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# Extended Abstracts

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**Hydrogeochemical characteristics of mineral and thermal waters**

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## INTRODUCTION

According to the density of occurrences and the diversity of physical properties and chemical features of the mineral waters, the territory of Serbia belongs to the one of the most resourceful areas of the European continent, but only a small quantity of these mineral waters is used for bottling. Currently, there are 30 bottling mineral water plants which delivered around 560 000 $m^3$ of bottled water to the market in 2008.

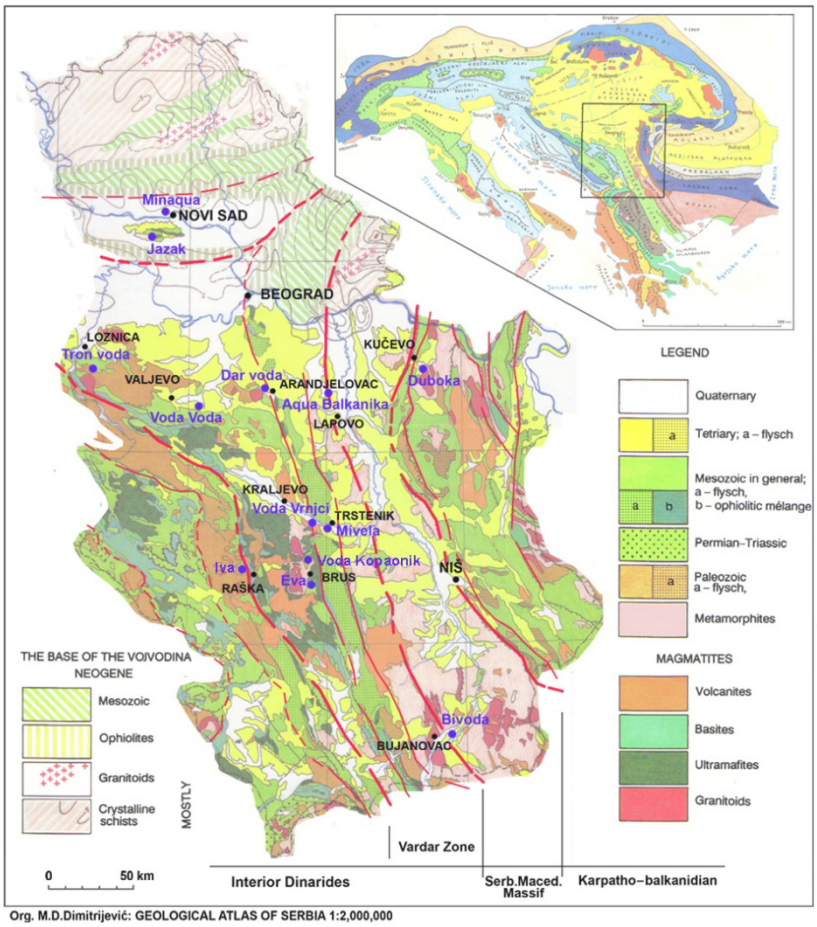


**Figure 1.** Features on the geological map of Serbia (Dimitrijevic, 1994).

The territory of Serbia is divided into 5 regional geological systems (Figure 1): Pannonian, Interior Dinarides, Vardar zone, Serbian-Macedonian massif and Carpatho-Balkans, which are significantly different according to the quantity and quality of ground water. In the Pannonian basin water is predominantly accumulated within the Neogene sediments, in the Dinarides and Carpatho-Balkans areas water is accumulated within limestone, and in the central part (Vardar zone, Serbian-Macedonian massif) within different rocks of a metamorphic complex. The geological conditions dictate the speed of water exchange, but they do not correspond completely to the quality of the ground water.

## PRESENTATION OF ANALYZED OCCURRENCES AND THEIR QUALITY

EuroGeo Survey Geochemistry workgroup (Reimann, Birke, 2010) examined 13 mineral water samples from the teritory of Serbia. The total of 71 parameters were examined for each sample, and some of the results are given in the Table 1.

**Table 1.** Review of the chemical composition of the analyzed mineral waters.

| Mineral water | Class | Subclass | Specific components | TDS (mg/l) |
|---|---|---|---|---|
| Minaqua | $HCO_3$-Cl | Na | J, $NH_4$, B, Fe | 1151 |
| Jazak | $HCO_3$ | Ca, Mg | | 352 |
| Dar voda | $HCO_3$ | Na | Fe, Mn, F, Li, Cs, Cu, Rb, B | 592 |
| Bivoda | $HCO_3$ | Na | B, Sr, Ge, K, Si | 3317 |
| Aqua Balkanika | $HCO_3$ | Ca | | 363 |
| Voda Vrnjci | $HCO_3$ | Na | Cs, Rb, Li, Sr, Ge, Si, Ni | 1081 |
| Mivela | $HCO_3$ | Mg | Rb, Si | 1286 |
| Eva | $HCO_3$ | Ca | Sb, Ni | 184 |
| Voda Kopaonik | $HCO_3$ | Na | Cs, Li, Sr, Ge, Fe, F | 1086 |
| Iva | $HCO_3$ | Ca, Mg | | 234 |
| Voda Voda | $HCO_3$ | Ca | Ti, W, Sb | 364 |
| Tron voda | $HCO_3$ | Ca, Mg | | 320 |
| Duboka | $HCO_3$ | Ca | | 836 |

Within the Pannonian basin we have analyzed the Minaqua and Jazak water.

**Minaqua** is genetically related to the Neogene sediments of the Pannonian basin. Since the water is formed in anaerobic conditions, higher concentrations of J (0.686 mg/l) and $HN_4$ (4.4 mg/l) in the mineral water have been observed and they are of a natural, organogenic origin. Higher concentrations of $NH_4$ indicate that the water was formed in areas where oil and gas are generated. All of the analyzed waters are $HCO_3$ according to their anionic composition, only Minaqua is $HCO_3$-Cl, which indicates that the waters are formed in a shallow environment of the Pannonian basin. From a medical point of view, iodine strengthens memory, mood, normal functioning of the thyroid gland, quality of hair, skin, teeth and nails, which gives this water a special value.

**Jazak** water from horst Fruska Gora, is being captured from Triassic sediments, which were developed in carbonated facies (limestone, dolomite) (Vukicevic, Demic, 2005). That is confirmed by a ratio of rCa/rMg of 1.68. The water is $HCO_3$-Mg, whereby we can say that a considerable amount of Ca (77.0 mg/l) and Mg (45.6 mg/l), as well as a low amount of Na (6.9 mg/l) and Cl (5.53 mg/l) contribute to the good water quality. It emerges through fracture-karst springs of a considerable volume, and according to these features the location is not typical for the Pannonian basin.

In the area of Interior Dinarides **Iva** water (Grabovacka banja – spa) is bottled. Water flows under pressure out of Middle Triassic limestone. The recharge is done through the infiltration of atmospheric water in the open part of the karst aquifer located North-East of the spa. The geological structure of the terrain is made of phyllite, schist and metasandstone, within layers of a Paleozoic age, above which Triassic sediments (marbly limestone) occur. Thick-bedded and massive dolomites and limestone are situated above them. The terrain is in tectonic respect significantly fractured which enables inflow of the water from serpentinite (Letic, Djokic, 2008).

Mineral water Iva is $HCO_3$-Ca, Mg. The ratio of rCa/rMg (2.83) as well as a total water hardness of 12.2 to 13.9° dH, indicate carbonate rocks as its primary circulation and accumulation environment, and the presence of serpentinite as the source of its chemical composition. Hydrochemical parameters are within the limits for drinking water which make it very suitable for bottling.

The majority of the analyzed samples of mineral water from the territory of Central Serbia contains higher concentrations of Cs, Li, Rb, and Sb, which indicate that the water emerges from granite intrusions. Higher concentrations of U, Th and K, which have been observed in **Bivoda** and **Dar Voda** confirm that the water emerges from acid igneous intrusions, and that they are related to **Voda Vrnjci** as well. Their specific chemical composition is the result of the forming and outflow of mineral water. The primary spring is fed by an infiltration of atmospheric water through the fault system in uncovered parts of the terrain built up of modified rocks and granite. Enrichment caused by mineral substances and generation of the primary chemical composition occur in deeper spring parts (Vujanovic et al., 1971). Water circulates through the fault system whereby it is enriched by gas $CO_2$ from the faults and then it arrives to the reservoir rocks in the Neogene sediments (sands), where it is captured.

**Dar Voda** (water) is drilled in the Bukovac fault. The pH value of 5.6 indicates a low acid environment, while according to water hardness (14.0-17.3°dH) it is classified as a fairly hard water (according to Clut). Higher concentrations of Fe (0.101 mg/l) and Mn (0.465 mg/l) in Dar Voda can be related to the decomposition of granite rocks, or the presence of basic rocks which are not found on the surface, or in the borehole. The presence of fluorine F (1.39 mg/l) in the water is related to minerals of igneous rocks (granitoide of Bukulja), apatite, biotite, fluorite (Dangic, Protic, 1995). By studying the migration of fluorine in the mineral waters of Serbia it was noted that the content of fluorine is the most common in the $HCO_3$- Na water, with nitrogen gas composition. With the increase in the ratio of rNa / rCa + Mg, the content of fluorine increases by certain regularity (Papic, 1994).

Considerable concentrations of $CO_2$ (600-1580 mg/l) give the water an acidic nature. Based on the balneology value of Dar Voda, the water is classified as a Na $HCO_3$-Li-F-Si-CO2-cool mineral water and it is recommended for the prevention of gastritis, stomach diseases, gall and liver diseases, diabetes and osteoporosis.

According to its ionic composition **Bivoda** has high contents of $HCO_3$ (3290 mg/l) and Na (1212 mg/l). This hydrochemical type of underground water is related to acidic igneous rocks such as granite and its products. The water is characterized by considerable amount of free $CO_2$ which emerges out of deep fault structures and gives the water an acidic flavor (Zlokolica-Mandic, 2000). The presence of free $CO_2$ is also related to the pH value which is somewhere at the cross point between low acid water and neutral water with a pH of 6.5. The quantity of Sr (1.9 mg/l) in higher concentrations is a direct consequence of the high mineralization (4891.0 mg/l) of Bivoda. The origin of B (5.66 mg/l) in Bivoda hasn't been definitely determined. The high percentage of boron indicates that boron in the ground water derives from a mineral named tourmaline, which emerges in pegmatite, present in the area of Bujanovac (Dragisic, 1997); but it is most likely that the origin of boron with carbon dioxide comes from deep fault structures. This water is rich with minerals which are recommended for the people exposed to the physical exertion.

The natural carbo-acidic water **Aqua Balkanika** is also related to igneous rocks. The presence of free $CO_2$ in the water is related to processes of regional metamorphism (cooling and solidification) of igneous intrusions in deeper parts of the Earth's crust. During magma crystallization, easily evaporating components, $CO_2$ among them, are partly built into the rock minerals, and a considerable part of them is released during consolidation with ground water. Water moves along joints and faults toward the terrain surface (Komatina, Popovic, 1994). Underneath these Neogene sediments there is crystalline schist with a considerable presence of calcschist and marble. In the south of the location, these rocks appear on the surface in the recharge area. The water is $HCO_3$-Ca of the low TDS (363.0 mg/l), and higher concentration of Ca (78.5 mg/l).

Vrnjacka Banja is the most popular spa-touristic center in Serbia. There are several springs of healing water in it. The „Sneznik" spring, which is used for balneotherapy, is also used for water bottling under the name **Voda Vrnjci**. Next to the spring there is a borehole made in serpentinite rocks. The oldest rocks in the wider area are Paleozoic schist and amphibolites, with layers of marble through which considerable quantities of mineral water circulate. The water circulates through serpentines and gabbros, that are tectonically quite disturbed, which implies very good filtration characteristics and also increased concentrations of Mg ions (55.4 mg/l) (Nikolic, 2009). The presence of geochemical assemblage Cs, Rb, Li, Sr, Ni, Ge, indicates a contact of this water with granodiorite, which is located 10 km to the South-East of Vrnjacka Banja (Zeljin, Crni Vrh), while higher content of Ni (9.12 mg/l) indicates the presence of ultrabasic rocks (gabbros and diabase). Voda Vrnjci is characterized by an increased TDS (1081 mg/l) and increased contents of $CO_2$ (700–1044 mg/l).

Mineral water **Mivela** is bottled in the Trstenik area (Veluce place). The water is $HCO_3$-Mg with a water hardness of around 80°dH, which means that it falls into the category of very hard waters, according to the Clut classification. The water is characterized by an extremely high concentration of Mg (324.0 mg/l), which is most probably due to the circulation of water through serpentine, peridotite and fault structures. Due to its high concentration of Mg, it is very helpful for the prevention of hypertension, regulation of blood sugar levels, heart arrhythmia, endocrinologic diseases and nervous system diseases.

At the foothill of the Kopaonik mountain (Brzece-Brus), the bottling of mineral water **Eva** is performed. The water is characterized by its low TDS of 184 mg/l, which classifies it among low mineralized water. The high content of Sb (2.03 mg/l) originates from hydrothermal alteration of serpentinite. According to the Alekin classification, the water is $HCO_3$-Ca, which indicates a limestone origin.

**Voda Kopaonik** is located in the vicinity of Eva water, yet has significantly different qualities. Voda Kopaonik is $HCO_3$-Na, according to its ionic composition. Increased concentrations of Cs, Li, Sr, and Ge indicate contact with igneous rocks. The presence of fluorine F (2.39 mg/l), like in Dar water, is in direct connection with the ratio of rNa/rCa + Mg (Papic, 1994). However, the presence of Ni, which is also found in Voda Kopaonik, is related to the presence of ultrabasic rocks (gabbro and diabase).

**Voda Voda** is bottled in the area of Gornja Toplica (Mionica). The water is $HCO_3$-Ca, originating from limestone found in the bottom of Neogene sediments, discharging in the form of a flowing well. Higher concentration of Ti, W and Sb are related to diabase and spilite.

The natural spring water from the Devet Jugovica spring is bottled under the name **Tron** water. Content of Na (1.8 mg/l) is the extremely low. The ratio of rCa/rMg (=2.144), indicates dolomite and dolomitic limestone as the primary environment for water circulation.

Natural mineral water **Duboka** of Kucevo belongs to the Carpatho-Balkanian hydrogeothermal province. It is characterized by increased concentrations of $HCO_3$ (956 mg/l) and Ca (241 mg/l) as a result of the decomposition of limestone and calcium feldspars in magmatic rocks (granite monzonite). The water temperature is 20°C, so it is classified as a thermomineral water. Based on the geological structure, it is obvious that the granodiorites, which are located near the mineral water findings below the limestone, have a great deal of influence on the water temperature. The content of $CO_2$ (450 mg/l) makes it a low acid water.

## CONCLUSION

The analyzed mineral waters of Serbia significantly vary regarding the TDS, from 184 to 3317 mg/l (Table 1). All waters are $HCO_3$, except Minaqua which also contains Cl among the leading anions. In the cation composition, there are two major groups: with a dominant content of Na, and with a dominant content of Ca or Ca+Mg. In this grouping, Mivela is an exception, because it is dominantly Mg ion. Generally, Na water contain a large number of micro components, which is of course a consequence of their high mineralization, but also of genetic relation to the presence of acidic igneous intrusions in the zone of mineral composition forming. However, these rocks are not always seen on the surface, in the nearest zone of infiltration, and are not registered in the exploitation wells. The analyses of mineral water prove the direct correlation between the hydrochemical composition of water and complex geological settings in which the formation and movement of water have been taking place, throughout the geological history.

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