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GEOCHEMICAL FEATURES OF THE THERMOMINERAL WATERS OF THE BOROVIC SITE, KRATOVO (THE REPUBLIC OF MACEDONIA)

Orce Spasovski, Vojo Mircovski[1]

[1]Faculty of Mining and Geology Stip, Republic of Macedonia, sorce@rgf.ukim.edu.mk

Abstract. The paper presents the results obtained during the geochemical examinations of the thermomineral waters of the Borovik site, Kratovo. The results are related to data of earlier geochemical examinations (drill hole ZD-3) and investigations carried out during 2003 and 2004 (drill holes ZD-3, ZD-77 and ZD-1).

The chemical composition of the hydrothermal fluids and the isotopic composition of some of the dissolved ions and gases are closely related to the thermal evolution of the hydrothermal systems. To date no isotopic examinations of the themomineral waters of Borovik have been carried out. The paper will present the calculated values only of hydrogeochemical geothermometers that are directly dependent on the temperatures prevailing in the collector.

The thermomineral waters of Borovik are sodium-potassium-hydrocarbonate, sulphate, sulphide and low acid carbon hypertherms. This can be inferred from the percentage of individual dissolved component parts (in mg/l). Dry residue at 180°C of the water studied amounts to 2.1743 gr/l, which indicates that it can be classified as mineral water.

It was determined that cations exceeding 20 millival% include those of sodium (42 mval%) and calcium (48 mval%), whereas of the anions, hydrocarbonate of up to 51 mval% and sulphate SO_4 to 42.0990 mval% were found. This allows the water to be classified as sodium-calcium-hydrocarbonate, sulphate mineral water.

The water contains free sulphurhydrogen H_2S of 0.0012 gr/l and free CO_2 of 0.8800 gr/l and allows us to classify it as sodium-calcium-hydrocarbonate, sulphate, sulphide and low acid carbon hypertherms.

The results of the chemical analysis of heavy metals indicate that all heavy metals studied are within the allowable values.

Latest investigations indicate that the water is characterized by increased contents of elements such as Sr, Se and As that, probably are the product of classical hydrothermal systems, located at depth.

Key words: Borovik, thermomineral water, examination, chemical composition, Kratovo-Zletovo volcanic area.

INTRODUCTION

The Borovik site is situated in the north-east part of the Kratovo-Zletovo volcanic area between the villages of Filipovci and Turalevo. The terrain is low mountainous with average heights of 450 to 700 m and several such as those of Gradiste, Borovik, Golak etc. characterized by pronounced weathering.

In 1988 hydrothermal investigations included geologic data provided by many authors and earlier research works. Of particular interest were the two shallow drill holes drilled in the riverbed of Povisnica inside the Turalevski crater. The first drill hole ZD-70 m revealed self-potential mineral water of cca 2 l/s and temperature of 30.80°C. The second drill hole did not discover any water, but the temperature in the middle of the drill hole amounted to 30.80°C.

Data obtained during these geophysical measurements and those of drill hole ZD-1, were also used in further investigations in the deeper drill hole (ZD-3) drilled 335 m to depth, which discovered self potential thermomineral water with water temperature of 50°C and flow rate of 12 l/s.

In 1991 three new drill holes were dug in the river bed of Povisnica (upstream to the west) (ZD-4 of 134 m, ZD-5 of 128 m and ZD-6 of 96 m) dense pattern being 1 km. The drill holes helped to determine the hydrogeological occurrences and determination of possible presence of geothermal water.

GEOLOGICAL FEATURES

The geological composition is heterogeneous and consists of volcanic materials, tuffaceous breccias, sandstones and marls. All rocks, starting with Oligocene tuffaceous breccias through sandstones and marls are intruded by biotite augite andsites, hornblende andesites. Small outflows present as larger or smaller slabs (fig. 1) have been seen over the rocks.

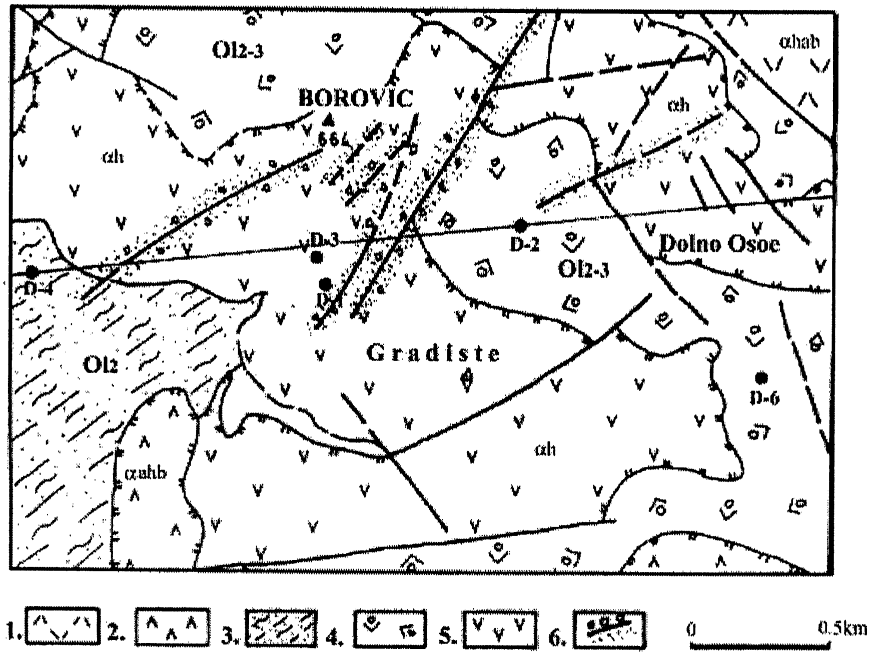

Fig. 1. Geological map of Borovik
1. Hornblende-augite andesite; 2. Labrador andesite; 3. Clayey tuffaceous sandstones and limestones; 4. Volcanic breccias and sandstones; 5. Hornblende andsites; 6. Altered fault zones, poorly mineralized.

The structural composition of Borovik site is similar to the composition of other parts of the area. Fault structures are of NE-SW and NW-SE strike, rarely E-W which at the Turalevo crater, particularly at Borovik intersect. This represents a favourable tectonic environment for the deposition of mineralization.
Fault structures are connected with many manifestations, first of all those of hydrothermal alterations and post volcanic occurrences. The most pronounced hydrothermal alteration is silicification present as quartz rifts striking on the relief. Rather pronounced are kaolinization, sericitization, chloritization, pyritization etc.
It has also been determined that the area abounds in hydrothermally altered zones that have been mineralized at some places.

RESULTS AND DISCUSSION

It is well known that hot water circulation dissolves the rocks that it comes across. The amount and ratio of dissolved elements depend on the temperature of the environment. The movement of such water to the surface does not necessarily change its chemical composition. However, it lowers its temperature compared to that at depth.
Field and laboratory physico-chemical analyses carried out on the water of ZD-3 (table 1) lead to the conclusion that:
The thermomineral water of Bukovik is of **sodium-calcium-hydrocarbonate, sulphide and low acid carbon acid hypertherms** that can be seen from the amount of individual dissolved component parts.
The analyses in Table 1 indicate that the dry residue at 180°C of the water of ZD-3 drill hole is 2.1743 gr/l, which means that it meets the requirements to be classified as mineral water. It can also be seen that the cations of over 20 milivals% present include sodium (42.7088 milival%) and calcium (48.4343 mval%), whereas anions present include hydrocarbonate (51.8153 mval%) and sulphate SO_4 (42.0990 mval%) which makes it possible to classify the water as sodium-calcic-hydrocarbonate, sulphate mineral water.
Based on the contents of SiO_2, Na, K, Ca and Li and based also on their relationship in hydrothermal fluids by the use of standard formulas of Fournier, Trusdell, Rowe and Micvhard, possible temperatures were calculated for the deep parts of the collector. Disregarding trivial data, it was determined that the temperature, on average, amounts to 174°C. This points out, among other, the close time of magma penetration (a heating body). It also leads to the logic conclusion that now very high temperatures prevail.

Table 1. Physico-chemical analysis of the mineral water of the Bukovik site, drill hole ZD-3

	Specific gravity			1.00172
Data of analysis	pH			6.5
22.06. 1991	Dry residue at 180°C			2.1743
Analyst	Water temperature			48°C
M-r Liljana Zivadinovic	Air temperature			26°C
	1 (ONE)LITER OF WATER CONTAINS			
	grams	***Millimols***	***millival***	***Millivals %***
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
Ammonium (NH_4^+)	0	0	0	0
Calcium (Ca^{++})	0.32000	8.0000	16.0000	48.4343
Manganese (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
Alluminium(Al^{++})	0.00005	0.0180	0.0054	0.0168
Anions :				
Hydrocarbonate (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
Iodite (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
Sulphate (SO_4^-)	0.7800	8.1250	16.2500	42.0990
			38.5986	**100.0000**
Weak electrolytes				
Metasilicite acids	0.6680			
Metaborine acids	0.0056			
Total dry materials			3.4579	
Gases				
Free CO_2	0.8800			
Free H_2S	0.0012			
Chemical properties	Chemical composition is sodium, calcium, hydrocarbonates and sulphates. Total concentration of the order of h/1000 amounts to Na (71.63); Ca (16.0); HCO_3 (20.0); SO_4 (16.25). Water is also characterized by the presence of free CO_2 (0.88 g/l) and H_2S (0.0012 g/l)			
Curul equation	$H_2S\ 0.0012\ CO_2\ 0.8800\ M\ 3.4579\ \frac{HCO_3 51.81 SO_4 42.09}{Na 42.70 Ca 48.43}\ T\ 43°C$			
Categorization	Water belongs to sodium-calcium-hydrocarbonate, sulphate, sulphide and low acid carbon hypertherms			

These waters contain about 1/3 of the volume of pure CO_2. Its content in drill hole ZD-3 for the past ten years of free outlet of mineral water has not changed significantly. significant amounts have been noticed in shallower drill holes, which did not yield (open) hydrothermal fluids. The development of large amounts of CO_2 is probably due to exhalations during the final stages of Tertiary volcanism. The presence of free CO_2 (0.8800 g/l) and H_2S (0.0012 g/l) makes it possible to say that it is sodium-calcium-hydrocarbonate, sulphate, sulphide low acidic carbohydrate hypertherms.
The water is characterized by high contents of sulphur and components that probably developed during hydrothermal systems at depth. As a result, the thermomineral water in the site received healing properties. In addition, it is used, in a

limited amount, as a good quality drinking water (known as Dobra Voda). The type of mineral water belongs to the volcanic waters whose demand on the world and European markets is high.
Latest investigations aimed at following the chemical composition of the water in March, April, July, August and September in 2004 in order to determine the presence and variation of individual elements and compare them with the results obtained during earlier investigations. The investigations included the waters of drill holes ZD-3, ZD-4, ZD-7 and ZD-4. The results obtained are shown in Tables 2 and 3.
Tables 2 and 3 indicate that the mineral water of Borovik contains a variety of components, most probably due to classical hydrothermal systems located at depth.
The contents of alkali metals Na and K vary from 30.54 mg/l (ZD-5) to 252.12 mg/l (ZD-3). K content is much lower than that of Na amounting from 1.28 mg/l (ZD-5) to 39.28 mg/l (ZD-4). Ca content varies between 273.79 mg/l (ZD-7) to maximum of 369.07 mg/l (ZD-4). Magnesium does not vary significantly amounting from 30.77 mg/l (ZD-3) to 71.08 mg/l (ZD-5).
Of the microcomponents of note are the contents of As, Se and Sr. The paper will discuss only part of microelements, and all elements can be seen in Tables 2 and 3.
Al contents are about 0.02 mg/l (ZD-3), whereas Mn is within 0.209 mg/l and 1.07 mg/l (ZD-5). Iron shows higher variations compared with manganese amounting from 0.164 mg/l (ZD-4). Strontium occurs in high amounts in all three samples amounting from 3.40 mg/l (ZD-7) to maximum 5.72 mg/l (ZD-3). Ni and Co have been found in all three samples, but the same do not indicate any significant variations with regard to contents.
According to the data presented on the macrocomponents and microcomponents it can be noticed that there are no significant changes in the contents of elements in samples during different time periods. It can also be seen that elements such as Na, Ca occur in high concentrations. This classifies the water as sodium-calcic type. Of note are also the high contents of As, Sr and Se.
The conclusions on the composition of the mineral water of Borovok are based on a small number of samples. However, they offer good data on the composition.

Table 2. *Contents of microelements in March and April in the thermomineral water from drill holes ZD-3, ZD-5, ZD-7, and ZD-4 (in mg/l).*

		Day the sample was taken		
Element	**Drill hole**	**23. 03. 2004**	**05. 04. 2004**	**20. 04. 2004**
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
Se	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

Table 3. *Contents of microelements in July, August and September in the thermomineral water from drill holes ZD-3 and ZD-7, (in mg/l).*

Element	Day the sample was taken						
	Drill hole	**10.07.2004**	**10.08.2004**	**20.08.2004**	**10.09.2004**	**20.09.2004**	**28.09.2004**
Mo	ZD-7		0,055		0,0494	0,0498	
	ZD-3		0,0381	0,0462	0,0329	0,0200	0,0311
Al	ZD-7	0,0202	0,0232		0,0353	0,0197	
	ZD-3	0,026	0,023	0,0246	0,0232	0,0243	0,0215
P	ZD-7	0,0197	0,0169		0,0107	0,0128	
	ZD-3	0,011	0,0078	0,0098	0,0065	0,0033	0,0047
Zn	ZD-7	0,0208	0,0143		0,0136	0,0144	
	ZD-3	0,0105	0,0015	0,0046	0,0075	0,0075	0,005
Ba	ZD-7	0,0139	0,0111		0,0113	0,0113	
	ZD-3	0,0231	0,0204	0,0208	0,0206	0,0217	0,0207
Ni	ZD-7	0,0012	0,0018		0,0014	0,0011	
	ZD-3	0,001	0,0032	0,0051	0,0086	0,002	0,0037
Co	ZD-7	0,003	0,001		0,001	0,0035	
	ZD-3	0,0010	0,0015	0,0004	0,0015	0,0008	0,0026
Cr	ZD-7	0,003	0,0041		0,0023	0,0046	
	ZD-3	0,004	0,0021	0,0041	0,0013	0,0033	0,0027
Cu	ZD-7	0,0121	0,0014		0,0099	0,0051	
	ZD-3	0,0086	0,0033	0,005	0,0034	0,0077	0,0024

Pb	ZD-7	0,0121	0,0134		0,018	0,0295	
	ZD-3	0,0087	0,0101	0,021	0,0122	0,0185	0,0232
Ag	ZD-7	0,0067	0,0061		0,0078	0,0054	
	ZD-3	0,0082	0,0026	0,0031	0,0058	0,0042	0,0069
Cd	ZD-7	0,0003	0,0001		0,0002	0,0005	
	ZD-3	0,001	0,0063	0,0027	0,001	0,0026	0,0025
Ti	ZD-7		0,0003		0,0006	0,0014	
	ZD-3		0,0003	0,0003	0,0003	0,0013	0,0003
As	ZD-7		<0,01		<0,01		<0,01
	ZD-3	<0,01	<0,01	<0,01	<0,01	<0,01	<0,01

CONCLUSION

The mineral water of Borovik belongs to the sodium-clacium-hydrocarbonate, sulphate, sulphide and low acid carbon hypertherms. This is obvious from the presence of individual dissolved component parts (said in mg/l). Table 1 shows that dry residue at 180°C of analyzed water from drill hole ZD-3 is 2.1743 gr/l which means that it satisfies the criteria for mineral water. The table also shows that the cations of over 20 mival% are sodium (42.7088 milival%) and calcium (48.4343 mval%), and of the anions hydrocarbonate (51.8153 mval%) and sulpahte SO_4 (42.0990 mbal%), which makes possible its classification as sodium-clacium-hydrocarbonate, sulphate, sulphide and low acid carbon hypertherms.

This composition gives the water medicinal and healing properties. Besides, it is used (in limited amounts only) as good water for drinking (called Dobra Voda). The water is also characteristic for its high concentrations of components that are products of hydrothermal systems located at depths.

The analysis of heavy metals indicates that they are within the normal values. Of note are the increased concentrations of Sr, Se and As. The type of mineral water belongs to the so-called volcanic waters whose demand in Europe and the world is high.

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Milivojevic (1990) carried out investigations on the origin of the gas in the thermal cold acidic waters in the region of Prokuplje – Bujanovac. He assumes that the gas is the result of transformation of carbonate rocks (marbles) with temperatures higher than 100°C. The same can be said for the gas in the Bitola valley since carbonate rocks can be seen in the surrounding. His opinion coincides with that of Kissin and Pakhomov (1967) that CO_2 develops by hydrolysis of carbonate rocks at temperatures higher than 100°C.
Isotopic analysis is necessary for the right determination of the gas in this area.

CONCLUSIONS

The hydrogeological investigations carried out indicate that the mineral water and CO_2 gas in the vicinity of Bac are located in several horizons in the Neogene Middle Pliocene sediments. The geological environment abounds in important water reserves that can be exploited and give economic effect.

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