GEOCHEMICAL CHARACTERISTICS OF THE WATERS FROM THE GEOTHERMAL SYSTEM ZDRAVEVCI

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Abstract

In this paper the results from the geochemical research of the waters from the geothermal system Zdravevci are presented. The geochemical research points to the fact that it is a case of sodium – calcium – hydrocarbonate, sulfide and low acid carbonic hyperterms, which is also evident from the participation rates of separate dissolved components in them. Due to this content, the thermal water from this geothermal system has bath and healing features. The waters from the researched geothermal system, apart from the other components, also contain 1/3 of the volume with pureCO_2, increased contents of sulfur and increased concentrations of sulfur and also increased concentrations of many other components that most likely a product of the classic hydrothermal systems located in greater depths.

Key words: Zdravevci, geothermal system, AES-ICP, major elements, microelements, thermomineral water.

INTRODUCTION

The chemical content of the hydrothermal fluids and the isotopic content of certain dissolved ions and gases are tightly connected to the thermal history of the hydrogeothermal systems. This hydrochemical property enables use of many practical methods to use the chemical content of the hydrothermal fluids in the geothermal symptomatology.

Without going into details, it should only be taken into consideration that the results from the research of the chemical content of many warm and hot waters in the world, many authors point to the fact that the content of Na, K, Ca, Mg and$SiO_2$and many others dissolved components can provide significant data also for the temperatures which exist in the volume of the accumulation of the hydrogeothermal fluids.

The chemical content of the hydrothermal fluids is mainly conditioned by the reactions among the minerals which constitute the rocks and the fluids and which are conditioned by the temperatures.

The examination of the chemical content of the thermomineral waters from the geothermal system 'Zdravevci', as well as the waters from other springs and wells in this area, has been done during this last few years but it is not systemized yet. In order to determine the chemical content of the waters, samples have been taken from various natural springs, wells or some examined holes in the areas surrounding the geothermal system 'Zdravevci'. The chemical analyses are done in various laboratories with different criteria and possibilities to determine the various components of the examined waters. Apart from that, it is also evident that the different laboratories have equipment with different perceptibility in the process of determining the content of separate components (comparing the data from the water from the examined hole ZD-3 from different laboratories).

The analyses are concerned with determining the content of the main elements, like Ca, Mg, Na, Kand other elements present in the concentrations from the scale mg/L but also determining the content of microelementspresent in the concentrations from the scale mg/L. The latest examinations are done with atomic emission spectroscopy with inductively joined plasma, i.t. AES-ICP method which satisfies the required needs for sample analyses of waters of different type.

RESULTS AND DISCUSSION

It is well known today that in the process of the examination of geothermal waters, the geochemical research has great application. These examinations are based on the fact that the warm waters in their circulation through the Earth's surface dissolve certain rocks they encounter along the way. The quantity and the proportions of the dissolved ingredients are directly depended on the temperature of the

surrounding area. During the flow of that water towards the surface its chemical content is significantly changed, but it can be stated that the thermal waters decrease the temperature compared to the temperature it had in the grater depths.

In the examination processes done in 2009, an attempt has been made to follow the chemical content of the thermomineral waters in order to determine the presence and the variability of the presence of separate elements, and also to make a comparison with the results from the previous examinations. These examinations only deal with the water from the holes ZD-3, ZD-4, ZD-7 and ZD-5. The results are presented in Table 1.

From the given Table 1 it can be seen that the mineral water from the geothermal system 'Zdravevci' is characterized with a presence of a great number of components which are most probably a product of classical hydrothermal systems, located in grater depths.

The content of the of the alcaline metals Na and K varies, for the Na from 30,54 mg/l (ZD-5) to 252,12 mg/l (ZD-3). The content of K is significantly lower that Na, varying from 1,28 mg/l (ZD-5) to 39,28 mg/l (ZD-4). The content of Ca is also different in the separate holes and it is the range from 273,79 mg/l (ZD-7) to maximum of 369, 07 mg/l (ZD-4). The magnesium does not show significant variations in terms of the content and it is the range from 30,77 mg/l (ZD-3) to maximum of 71,08 mg/l (ZD-5).

From the microcomponents of the examined samples, it is significant to notice the content of Al, Cu, Fe, Pb, Zn, Ni, Co, Sr, Ce, Cd, As and Cr. Special attention deserve the contents of As, Ce and Sr. Further on, there will be interpretation of only a small part of the microelements, while the complete content of all analyzed elements can be seen in Tables 1.

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Table 1. *The content of microelements in the thermomineral watersfrom the holesZD-3, ZD-5, ZD-7 and ZD-4(mg/l)*

Element	Hole	Results from the examination(mg/l)		
Ca	ZD-3	353,03	353,03	338,19
	ZD-5	286,88	286,88	293,63
	ZD-7	294,61	294,61	273,79
	ZD-4	369,07	369,07	340,42
Mg	ZD-3	38,61	30,77	32,25
	ZD-5	71,08	49,02	58,48
	ZD-7	43,57	26,93	34,06
	ZD-4	43,67	31,56	38,32
Na	ZD-3	223,50	199,86	252,12
	ZD-5	36,54	30,54	41,34
	ZD-7	96,93	68,98	89,96
	ZD-4	214,29	301,21	213,03
K	ZD-3	37,504	36,32	36,10
	ZD-5	36,359	1,39	1,27
	ZD-7	34,050	36,82	26,53
	ZD-4	39,281	39,21	40,51
Sr	ZD-3	5,72	5,31	5,27
	ZD-5	3,71	4,15	4,71
	ZD-7	4,78	3,40	4,18
	ZD-4	5,71	5,23	5,21
Mn	ZD-3	0,230	0,245	0,209
	ZD-5	0,797	1,076	0,98
	ZD-7	0,712	0,839	0,66
	ZD-4	0,227	0,254	0,24
Fe	ZD-3	0,171	0,205	0,313
	ZD-5	0,209	1,36	1,204
	ZD-7	3,065	4,99	3,685
	ZD-4	0,164	1,78	1,003
Zn	ZD-3	0,0069	0,008	0,03
	ZD-5	0,011	0,011	0,015
	ZD-7	0,013	0,013	0,013
	ZD-4	0,632	0,012	0,011
Pb	ZD-3	0,029	0,015	0,016
	ZD-5	0,017	0,039	0,014
	ZD-7	0,0067	0,0051	0,0048
	ZD-4	0,023	0,015	0,019
Cu	ZD-3	0,0015	0,0028	0,0040
	ZD-5	0,0036	0,0130	0,0041
	ZD-7	0,0078	0,0013	0,0071
	ZD-4	0,0016	0,0016	0,0044
Ni	ZD-3	0,002	0,003	0,001
	ZD-5	0,008	0,002	0,006
	ZD-7	0,001	0,006	0,004
	ZD-4	0,001	0,0082	0,001
Cd	ZD-3	0,0016	<0.001	<0,001
	ZD-5	<0.001	0,0012	0,0005
	ZD-7	0,0013	<0.001	0,0018
	ZD-4	0,0002	<0.001	<0,001
Co	ZD-3	0,0038	0,0030	0,0026
	ZD-5	0,0036	0,0038	0,0039
	ZD-7	0,0042	0,0083	0,0030
	ZD-4	0,0049	0,0041	0,0040
As	ZD-3	0,301	0,133	0,091
	ZD-5	0,090	0,067	0,062
	ZD-7	0,097	0,035	0,107
	ZD-4	0,069	0,276	0,024
Ce	ZD-3	0,347	0,151	0,148
	ZD-5	0,114	0,137	0,158
	ZD-7	0,296	0,129	0,284
	ZD-4	0,130	0,414	0,233

Note:*The analyses are done at the Faculty of natural and technical sciences in Stip 2009.*

Special attention deserve the contents of As, Ce and Sr. Further on, there will be interpretation of only a small part of the microelements, while the complete content of all analyzed elements can be seen in Tables 5 and 6.

The content of Al is in most cases 0,02 mg/l, while Mn is in the range between 0,209 mg/l (ZD-3) to maximum 1,07 mg/l (ZD-5). The Iron showed greater variations in the content than the manganese and is mostly in the range between 0,164 mg/l (ZD-4) to maximum of 4,99 mg/l (ZD7).

The arsenic is mostly in content of 0.024mg/l (ZD-4) to maximum of 0,301 mg/l (ZD-3). The content of Ce is slightly higher and it is the range of 0.114 mg/l (ZD-5) to maximum of 0.414 mg/l (ZD-4). The Strontium is in increased content and all these three analyzed samples are the same and are in the range of 3,40 mg/l (ZD-7) to the maximum of 5,72 mg/l (ZD-3). Ni and Co are also present in the all three analyzed samples but none of them show any significant variations in their contents.

After the performed field and also laboratory physical-chemical analyses of the mineral water in the researched hole ZD-3 (Table 2) the following can be deduced:

The thermomineral water from the geothermal system 'Zdravevci' belong to the category of *sodium – calcium – hydrocarbonate, sulfide and low acid carbonic hyperterms*, which is also evident from the participation rates of separate dissolved components in them.

In the direction of movement of that water towards the surface of the field, its chemical content is significantly changed, but it can be stated that the thermal waters decrease the temperature compared to the temperature it had in the grater depths in the holes.

From the presented analyses (Table 2) it can be seen that the dry residue of 180°C of the examined water from the hole ZD-3 is 2.1743 gr/l, which means that it satisfies the criteria to be classified as mineral water.

From the presented analyses it can also be stated that the cations are above 20 milival% present in sodium (42.7088 milival%) and calcium (48.4343 milival%) and as for the anions hydrocarbonat (51.8153milival%) and the sulfate CO_4 (42.0990 milival%) which makes this water belong in the category of sodium – calcium – hydrocarbonate, sulfide mineral water.

Table 2. *Physical-chemical analysis of the mineral water from the locality Borovik, researched hole ZD-3*

Specific gravity	1.00172			
Ph	6.5			
Dry residue at 180°C	2.1743			
Temperature of the water	48°C			
Temperature of the air	26°C			
1 (ONE) LITRE WATER CONTAINS				
	Grams	*Millimole*	*Millival*	*Millival%*
Cations:				
Sodium (Na^+)	0.32450	14.1086	14.1086	42.7088
Potassium (K^+)	0.02500	0.6410	0.6410	1.9404
Lithium (Li^+)	0.00020	0.0288	0.0288	0.0871
Ammonia (NH_4^+)	0	0	0	0
Calcium (Ca^{++})	0.32000	8.0000	16.0000	48.4343
Magnesium (Mg^{++})	0.02500	1.0285	2.0570	6.2268
Strontium (Sr^+)	0.00660	0.0753	0.1506	0.4558
Manganese (Mn^{++})	0.00030	0.0054	0.0108	0.0326
Iron (Fe^{++})	0.00090	0.0161	0.0322	0.0974
Aluminum (Al^{++})	0.00005	0.0180	0.0054	0.0168
Anions:				
Hydrocarbonat (HCO_3^-)	1.2200	20.0000	20.0000	51.8153
Chlorine (Cl^-)	0.0800	2.2535	2.2535	5.8394
Bromine (Br^-)	0	0	0	0
Iodide (J^-)	0	0	0	0
Fluoride (F^-)	0.0018	0.0947	0.0947	0.2453
Nitrate (NO_3^-)	0	0	0	0
Phosphate (HPO_4^-)	0.00002	0.0002	0.0004	0.0010
Sulfate (SO_4^-)	0.7800	8.1250	16.2500	42.0990
			38.5986	100.0000
Weak electrolytes				
Metasilicic acids	0.6680			
Metaboron acid	0.0056			
Total dry substance, dissolved in water			3.4579	
Gases				
Free: CO_2	0.8800			
Free: H_2S	0.0012			
Chemical property	The chemical content is charactarized with sodium, calcium, hydrocarbonate and sulfide. The total concentration based on measures H/1000 is for Na (71.63); Ca (16.0); HCO_3 (20.0); SO_4 (16.25). The water is also characterized with presence of free CO_2 (0.88 g/l) and H_2S (0.0012 g/l).			
Kurlov formula	H_2S 0.0012 CO_2 0.8800 M 3.4579 $\frac{HCO_3 51.81 SO_4 42.09}{Na 42.70 Ca 48.43}$ T 45°C			
Type of water	The water belongs in the category of sodium – calcium – hydrocarbonate, sulfide and low acid carbonic hyperterms.			

Based on the content of SiO_2, Na, K, Ca and Li, and also based on their mutual relations in the hydrothermal fluids in the locality Borovik, by using appropriate standard formulas of Phournier, Trusdell, Ronje and Michard, the possible temperatures of the

deeper parts of the collector are also calculated. Without going into details, the temperature is estimated to be approximately 174 °C. That points to the fact that, apart from the other things, in a tight impact in time on the magmatic intrusion, i.e. the heating object, and also it can be concluded logically that there are much higher temperatures existing today.

The examined water, among the rest contains 1/3 pure CO_2. Its quantity in the researched hole ZD-3, with a free flow of the mineral water, estimated in the last ten years, has not changed significantly. Significant quantities of CO_2 are noticed in the more shallow holes which have not opened the hydrothermal fluids. The great quantities of CO_2 are probably due to the escalations of the final stages of the tertiary volcanism. The presence of the free CO_2 (0.8800 g/l) and H_2S (0.012 g/l) gives this water another attribute to its categorization, that it belongs to sodium – calcium – hydrocarbonate, sulfide and low acid carbonic hyperterms.

This water is characterized with great content of sulfur and increased concentrations of a great number of components which are most probably a product of the classical hydrothermal systems located in the greater depths. Due to the content, the water from the mentioned locality has bath and healing characteristics. Apart from this, it is used today, only in limited quantities, as a high quality drinking water (Dobra Voda). This kind of mineral waters belongs to volcano waters, which makes them most demanded on the European and world market of mineral waters.

For the illustration of the chemical content, the data presented in the trilinear diagram (Figure 1 and 2) which clearly presents that the thermomineral waters coming from the hydrothermal system 'Zdravevci' all have similar but in occasions different chemical content depending on the environment they originate, the length and the content of the transiting paths from the primary collector to the place of their outflow, the temperature of the collector and the one in the transiting paths, etc., does not exclude the opportunity that it influenced the accuracy of separate laboratories.

It can be seen, in the trilinear diagram, that all analyzed waters belong to hydrocarbonate, and the content of other dissolved elements (Ca, K, Na and Mg) they can be categorized and named as certain subtypes.

For example, the thermomineral water from the researched hole ZD-3, based on the chemical analysis from the Republic Institute for Health Protection – Skopje, it can be defined as *hydrocarbonate - sulfide – calcium, sodium – potassium type of water* with the following formula:

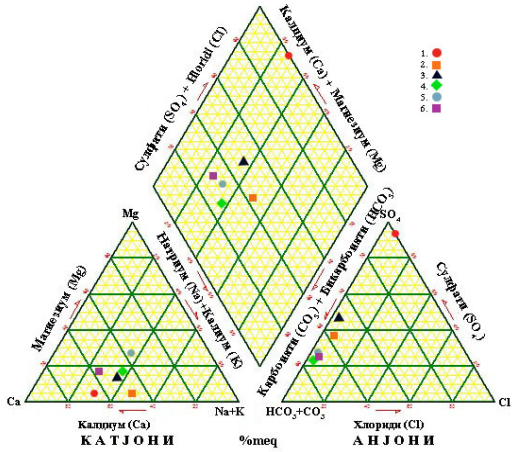

Figure 1. Trilinear diagram for the chemical content of the thermomineral waters by Piper for the geothermal system 'Zdravevci' (taken from the Analysis from 1993) 1. ZD-1, 2. ZD-3 (1), 3. ZD-3 (2), 4. ZD-5, 5. ZD-4, 6.ZD-2.

Based on the chemical analysis of the water done by the chemical laboratory at the Institute for Rehabilitation in Belgrade, it is categorized as sodium – calcium – hydrocarbonate, sulfide and low acid carbonic hyperterms, which is evident in presence of separate dissolved components in them (given in mg/l). The dry residue of 180^0C from the examined water is 2,1743 g/l which points to the fact that it satisfies that criteria to be classified as mineral water.

The analyzed sample from the water from the researched hole ZD-3 can be presented with the following formula (by Kurlov):

It can also be stated that the cations of over 20 millival% are present: sodium (42,7088 millival%) and calcium (48,4343 millival%) while from the anions, we have hydrocarbonate 51,8153 millival% and the sulfate SO_4 - 42,0990 millival%, which makes this water to be categorized as sodium – calcium – hydrocarbonate, sulfide mineral water.

This water contains free sulfur-hydrogen H_2S – 0.0012 g/l and free CO_2 – 0,8800 g/l and it categorizes this water as sodium – calcium – hydrocarbonate, sulfide and low acid carbonic hyperterms.

During 2009 we have performed research of five samples taken from the holes where today we have an overflow of the water and one sample from the water of the spring in the river Povisnica (Table 3). The results from this research confirmed that the water from this geothermal system belongs to the category of sodium – calcium – hydrocarbonate, sulfide and low acid carbonic hyperterms (Picture 2).

Table 3. *Chemical content of the thermomineral water of the geothermal system 'Zdravevci' (mg/l)*

Components	Label on the samples					
	ZD-4 (1)	ZD-4 (2)	ZD-3 (1)	ZD-3 (2)	ZD-7	Source
Na	214	260	252	223	90	175
K	40	39	36	37	38	53
Ca	319	340	262	320	295	271
Mg	52	38	36	32	45	79
Cl	33	34	44	80	28	39
SO_4	374	492	430	560	480	332
HCO_3	658	662	483	769	674	632
pH	6.8	6.8	7.0	6.9	7.1	6.8

Note: The analyses are done at the Institute for Health Protection in Veles.

The total mineralization of the analyzed water is significantly high and is in most cases higher that 1 g/l i.e. it is between 0.33 – 2.88 g/l.

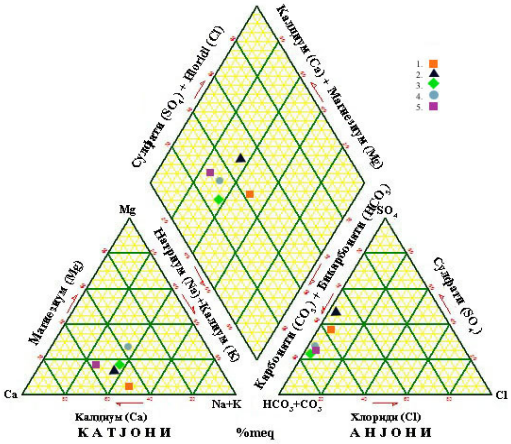

Figure 2. Trilinear diagram of the chemical content of the thermomineral waters by Piper for the geothermal system 'Zdravevci
1. ZD-3, 2. Source, 3. ZD-5, 4. ZD-4, 5.ZD-2.

The analyzed waters concerning the physical properties, they are clear, no color, no smell or a slight smell of H_2S, no taste or a slightly acid taste. The temperatures vary greatly, so some can be categorized as hypothermal, others as hymoethermal, while the water from ZD-3 is hyperthermal.

The pH values vary greatly and those are natural waters (with pH from 6.5 to 7.5). The extremely acid (pH 2.6) is only the water from one well on Plavica, where there is an intense dissolving of sulphide minerals.

Taking the gas content in consideration, it can be said that the mineral waters from this area where gases are present belong to carbon-acid waters where the content of CO_2 is over 90%, and in certain cases a presence of 100% CO_2. The presence of N_2 and O_2 which are a result of air pollution due to the old equipment when taking and examining the samples.

The immense presence of CO_2 in most natural springs and in some researched holes point to the high temperature of the collector of the geothermal system and also to its great dimension. On the other hand, the immense presence of CO_2 in thse waters confirms the possibility of the existence of great masses of carbonate within the collector of the geothermal system 'Zdravevci'.

By analyzing the results from the chemical analyses of the hard metals, it can be stated that from the examined hard metals in the theromineral water from the geothermal system 'Zdravevci', they are within normal ranges.

The latest examinations of the thermomineral water of the geothermal system 'Zdravevci', show that this water is characterized with higher concentrations of the great number of components, primarily Sr, Ce and As, which are most probably a product of classical hydrothermal systems, located in greater depths.

CONCLUSION

The mineral water of the researched area belongs to the category of sodium – calcium – hydrocarbonate, sulfide and low acid carbonic hyperterms, which is evident with the presence of separate dissolved components in it (given in mg/l). Due to this content this mineral water has bath and healing characteristics. Apart from this, it is used today, only in limited quantities, as a high quality drinking water (Dobra Voda). This water from the mentioned locality, is characterized with increased concentrations of a great number of

components which are most probably a product of the classical hydrothermal systems located in the greater depths. From the analyses of the hard metals, it can be stated that they are in normal values.

Based on the presented so far about the content of macrocomponents and microcomponents, it can be noticed that the examined samples from the thermomineral water of the researched geothermal system is characterized with presence of great number of microelements which is a result of the geological constitution of the field and the paths where the fluids have passed. It is also evident that the elements such as Na, Ca are present in significant high concentrations, which confirms their classification as sodium-calcium type. Special attention deserve the high contents of As, Sr and Se and the high concentrations of the great number of components of primary importance Sr, Ce and As which are most probably a result of classical hydrothermal systems, located in greater depths.

Taking the gas content in consideration, it can be said that the mineral waters from this area where gases are present belong to carbon-acid waters, the content of CO_2 is over 90%, and in certain cases a presence of 100% CO_2.

The presented conclusions about the content of the mineral water from the geothermal system 'Zdravevci' are based on a small number of analysed samples but they still give solid information about the content of the water.

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