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Hydrogeochemical characteristics of mineral and thermal waters

title: **Hydrogeochemical characteristics and their basic types thermomineral waters in Serbia**

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ABSTRACT

The title of this paper sufficiently points out the essential presentation as a whole. Together with the state of research and exploitation of the thermomineral water in Serbia, the paper presents the categorization of these waters in accordance with the anion end cation contents, basic types i.e. the way and extend of the utilization, the origin and the processes occurring in the Earth's crust, zone in the relation to the environment where they ere formed, as well as the assessment of these waters in Serbia. The paper especially emphasizes the fact that geological composition and certain conditions and processes occurring in the Earth's crust represent the decisive factors for the genesis of these waters, well as the differences rep resenting the essence of these waters as a natural mineral resource. Serbia, in its whole territory, is country rich with mineral waters representing a natural treasure that should be appreciated. According to the registered natural occurrences (spring) up-to-now established by the research drilling, there are 272 locations in Serbia (as per recent data probably more than 300), out of which 230 locations have been tested in details. As far as the form and content are concerned, this paper represents a new conceptual approach to the treatment of thermo mineral waters – not only in classifying basic types of these waters, but in separating and defining hydro geochemical conditions of geological environment in which occurrences are noticed as well. There have been data about the depth of drilling, the kind of collector and its depth, for most boreholes. It is more important, however, that research work so far shows that thermomineral occurrences and their spread within the territory of Serbia depend very much on neotectonic movements reflecting in transformation of older structures, by activating existing dislocations, general relief raising, depression formation and horsts. The effect of neotectonic movements is followed by volcanic activity, namely geothermal anomaly formation in particular regions, of which contemporary manifestations on the surface of the terrain are, among the others, thermo mineral water occurrences as well. Tertiary igneous activity is another important factor for thermomineral water occurrences. Masses of vulcanite following faulting contributed to geothermal anomalies formation considerably. With regard to that, practically, it is very difficult, almost impossible, to draw a boundary among particular mineral water types in natural conditions, for different types of mineral waters are present on the terrain, it is very difficult to make an entire mineral water classification. Systematizing the presented results of former researches according to ion composition, mineralization, gas composition and radioactivity, the following types of thermo mineral waters in Serbia can be singled out by specific components: HCO_3-Ca, Mg-Ca, Mg-Ca-Na with M to 5 g/l, HCO_3-Na with M to 15 g/l, Complex anion composition Na or Ca-Na, raised t with M to 10 g/l, SO_4-HCO_3, Mg-Ca and Na-Mg-Ca with M to 5 g/l, SO_4-Cl-Na, Ca-Na with M to 15 g/l, SO_4-Cl and HCO_3-SO_4-Cl-Na, SO_4-Na and Mg-Na, HCO_3-Cl-Na rarely Cl-Na-Ca, Cl-Na and Ca-Na, in the last three types M is raised. The pH values of mineral and thermomineral water varies from 2.5 (hyperacid) up to 12 (hyperalcaline). Values of TDS vary from 0.2 gr/kg to 20 gr/kg. Maximal temperature of the natural springs is 96°C . Maximal temperature of thermal water from wells is 111°C.

INTRODUCTION

Serbia is situated in western part of Balkan Peninsula. The Balkan Peninsula is located in the South Eastern Europe and geographically it represents its largest section. Serbia covers relatively small area (about 88 000 km^2) but its geology is quite complex. Upper part of the earth

crust at the territory of Serbia, 250 natural springs are situated. This paper shows main characteristics of thermomineral water of Serbia such as: yield, temperature, chemical content, and utilization.

REGIONAL GEOTHECTONICS AND GEOLOGICAL OVERVIEW

The most of the thermal springs are locatedin the Inner Dinarides their is situated in the southern periphery of the Pannonian Basin. It ranges from Belgrade at the east to Sisak at the west and from the Sava River at the north towards the cities of Banja Luka and Sarajevo (Fig. 1). Inner Dinarides represents the nothen branch of the Dinaric Formations, which are the largest geotectonic unit of thr Balkan Peninsula. According to conventional tectonics concepts the Dinaric Formations represen the central part of the former large geosinklyne inside Alpine Orogeny, wich also encompass the following large geotectonic units: Serbian-Macedonian Massif, Carpatho-Balkanides and Pannonian Basin and a small part of Mesian Platform (Grubić, 1980). According to the lates interpretations of the tectonics of Balkan Peninsula, which, are the result of the applied „global tectonic" theory, the Eart"s crust in the teritory „Yugoslavia" consists of terranes (Keppie & Dallmeyer, 1990). The terranes in the central and western parts of the Balkan Peninsula are the consequence of subduction that occurred during the Jurassic Period(Karamata & Krstić, 1996). According to these authors the hydrogeothermal system of Inner Dinarides is situated in the extreme southern section of the Pannonian Basin and the following Dinaric terranes: The dinaric Ophiolite Belt terrane (DOBT), The Central Bosnian Mts.terrane (CMBT), The Jadar Block terrane (JBT), The Vardar Zone composite terrane (VZCT). The Pannoniana Basin, or its south part in Serbia and Bosnia and Herzegovina, consists of Paleogene, Nogene and Quaternary sediments with a total maximum thicness of about 4 000 meters.

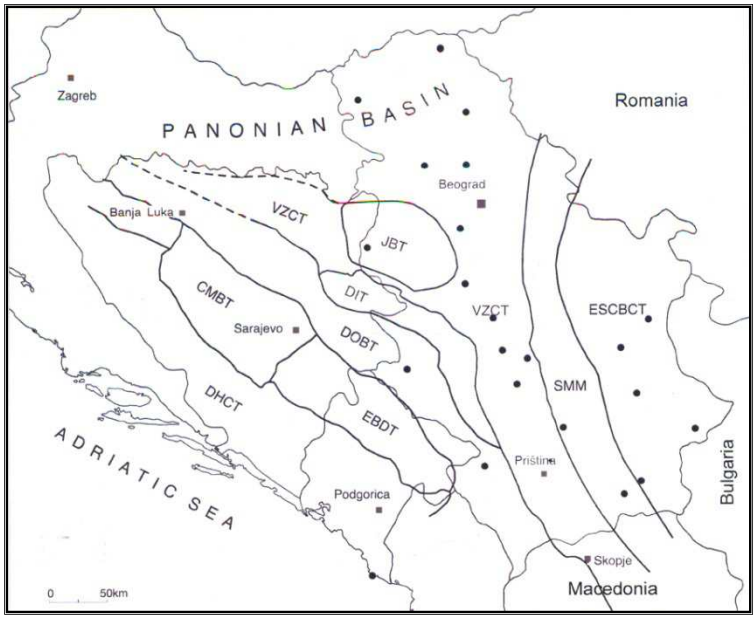

Figure 1. Geotectonic map.

HYDROGEOCHEMICAL CHARACTHERISTICS OF THERMOMINERAL WATERS IN SERBIA

Pannonian Basin. Within this geotectonik unit comprising a complex hydrogeothermel conductive system with a number of separate reservoirs, four groups of reservoirs are individualized by depth. First group of reservoirs have a maximum depth of 2000 m. The highest water temperature in the reservoirs is 120°C. The average flowing well yields are 1-13 kg/s. Total mineralization of thermal water is 1-9 g/kg, mostly 3-5 g/kg. Chemically, thermal waters are of HCO_3-Na type. Water temperature at well-heads are mostly 40-55°C, maximum 82°C (Tonic et al, 1989). The second group of reservoirs are in Lower Pliocen and Pannonian sediments, composed of sandstones of a lower porosity than the aquifers of the first group. Thermal waters in this reservoir are of HCO_3-Cl-Na typa and of mineralization rate 4-20 g/kg, mostly 5-12 g/kg. The maximum expected water temperature in this reservoir group is up to 160°C. Average yields of flowing wells are 2.5 to 5 g/kg, and the well-head water temperatures are 50-65°C on average. The third group of reservoirs are those at the base of Neogene or Paleogene sediments. These are Miocene limestones, sandstones, basal conglomerates, and basal breccias. Thermal water contained in these rocks is higly mineralized (to 50 g/kg), and its chemical composition is of the HCO_3-Na type. Average well yields are 5-10 kg/s and water temperature at well-heads are 40-50°C. The fourth group of reservoirs are in Mesozoic and Paleozoic rocks under Paleogene end Neogene sediments. The most important reservoirs of this group and of the entire Pannonian hydrogeothermal system and Republic Srpska are Triassic karstifield and fractured limestones and dolomites. Similar reservoirs extend beyod the border, in the Pannonian basin, in Hungary, Romania and Slovakia. Far from the basin's margin, at depths exceeding 1500 m, thermal waters in Triassic limestones are of Cl-Na type. In the marginal zone of the basin, where Neogene sediments are 1000 m deep over Triassic limesstones and where water-exchange is active thermal waters are of HCO_3-Na type and have mineral contents of up to 1 g/kg. Average well-yields is 12 kg/s, or 40 kg/s from reservoirs near the basin"s margin. The water temperatures at well-heads are mostly 40-60°C.

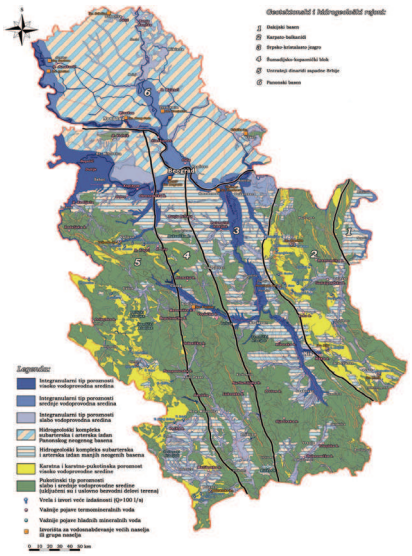

Figure 2. Hydrogeological map of Serbia.

Dinarides. Hydrogeothermal system in this geothermal province differ in their types, kinds of reservoirs and their extend,etc., as a result of varying geology. Rocks that have the largest distribution are Mesozoik in age (1), karstifited Triassic limestones and dolomite, (2) ophiolitic melange including large Jurassic peridotite massifs (3), Cretaceous flysch (4) Paleozoik metamorphic rocks (5), Paleogene and Neogene granitoid and volcanic rocks, and (6) isolated Neogene sedimentation basins. Hydrogeotherml system have formed in terrains: (1) Neogene sedimentation basins with reservoirs in Triassic limestones under them, (2) peridotite massifs and ofhiolitic melange with reservoirs in Triassic limestones; (3) granitoid intrusions and respective volcanic rocks with reservoirs in the same rocks, and(4) Paleozoic metamorphic rocks with reservoirs in marbles and quartzites. The best aquifers are Triassic limestones, as the thermal water contained has low mineral content (<1 g/kg) of HCO_3-Ca-Mg type. Springflows are very high, up to 400 kg/s, and well yields are up to 60 kg/s. Maximum temperatures of water at well –heads are 80°C. The second important reservoirs are those in granitoid intrusions and their marginal thermometamorphosed fracture zones. The contained thermal waters are also low in total mineralization (>1g/kg) of HCO_3-Na type, and maximum yield to 15 kg/s.The highest temperature of waters at well-heads are 78°C.There are few occurences of thermal water in Paleozoik metamorphic rocks.Such springs have low flows (< 1 kg/s), low water temperatures (< 20°C), mineralizations rates 5-7 g/kg, HCO_3-Na in type, and high concentrations of free CO_2 gas.

Serbian-Macedonian Massif. There are two types of hydrogeothermal system in this geothermal province. One is the type formed in the Proterozoik matamorphic complex, with the reservoir in marbles and quartzites up to 1500 m in thickness.Thermomineral waters in the reservoir have total mineral content of 5-6 g/kg.Their chemical composition is HCO_3-Na –Cl type water with high concentration of free CO_2. This gas is formed by thermolysis of marble at temperatures above 100°C in the presence of water, as verified by isotopic studies (Milivojevic, 1989). Thermal water temperature at springs is 24-72°C and springflow is of gas-lift type due to the high CO_2 gas content. The second type hydrogeothermal system was formed in contact with and in the marginal zones of the Neogene granitoid intrusions. The reservoir rocks are granitoids, metamorphic and contact-methamorphic rocks, heavily fractured as a result of heating and cooling. The thermal springs of Vranjska spa belong to this system type and have the warmest water in Serbia, 80-96°C.Its mineral content varies from 0.1 to 1.2 g/kg. The water type is HCO_3-Na-SO_4-Cl. Springflows are up to 80 kg/s.

Carpatho-Balkanides. This geothermal province has many hydrogeothermal system, most of them formed in regions of isolated Neogene sedimentary lake basins. Reservoir rocks are karstified Triassic, Jurassic or Cretaceous limestones. Thermomineral karst springs have flows of 60 kg/s, with water temperatures to 38°C. Total mineralization is 0.7 g/kg and the water type is HCO_3-Ca. Another type of hidrogeothermal system in this geothermal province was formed in the Upper Cretaceous paleorift of Eastern Serbia, where Mesozoic limestones were penetrated and thickly covered with andesite lavas and pyroclastics. The mineralization of these contained water are up to 0.8 g/kg and the water is of SO_4-Na-Cl type, or HCO_3-Na-SO_4-Cl type where it is limestones.Water temperatures at thermomineral springs are up to 43°C, and springflows are up to 10 kg/s.

Table 1. Review of represented classes and subclasses of mineral water in Serbia in the selected regions.

Region	Subclass	Ca	Ca Mg	Ca Na	Ca Mg Na	Mg Na	Na	Ca Na Mg	Mg Ca	Mg Na Ca	Mg Ca Na	Na Ca	Na Mg	Na Ca Mg	Na Mg Ca	NH_4 +Na	H, Fe	Σ
	Class																	
Carpatho-Balkanides	HCO_3																	
	HCO_3-SO_4	5	13		1									1				20
	SO_4-HCO_3						2											2
	HCO_3-Cl-SO_4							1				1						2
Serbian-Macedonian Massif	HCO_3													1				1
	HCO_3-SO_4		7		1		15				1	1						25
	SO_4-HCO_3		2				3											5
	HCO_3-Cl						1											1
	Cl-SO_4						1						1					2
	SO_4																1	1
	Cl		1															1
Šumadija-kososvo-Kopaonik area	HCO_3						1											1
	HCO_3-Cl	4	7		1	5	30	1	6	1	1	6	4	1	7			74
	SO_4-HCO_3						3		1				2	1				7
	SO_4-Cl			1														1
	Cl																1	1
Dinarides	HCO_3						1											1
	HCO_3-SO_4	2	21	2	1		24		2	1		5		2				60
	HCO_3-Cl											1						1
	Cl						2						1					3
Pannonian Basin	HCO_3						1											1
	HCO_3-Cl						13					1						14
	Cl-HCO_3						3									1		4
	Cl						5											5
Total	10	11	51	3	4	5	113	2	9	2	2	17	8	6	7	1	2	243
u (%)		4,53	20,99	1,23	1,65	2,06	46,5	0,82	3,70	0,82	0,82	7,0	3,3	2,47	2,88	0,41	0,82	100

CONCLUSION

Researched and analyzed thermomineral water occurrences of Serbia, are differed by their chemical composition. The result of varying composition is different lithological rock masses and other physical and chemical conditions that influence on water in their underground movement from infiltration zone to discharge zone. Test results are presented in the form of macro components content (anions and cations) that are served to extract the basic types of mineral water.

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