ type are present. By using the cluster analysis based on 23 samples (considered variables in the diagram), considering the parameters: temperature, electrical conductivity, pH, Eh, dissolved oxygen,
dissolved CO2, HCO3-, Cl-, SO42-, Na, K, Ca, Mg we tried to define the grouping of the different types of mineral waters.

Fig. 3. Piper-diagram of the 23 mineral water springs

The main influencing parameters were the electrical conductivity, temperature, dissolved gases, pH and Eh because they were mostly linked to each other. According to these the mineral waters are grouped (Fig. 4). As Fig. 4 shows there is a tendency of decreasing from the high conductivity values towards the lower and mineral waters are grouped according to their similarities in the chemical composition. The well Sz2 from Odorhei Seiche Spa is clearly separated from the rest of the samples due to its extreme high conductivity, above 240 mS/cm. The second and third group of >90 mS/cm, and >20 mS/cm respectively, are mineral springs from Odorhei Kápolnás Spa of Na+ – Cl- type. The rest of the mineral waters are of relatively low conductivity (around 2-4 mS/cm) comparing to the ones discussed before. These represent the transition from Na+ – Cl-type to Ca2+ – Mg2+ – HCO3- type.

In the first group (fig. 5) there are mineral waters from Kápolnás Spa which are of Na+ – Cl- type, but lower conductivity. The second group mainly contains mineral waters from the Upper Vârghiș Valley, being, as shown by the Piper-diagram between the two main mineral water types, and the third group contains the mineral waters from Chirui Spa which are dominantly of HCO3- type without any dominant cation.

A scatter between the CO₂ content and conductivity was performed (Fig. 6). On the X-axis we represented the conductivity, and on the Y-axis the CO₂ content. Two main groups can be distinguished, the group of mineral waters with high CO₂ values (> 1450 mg/l) and with relatively low CO₂ content (< 720 mg/l). The mineral water springs with high CO₂ values are located at Chirui, Vârghiș and Seiche. The mineral waters with low CO₂ values are those of Kápolnás Spa, but these have a higher conductivity.
There is a tendency of reverse proportionality between the electrical conductivity and the CO₂ content. The extreme high values in CO₂ content and electrical conductivity are present at sample Sz2 of Seiche.

The variations in the composition of mineral waters are explained by the fact that the study area is located at the contact between the volcanic area and the sedimentary deposits, including the Badenian salt. The mineral waters located on the volcaniclastic plateau differ from a chemical point of view from those located in the Transylvanian Basin, mineral waters from Kápolnás Spa respectively.

The mineral waters closer to the volcanic edifices, located at Chirui Spa are dominantly of HCO₃⁻ type without any dominant cation, since the water dissolves mostly volcaniclastic material. The mineral waters from Upper Vârghiş Valley are dominantly of Na⁺ – HCO₃⁻ – Cl⁻ and one is of Na⁺ – Cl⁻ type probably due to the presence of Sarmatian deposits, salty clays which are covered by the volcaniclasts of the Harghita plateau. Tectonics have also a great influence on the chemical composition of waters.

At Seiche Spa the geological structure mainly consists of the Miocene sedimentary of the Transylvanian Basin, but the mineral waters are located on a fault which is probably responsible for the circulation of gases, explaining high CO₂ values and the unusually high conductivity of sample Sz2.

The present paper deals with all the existing mineral water springs in the area providing information in a high resolution about the local hydromineral system. The mineral water types were defined using physico-chemical data from the field and major constituent chemistry.
We conclude that there are mixing zones between the waters related to the sedimentary of the Transylvanian Basin and the waters related to post-volcanic phenomena. These potential mixing zones are present in the study area and are located at the Upper Vârghiș Valley. More detailed investigation on the origin of mineral waters should be made by using stable isotopic methods or microelement investigations.

7. Conclusions

In our paper we focused on the hydrogeochemical features of the mineral water springs in a contact area between two main geological units, the volcanic range of the Eastern Carpathians and the Transylvanian Basin. These mineral waters are used in spas or for drinking and have different chemical composition.

The geological structure of the area includes volcanic rocks, sedimentary rocks and salt diapirs that may arrive at the surface. Tectonics have also an important contribution to the circulation of underground water and gases. At Odorheiu Secuiesc Seiche Spa the NE-SW driven fault brings to the surface mineral waters with high salinity and also with high CO₂ content.

Two main water types can be described, mineral waters of Na⁺ – Cl⁻ type, present at Odorheiu Secuiesc, Kápolnás Spa and of HCO₃⁻ type with no dominant cation at Chirui Spa.
We could identify mixing zones between the two types which are present in the Upper Vârghiș Valley. The mixing is reflected not only by the chemical composition including CO$_2$, and also supported by the local geological structure. At Vârghiș Valley the sedimentary Sarmatian deposits might be closer to the surface and responsible for the type of mineral waters.

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