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HYDROCHEMICAL CHARACTERISTICS OF THE THERMOMINERAL WATER FROM THE SPA OF KEŽOVICA – ŠTIP, REPUBLIC OF MACEDONIA

Vojo Mirčovski[1], Biljana Gičevski[2], Đorđi Dimov[1]

[1]*Faculty of Natural and Technical Sciences, Institute of Geology, "Goce Delčev" University in Štip, Blvd. Goce Delčev 89, Štip, Republic of Macedonia*
[2]*Exploring Society "Ursus Speleos", Dobromir Hrs 20a, 1000 Skopje, Republic of Macedonia,*
vojo.mircovski@ugd.edu.mk

A b s t r a c t: Hydrochemical characteristics of thermomineral water samples from four wells (B_1, B_2, B_3 and S_3) were analyzed. They are located in the vicinity of the Kežovica spa, southwest from the city of Štip. With regard to geotectonic view, the wider area around the wells belongs to Serbo-Macedonian massif and Vardar zone. The Kežovica spa is located in a contact between granite and Upper Eocene sediments. Several grapho-analytical methods (Piper diagram, Stiff diagram, Chadha diagram and D'Amore) have been used for the analysis of water samples. The hydrochemical analyses point out that the water from all wells have the same origin. The major cations in the water are Na^+ and Ca^{2+}, and anions are Cl^- and SO_4^{2-}. All waters belong to NaCl water type.

Key words: hydrochemistry; thermomineral water; spa of Kežovica; Jurassic granites

INTRODUCTION

Thermomineral spa of Kežovica is located 2 km southwest of the city of Štip in the vicinity of Novo Selo. It has been known since the time of Turkish rule in Macedonia, which at that time was used as a healing thermal spa.

Near the spa are located two wells marked as B_1 and S_3. Thermomineral water from these wells is used for the spa and physical therapy. Also two wells marked as B_2 and B_3 are located in Ldži in the vicinity of Bregalnica about 0.5 km away from the spa of Kežovica. Currently thermomineral water from these two wells is not used. On this locality near Novo Selo is situated a source of thermomineral water used by the local population.

All four wells are made from Geological Institute in Ljubljana, well S_3 was made in 1953 and wells B_1, B_2 and B_3 in the 1976/77 year. The depth of the well B_1 is 30.7 m, B_2 is 101.1 m, B_3 is 44 m, and S_3 is 22.5 m. Yield of the wells is: B_1 is 1.3 l/s, B_2 is 11.5 l/s, B_3 is 6.5 l/s and S_3 is 2.7 l/s and the total capacity of the wells is 22 l/s.

The static level in the well B_1 is of 1.7 m, B_2 is 2.3 m, B_3 is 2.5 m, and S_3 is 2.3 m, which indicates that it is for subartesian aquifer located in the Jurassic cracked granites.

The temperature of the thermomineral water is in range between 53 and 62 °C.

According Miholić (1953) the radioactivity of water from the Kežovica spa is 42.82 moch units and of the source Ldži is 11.57 moch units. According to these data this spa belongs to the most radioactive spas in Macedonia.

Thermomineral waters from the Kežovica spa and Ldži source were explored by a number of researchers: Miloević (1953), Miholić (1953), Baić (1955), Netkov (1968), Nastić (1968), Gjuzelkovski and Stračkov (1973), Kotevski (1974), A. Kekić and G. Mitev (1973–1978), Mirčovski, Petrov and Delipetrov (2001) and Kekić, Mirčovski (2001–2002).

GEOLOGICAL AND TECTONICAL FEATURES

According to tectonic regionalization, the wider environment of the Kežovica spa is situated on contact between two major regional tectonic units: Serbo-Macedonian massif and Vardar zone (Arsovski, 1997).

Geological structure of the vicinity of the Kežovica spa is shown on the geological map (Figure 1) [Rakičević et al. (1969); Arsovski (1997)]. In geological structure participate Precambrian, Mesozoic, Tertiary and Quatenary rocks.

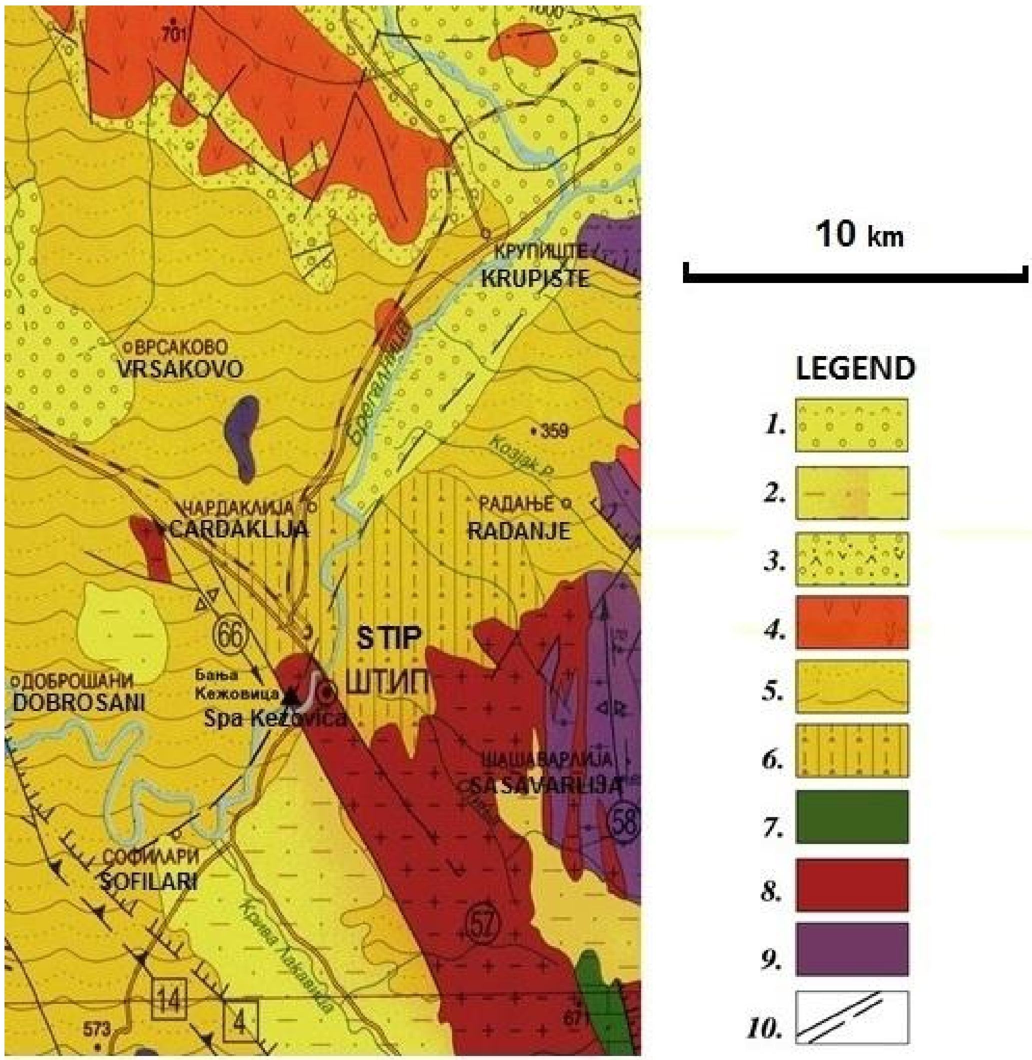

Fig. 1. Geological map of the vicinity of the Kežovica spa according Arsovski (1997).
1. Quarter; 2. Pliocene sediments; 3. Tertiary volcanogenic sedimentary rocks; 4. Tertiary volcanic rocks; 5. Eocene flysch sediments; 6. Eocene conglomerates, marls and sandstones; 7. Cretaceous sediments; 8. Jurassic granites; 9. Gneiss and mica; 10. Faults

Precambrian rocks build a small area east of Štip. They are represented by different types of gneiss and mica.

Mesozoic rocks are represented by magmatic and sedimentary rocks. Magmatic rocks are represented by granites which in the literature are known as Štip granites which appear southeast and east of the spa. Granites have heterogeneous lithological composition and are represented by: biotite adamelites, biotitic aplitoide granites and granite. The age of these granites is 155 ± 5 million years (middle Jurassic) (Šoptrajanova, 1967).

Mesozoic sedimentary rocks are presented in a small area southeast of the spa and are represented by conglomerates fascia and fascia of sandstones, clay and marls.

Tertiary rocks are represented by basal series of Upper Eocene conglomerates, sandstones and marls, Upper Eocene flysch sediments, volcanic rocks and volcanogenetic sedimentary rocks.

Conglomerates, sandstones and marls of the basal series are represented in the vicinity north of Štip.

Upper Eocene flysch sediments build a larger area and are represented by: sandstones, marls, conglomerates and limestones.

Volcanic rocks are represented by andesites and volcanogenetic sedimentary rocks with andensite tuffs, breccias and tuffs.

Pliocene sediments are represented by two large masses south of Štip and Lakavica graben and one small mass locate western of Štip. They consist of sandstones, clays and gravels.

Quaternary rocks occur along the river of Bregalnica and are represented by the old river terraces built from pieces of andesites, rarely quartz and gneiss and alluvial sediments represented by gravels and sands.

HYDROGEOLOGIC CHARACTERISTICS

The aquifer from which originate these waters was formed in cracked Jurassic granites which have fissure porosity Cracked granite in this area been detected with boreholes B_2 and B_3 from the surface of the ground up to a depth of 101 m.

According to the hydrodynamic characteristics of the level in these areas with previous research has been identified only subartesian aquifer.

Thermomineral waters of the Kežovica spa and Ldži source basically have tectonic origin. Their occurrence is probably related to the intersection of Štip fault which goes along the river of Bregalnica from Krupište, through Karaorman, Čardaklija, Štip and Sofilari with stretching northeast-southwest, and Lakavica fault which extends northwest-southeast and is located between the granites and Eocene sediments (Figure 1).

Thermomineral water from the Kežovica spa is occurs on the fault zone which is located at the contact between granite and Upper Eocene sediments. Ldži source is located on fault zone in the granite. Probably in depth these fault zones are in connection, which indicates the similarity of the chemical composition of water from the two localities.

METHODOLOGY

For determining the hydrochemical characteristics of thermomineral water from the Kežovica spa during October 2015 were taken 4 samples of thermomineral water from wells B_1, B_2, B_3 and S_3.

Physical-chemical analysis of the samples of thermomineral water is made at the University "Goce Delčev" in Štip, with the methods of ICP-AES (atomic emission spectrometry with inductively coupled plasma), and the results are presented in Table 1.

These hydro-chemical data are analyzed in order to see if there is a change in the chemical composition of the thermomineral water into time period 1977–1987 and 2015. There are the results of chemical analyses of wells B_1, B_2 and B_3 made in the Geological Institute in Ljubljana in 1977 (Geological Survey Ljubljana) (GSLj) and chemical analyses made by Kotevski 1987 for a wells B_1 and B_2.

RESULTS AND DISCUSSION

For the interpretation of the hydro-chemical analyses, several grapho-analytical methods were used.

The data were plotted on a trilinear Piper diagram (Piper, 1944). The major cations and anions are plotted in milligram per liter, in each triangle, then the plotting from triangular fields was extended further into the central diamond field. Piper diagram was used to identify the hydrochemical type of the water.

T a b l e 1

Hydrochemical analyses of the thermomineral waters

	B_1	B_2	B_3	S_3
pH				
GLj (1977)	7.9	7.9	7.9	
Kotevski (1987)	7.6	7.8		
2015	8.2	8.2	8.2	8.2
TDS ($mg \cdot l^{-1}$)				
GSLj (1977)	1305.8	1200.6	1279.8	
Kotevski (1987)	1334.6	1371.3		
2015	1251.1	1271.6	1274.3	1214.9
Ca^{2+} ($mg \cdot l^{-1}$)				
GSLj (1977)	14.8	28.8	21.0	
Kotevski (1987)	15.0	18.2		
2015	14.4	14.4	15.2	14.4
Mg^{2+}($mg \cdot l^{-1}$)				
GSLj (1977)	0.9	5.9	2.9	
Kotevski (1987)	33.0	–		
2015	0.5	0.5	0.6	0.5
Cl^- ($mg \cdot l^{-1}$)				
GSLj (1977)	468.0	370.0	436.0	
Kotevski (1987)	511.2	538.0		
2015	567.2	596.4	596.4	500.0
Na^+ ($mg \cdot l^{-1}$)				
GSLj (1977)	440.0	370.0	390.0	
Kotevski (1987)	407.6	472.8		
2015	493.6	498.9	503.6	493.6
K^+ ($mg \cdot l^{-1}$)				
GSLj (1977)	21.0	14.5	16.0	
Kotevski (1987)	11.6	10.5		
2015	13.2	12.8	12.8	13.2
Fe^+ ($mg \cdot l^{-1}$)				
GSLj (1977)	0.06	0.01	0.01	
Kotevski (1987)	0.15	0.02		
	0.01	0.09	0.02	0.01
SO_4^{2-}($mg \cdot l^{-1}$)				
GSLj (1977)	174.0	155.0	154.0	
Kotevski (1987)	162.4	164.4		
2015	162.9	148.9	144.3	162.9
HCO_3^- ($mg \cdot l^{-1}$)				
GSLj (1977)	171.0	202.0	193.0	
Kotevski (1987)	195.2	169.0		
2015	31.4	31.6	33.3	31.4

Stiff diagram (1951) show a very simple manner changes in the composition of the major constituent of water by observing the change in shape of a reference irregular polygon. It is constructed from four parallel horizontal axes extending on either side of a vertical zero axes. Cations are plotted on the left side of the zero axes, and anions are plotted on the right side, both in milliequivalents per liter. Each different pattern represents a different type of water.

In the Chadha diagram (Chadha, 1999) the difference in milliequivalent percentage between alkaline earth metals (Ca + Mg) and alkali metals (Na + K), expressed as percentage reacting values, is plotted on the *X*-axis, and the difference in milliequivalent percentage between weak acidic anions (carbonate + bicarbonate) and strong acidic anions (chloride + sulphate) is plotted on the *Y*-axis. The milliequivalent percentage differences between alkaline earths and alkali metals, and between weak acidic anions and strong acidic anions, would plot in one of the four possible sub-fields of the proposed diagram. The square or rectangular field describes the overall character of the water.

Using basic cations and anions D'Amore *et al.* (1983) determined six new parameters for distinguishing water groups based on the geological features of the main reservoir crossed by each water sample. Hydrochemical parameters are marked by letters from A to F:

$$A: \quad \frac{100}{\Sigma(-)}\left(HCO_3^- - SO_4^{2-}\right)$$

$$B: \quad 100\left(\frac{SO_4^{2-}}{\Sigma(-)} - \frac{Na^+}{\Sigma(+)}\right)$$

$$C: \quad 100\left(\frac{Na^+}{\Sigma(+)} - \frac{Cl^-}{\Sigma(-)}\right)$$

$$D: \quad 100\left(\frac{Na^+ - Mg^{2+}}{\Sigma(+)}\right)$$

$$E: \quad 100\left(\frac{Ca^{2+} + Mg^{2+}}{\Sigma(+)} - \frac{HCO_3^-}{\Sigma(-)}\right)$$

$$F: \quad 100\left(\frac{Ca^{2+} - Na^+ - K^+}{\Sigma(+)}\right)$$

Parameters define the ratio between dissolved species where square brackets represent concentrations in $meq \cdot l^{-1}$, and range from +100 to –100 meq l^{-1}. Sum Σ represents the sum of cation and anion concentrations. Parameter A assists in distinguishing between water circulations through calcareous terrains and those occurring in evaporitic rocks. Parameter B discriminates between sulphate-enriched waters circulating in evaporitic terrains and sodium-enriched waters that encountered marly, clayey sedimentary terrains. Parameter C tends to distinguish between waters deriving from 'flysch' or 'volcanites' and those coming from carbonate-evaporitic series or from a regional quartizitic schistose basement. Parameter D individuates waters that have circulated in dolomitized limestone. Parameter E distinguishes between circulations in carbonate reservoirs and those in sulphate-bearing reservoirs. Parameter F reveals the increasing K^+ concentration in the water samples.

The saturation indices (SI) describe quantitatively the deviation of water from equilibrium with respect to dissolved minerals. If the water is exactly saturated with the dissolving mineral, saturation index equals to zero. Positive values of saturation index indicate saturation/supersaturation, and negative ones indicate undersaturation. Saturation indices for anhydrite, aragonite, calcite, dolomite, gypsum and halite minerals were calculated using WATEQ4F computer program (Plummer et al., 1976).

Hydrochemical properties of the water samples

The hydrochemical analyses of the waters are presented in Table 1. The pH values showed that all water samples belong to the water group with alkaline reaction, oscillating in an interval from 7.6 to 8.2 (B_1), between 7.8 and 8.2 (B_2) and from 7.9 to 8.2 (B_3).

Grapho-analytical methods

All analyzed water samples of the study area showed similar characteristics.

Cation and anion concentrations are presented on Piper diagram (Figure 2). All water samples are plotted near the right-hand side of the diamond which showed that the water is reach in $Na^+ + K^+$ and $Cl^- + SO_4^{2-}$. The results showed that alkali metals exceeds alkaline earths, whereas strong acids exceeds weak acids. The chemical composition of the water is characterized by Cl–Na type which is typical of deep ground waters.

Stiff diagrams (Fig. 3) show that all water samples (B_1, B_2, B_3, S_3) had the same origin. Sodium and chloride had the dominant influence in the water, whereas carbonates had weak impact in the water.

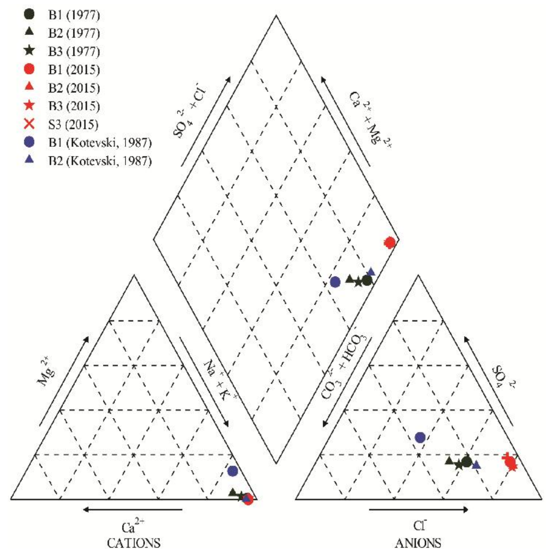

Fig. 2. Piper diagram for the water samples

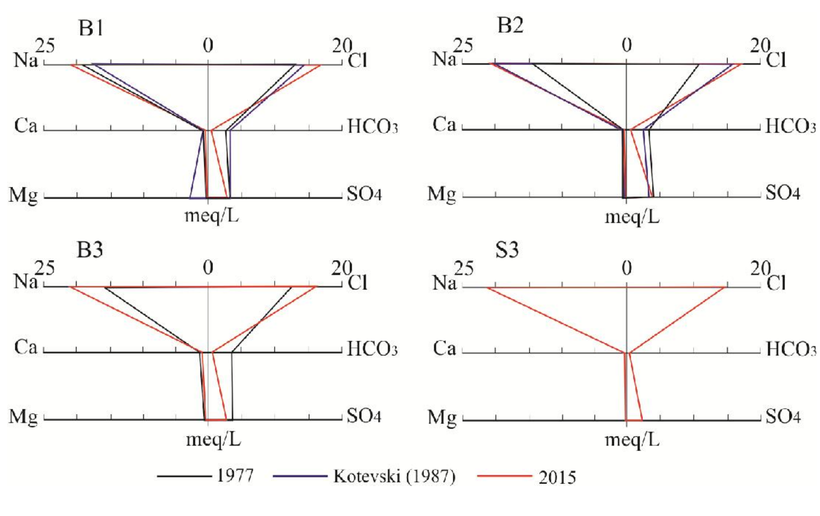

Fig. 3. Stiff diagrams for the water samples

The Stiff diagram of B_1 water sample shows that sulphate and calcium concentrations are almost constant throughout the analyzed period. Lower bicarbonate content was noticed in 2015, and higher magnesium content was recorded by Kotevski (1987).

The Stiff diagrams of B_2 and B_3 water samples point out that in 1977 content of chloride and sodium was lower than in 2015. On the other hand, bicarbonate content in 2015 was lower than in the rest analyzed years.

All analyzed water samples fall in the 7th subfield of Chadha diagram (Fig. 4). The positions of data points in the diagram represent C–Na type waters. The alkali metals ($Na^+ + K^+$) exceed alkaline earths ($Ca^{2+} + Mg^{2+}$) and strong acidic anions ($Cl^- + SO_4^{2-}$) exceed weak acidic anions (CO_3^{2-} + HCO_3^-). Such water generally creates salinity problems both in irrigation and drinking uses (Chadha, 1999).

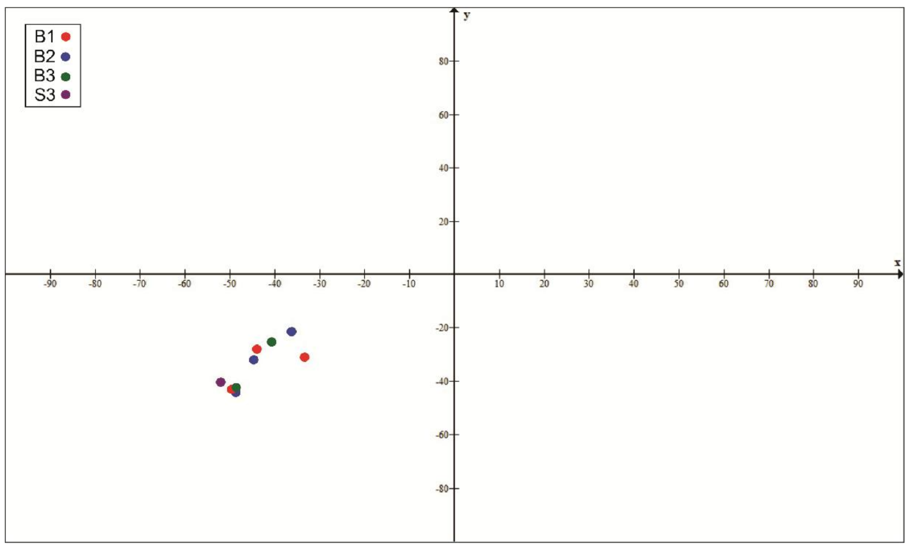

Fig. 4. Chadha diagram

The calculated values of the parameters A–F for the water samples have been plotted in rectangular D'Amore diagrams (Figure 5). All water samples had nearly identical shapes mutually. They belong to γ type which is characterized by Na–Cl type water and very deep circulation. The negative values of the A parameter point out that water is in contact with evaporative rocks. Only two water samples (B_2 and B_3), taken in 1977, have different values. The values above and below zero show the low impact of evaporatic series. The negative values of the B parameter emphasize sodium enriched water that encountered clay sediments. The positive values of the C parameter point out the influence of flysch and volcanites in the formation of the water. The high values of the D parameter show that the influence of the dolomitized limestone on the water is low. The values of the E parameter emphasize water movement through rocks that contain sulphates. The negative values of the F parameter point out that sodium and potassium content in the water is higher in relation to calcium content.

Saturation state

Saturation indices of the water samples are given in Table 2. All water samples of B1 were undersaturated with respect to anhydrite, aragonite, dolomite, gypsum, halite and magnesite, and undersaturated or slightly saturated with respect to calcite. Water samples of B2 were undersaturated with respect to anhydrite, gypsum, halite and magnesite, and generally undersaturated or slightly saturated with respect to aragonite, calcite, and dolomite. Sampling point B3 showed that water is undersaturated with respect to anhydrite, gypsum, halite and magnesite, and undersaturated or slightly saturated with respect to aragonite, calcite and dolomite. Undersaturation occurred in all water samples of S3 with respect to anhydrite, aragonite, calcite, dolomite, gypsum, halite and magnesite.

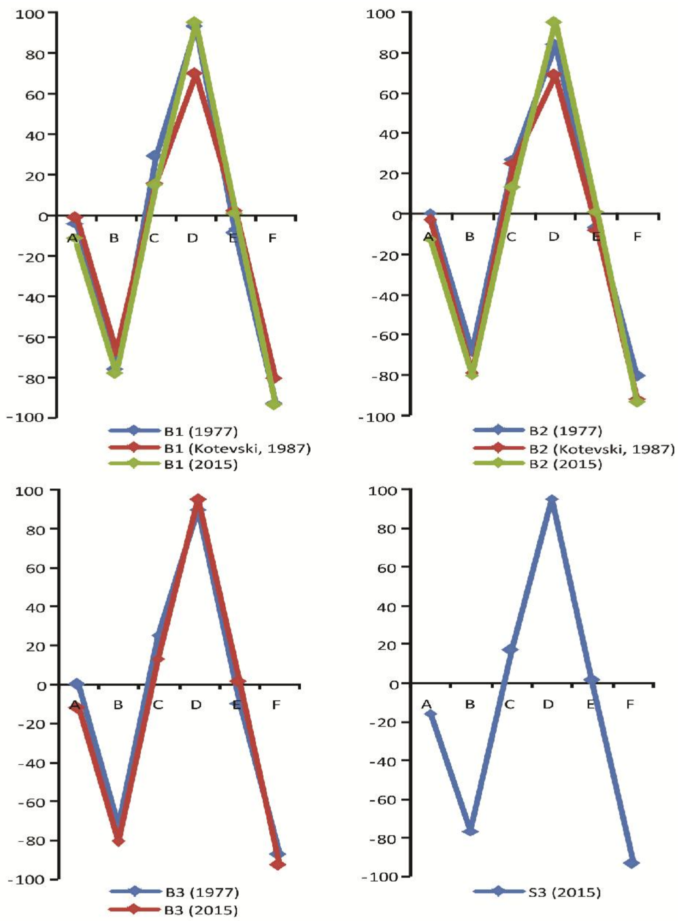

Fig. 5. D'Amore rectangular diagrams

T a b l e 2

Saturation indices of the water samples

Date of sampling	Anhydrite	Aragonite	Calcite	Dolomite	Gypsum	Halite	Magnesite
			Sampling point: B1				
1977	–1.893	–0.046	0.077	–0.722	–2.225	–5.383	–1.186
Kotevski, 1987	–1.950	–0.802	–0.679	–0.654	–2.274	–5.380	–0.376
2015	–2.146	–0.972	–0.828	–2.824	–2.184	–5.175	–2.488
			Sampling point: B2				
1977	–1.665	0.282	0.408	0.489	–1.956	–5.575	–0.333
Kotevski, 1987	–1.818	–0.814	–0.692	/	–2.158	–5.296	/
2015	–2.184	–0.890	–0.746	–2.607	–2.222	–5.149	–2.352
			Sampling point: B3				
1977	–1.766	0.205	0.326	0.150	–2.114	–5.466	–0.551
2015	–2.176	–0.926	–0.782	–2.673	–2.214	–5.145	–2.382
			Sampling point: S3				
2015	–2.139	–0.968	–0.824	–2.825	–2.177	–5.228	–2.492

CONCLUSION

The hydrochemical properties of thermomineral water from the wells B_1, B_2, B_3 and S_3 (Kežovica spa, Štip and Ldži) were analyzed. They are located in granite or in a contact between granite and Upper Eocene sediments.

The temperature was oscillating between 53 and 62°C. According to the pH index the water belongs to the water group characterized by alkaline reaction. The thermomineral waters have high mineralization which ranges within the 1200.6 – 1305.8 mg/l^{-1}. Hydrochemical features of the wells are represented by Piper diagram, Stiff diagram, Chadha diagram and D'Amore diagram. The results showed that all water samples have the same origin. The major ions in all water samples were dominantly $Na^+ > Ca^{2+} > K^+$ for the cations and Cl^- > SO_4^{2-} > HCO_3^- for the anions. All analyzed thermomineral water samples belong to NaCl water type.

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Р е з и м е

ХИДРОХЕМИСКИТЕ КАРАКТЕРИСТИКИ НА ТЕРМОМИНЕРАЛНИТЕ ВОДИ ОД БАЊАТА КЕЖОВИЦА – ШТИП, РЕПУБЛИКА МАКЕДОНИЈА

Војо Мирчовски[1], Биљана Гичевски[2], Ѓорѓи Димов[1]

[1]*Факултет за природни и технички науки, Институт за геологија, Универзитет "Гоце Делчев" во Штип, бул. „Гоце Делчев" 89, 2000 Штип, Република Македонија*
[2]*Истражувачко друштво "Урсус спелеос", ул. Добромир Хрст 20а, 1000 Скопје Република Македонија*
Vojo. mircovski@ugd.edu.mk

Клучни зборови: хидрохемија; термоминерални води; бања Кежовица; јурски гранити

Во овој труд се анализирани хидрохемиските својства на примероци од термоминерална вода од четири бунари (B_1, B_2, B_3 и S_3). Бунарите се наоѓаат во близина на бањата Кежовица, југозападно од градот Штип. Од геотектонски аспект, поширокиот простор околу бунарите му припаѓа на српско-македонскиот масив и вардарската зона. Бањата Кежовица се наоѓа на контактот помеѓу гранити и горноеоценски седименти.

Користени се неколку графичко-аналитички методи (Piper-ов дијаграм, Stiff-ов дијаграм, Chadha-ов дијаграм и D'Amore-ов дијаграм) за анализа на примероците од термоминералната вода. Извршените хидрохемиски анализи укажуваат дека водата од сите бунари има исто потекло. Главните катјони во водата се Na^+ и Ca_2^+, а анјони Cl^- и SO_4^{2-}. Сите анализирани примероци од термоминералната вода припаѓаат на NaCl-типот на вода.