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# HYDROGEOLOGICAL FEATURES AND ASSESSMENT OF TEMPERATURE IN PRIMARY COLLECTOR OF THE THERMOMINERAL WATER FROM THE HYDROGEOTHERMAL SYSTEM OF THE SPA KEŽOVICA AND L'DŽI – ŠTIP

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A b s t r a c t: This paper presents the hydrogeological features of the wider environment of hydrogeothermal system of the spa Kežovica and L'dži, and based on the chemical composition of thermal mineral water analyzed in the period from 1977 to 2016, with the help of hydrogeothermometers has made an estimate of the temperatures in the primary collector of these water. According to the structural type of porosity of the rocks present in the wider environment of the investigated field have been developed: boundary type of aquifers, fissure type of aquifers and waterless rocks. According to the hydrodynamic characteristics of the water level in this system there are aquifers with free level and subartesian aquifers. Thermomineral water from the hydrogeothermal system Kežovica and L'dži origin of fractured type of aquifer with subartesian pressure formed in tectonically cracked Štip granite. With the help of hydrogeothermometer on chalcedony, Na–K and Na–Li, is determined temperature in the primary collector of thermomineral water which are ranging from 90 to 120 °C.

Key words: thermomineral water; hydrogeothermal system; spa Kežovica; Jurassic granites; hydrogeothermometers

# INTRODUCTION

Hydrogeothermal system of the spa Kežovica and locality L'dži are located in the eastern part of Macedonia about 3 km southwest of the city of Štip, near Novo Selo.

Thermomineral water from this system is operated with only one well to the needs of the spa Kežovica and physical therapy. This well is marked as B-1. On the site L'dži in Novo Selo in the vicinity of Bregalnica river has a source of thermal mineral water, which is captured and used by the local population. Right above the source are located drilling wells market as B-2. The temperature of the thermomineral water is in range between 50 and 62 °C. The static level in the well B1 is of 1.7 m and B2 is 2.3 m, which indicates that it is for subartesian aquifer.

In the past, thermomineral waters of the spa Kežovica and source L'dži have been studied by a growing number of researchers: Miloevik (1953), Miholik (1953), Baik (1955), Nastić (1968), Gjuzelkovski and Stračkov (1973), Kotevski (1974), Kekić and Mitev (1973–1978), Ѓорѓиева (1995), Kekić and Mirčovski (2001–2002), Mirčovski and Stefanova (2016).

### GEOLOGICAL FEATURES

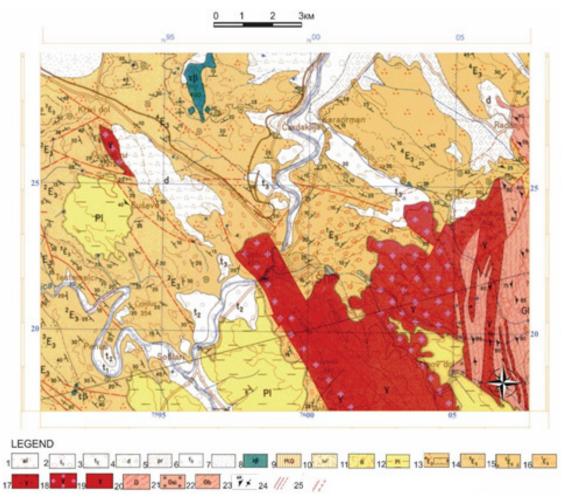
Wider surroundings of hydrogeothermal system of the spa Kežovica and L'dži is constructed from Precambrian, Mesozoic, Tertiary and Quaternary rocks (Rakičevič et. al., 1969) (Fig. 1).

The basis of the terrain is built from Precambrian rocks represented by biotite fine grain gneiss (Gb), sillimanite–cordierite gneiss (Gsi) and vesicular-amygdaloidal gneiss (G). They occur in the eastern part of a contact with Štip granite.

Mesozoic is represented by rocks of Jurassic age represented by granites which in the literature are known as Štip granites. Granites occurring southeast and east of the spa Kežovica. They have heterogeneous lithological composition representted by adamelit biotite, biotite granites and aplitoid granite. The age of these granites according Šoptrajanova (1967) by Rb/Sr method is set at  $155 \pm 5$ million years (Middle Jurassic). After their creation, Štip granites are cut by dacite dyke from a younger stage.

Tertiary rocks are represented by Paleogene and Neogene rocks. Paleogene is represented by flysch sediments from basal series built from sandstone, marls and conglomerates, lower zone of the flysch built from grey sandstone and purple claystones and conglomerates, sandstones and claystones, underscores yellow sandstones and an upper zone of the flysch represented by claystones and sandstone, marls, limestone and claystones. Neogene is represented by Pliocene sediments built of sands, clays and gravels, then volcanic sedimentary rocks represented by andesite tuff and andesite breccias and sedimentary rocks represented by calcareous limestone.

Quaternary rocks are heterogeneous and they are represented by several genetic types, such as: sand, clay and gravel, old river terraces, proluvial and diluvial deposits, higher and lower river terraces and alluvial sediments. And the small effusions and punches of cyanide and basalts in the locality of Eževo Hill northwest of Štip are also of the Quaternary age.



#### Fig. 1. Geological map of the investigated area.

QUATERNARY: 1 – Alluvium; 2 – Lower river terraces; 3 – Upper river terraces; 4 – Diluvium; 5 – Proluvium; 6 – Old river terraces; 7 – Sands, clays and gravels; 8 – Cyanide and basalts. TERTIARY: 9 – Calcareous limestone; 10 – Andesite breccias; 11 – Andesite tuff; 12 – Sands, clays and gravels; 13 – Upper zone of the flysch: claystones and sandstone, marls and limestone; 14 – Underscores yellow sandstones; 15 – Lower zone of the flysch: grey sandstone and purple claystones sandstones and claystones; 16 – Basal series: marls and conglomerates; MESOZOIC: 17 – Aplitoid granite; 18 – Biotite granite; 19 – Adamelit. PRECAM-BRIAN: 20 – Vesicular-amygdaloidal gneiss; 21 – Sillimanite-cordierite gneiss; 22 – Biotite fine grain gneiss; 23 – Slope elements of foliation; 24 – Fault: determined, covered and asuumed; 25 – Front of the peel

In tectonic view, wider environment of the investigation area comes within two tectonic units: the Serbian-Macedonian mass and Vardar zone (Arsovski, 1997).

The border area between the Serbian-Macedonian mass and Vardar zone is represented by a remarkable rupture, which passes through Mt.

### HYDROGEOLOGICAL FEATURES

Hydrogeological characteristics of the wider environment of the spa Kežovica and L'dži are shown on the hydrogeological map (Fig. 2) and hydrogeological profile (Fig. 3).

According to the structural type of porosity which occurs in rocks that are present within the wider environment of the investigated field can be distinguished:

Plačkovica and move towards Kratovo-Zletovo

area. This rupture along the Serbian-Macedonian

mass is scales bundled through the Vardar zone at

an angle of 40–70° with peeling to several kilometres. Hydrogeothermal system spa Kežovica and

- Boundary type of aquifer;

L'dži belongs within the Vardar zone.

- Fissure type of aquifers;
- Waterless rocks.

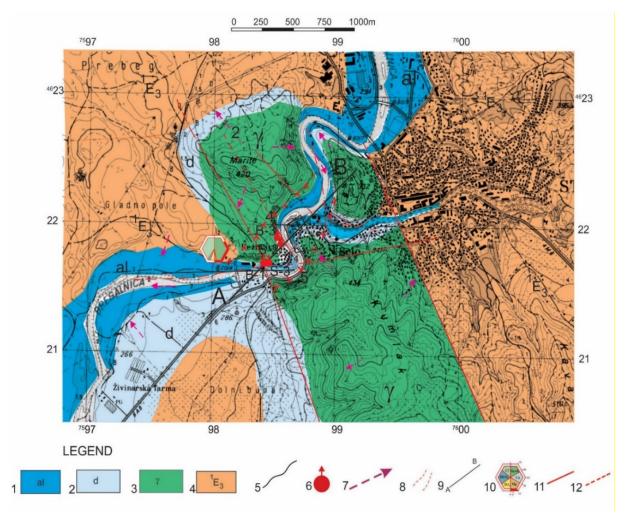


Fig. 2. Hydrogeological map of the hydrogeothermal system of the spa Kežovica and L'dži.
1 and 2 – Boundary type of aquifer; 3 – Fissure type of aquifers; 4 – Waterless rocks; 5 – Hydrogeological boundary;
6 – Subartesian wells; 7 – Assumed direction of movement of ground water; 8 – Assumed boundary of subartesian water;
9 – Profile line; 10 – Chemical composition of the water; 11 – Fault determined; 12 – Fault assumed (Mirčovski et. al., 2016)

Hydrogeological profile A-B

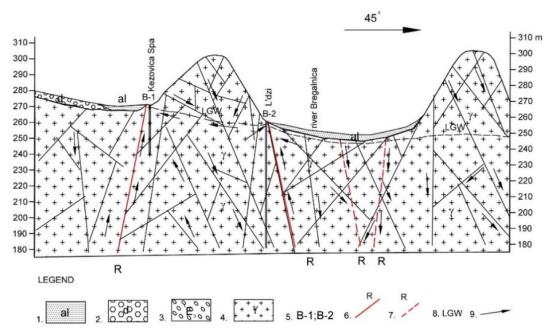


Fig. 3. Hydrogeological profile of the hydrogeothermal system of the spa Kežovica and L'dži.
 1 – Alluvium; 2 – Diluvium; 3 – Eocene; 4 – Granite; 5 – Exploitation borehole; 6 – Fault: determined, 7 – Fault: assumed;
 8 – Assumed level of ground water; 9 – movement of ground water (Mirčovski et al., 2016);

#### Boundary type of aquifer

Boundary type of aquifer is formed in incoherent rocks from the Quaternary age in which it is present intergranular porosity. There are represented by: alluvial and diluvial sediments. Alluvial sediments are developed in Bregalnica and Otinja, and are built of sand-gravel sediments deposited through the Eocene sediments and Jurassic granites. Based on data from the B-1 borehole their thickness ranges to about 4.5 m.

Diluvial sediments are represented on a larger area around the Merite hill and the locality of Dolni Bunar southwest of Kežovica spa. These sediments have heterogeneous composition which originated from the surrounding rocks. Mostly it is a loose cover which is composed of pieces of Štip granites and Paleogene sediments. The thickness of these sediments quite varied, ranging from 5 to 10 m.

According to the hydrodynamic characteristics of the aquifer levels within boundary type of aquifers are represented only by a aquifer with free level.

The feeding of these aquifers mainly down to the water from river flows and infiltration of precipitation.

#### Fissure type of aquifers

Fissure type of aquifers was formed in the Štip granites of Jurassic age which in this area is represented by adamelit, biotite and biotite granites, which has developed a fissure type of porosity. On the surface of the ground in these rocks has developed cracks in different sizes and directions of stretching arising as a result of tectonic movements (Fig. 4).

Also, the deep drilling which are performed at the site of Kežovica and L'dži during the 1975/76 year by the Geological Institute in Skopje to capture thermal water from greater depth was determined that the granites affected by tectonic movements are intensely cracked up 450 m depth. In deeper parts of 150 m, cracks mostly filled with calcite, which is deposited from the hot waters.

With fissure type of aquifers is connected and appearance of subartesian thermal waters in Kežovica and L'dži. Appearance of these waters is related to the deep fault structures which appear in this space.

The level of thermal water according to data from wells B-1 and B-2 is located at a depth of 1.7–2.5 m, and the temperature of thermal water is between 52 °C on the site of L'dži to 62 °C in the spa Kežovica.

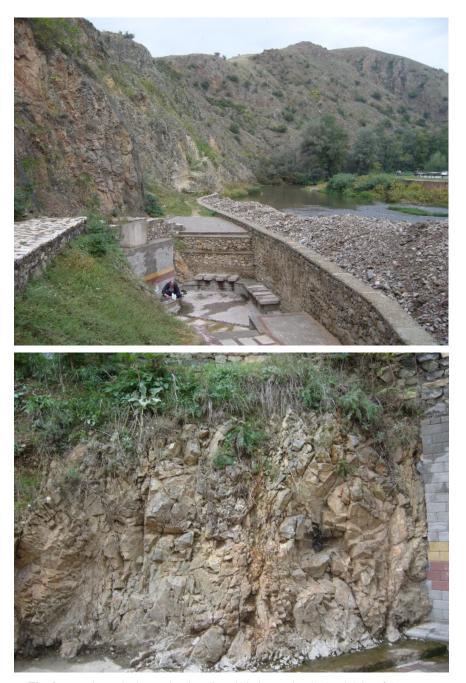


Fig. 4. Tectonic cracked Jurassic adamelit and biotite granites in the vicinity of the source

L'dži and well B-2. According to the hydrodynamic characteristics within the fissure aquifers, in shallow parts represented by aquifers with free level media of cold ground water and sub artesian aquifers where the thermal waters is accumulated, as is the case on the site of Kežovica and L'dži.

As the feeding zone or catchment area of source of thermomineral water Kežovica and L'dži we believe that is part of the area of Štip granite massif (northwest, southeast and east) and faults structures that are present in this area, which may be seen from the hydrogeological map (Fig. 2).

For the most part aquifer is fed by water by infiltration from precipitation through tectonic cracked granite rocks and through fault structures developed in this area. There is a possibility that this aquifer have nourishment also from other aquifers but this has not been confirmed.

#### Waterless rocks

The group of waterless rocks are categorized as Paleocene flysch sediments. These sediments

### ORIGIN OF THE THERMOMINERAL WATER

Thermomineral water from the spa Kežovica and source L'dži basically have tectonic origin. Their appearance is related to the intersection of Lakavica fault which extends northwest-southeast and is located between the granites and Eocene sediments and cross fault that goes along the river of Bregalnica which extends in east-northeastwest-southwest (Fig. 2). Thermomineral water from spa Kežovica, as seen from the presented hydrogeological profile (Fig. 3), occurs on the fault zone which is on contact between the granite and Upper Eocene sediments, and the source L'dži is located on fault zone which located in the granite. Probably in depth these fault zones are in connection which indicated the similarity of the chemical composition of water from the two localities.

are developed on a larger area east and west of the investigated area and they represent a geological sedimentary complex. It consists of sandstones, marls, conglomerates, clay and limestone.

For the tectonic origin of thermal water in Kežovica and L'dži also indicates the high temperature of water. With the latest measurements from 2016, the temperature is between 52 and 62 °C, and high total mineralization of the water ranges from 1537 to 1585 mg/l.

According Miholić (1953) the radioactivity of water from the Kežovica spa is 42.82 moch units and of the source L'dži is 11.57 moch units. According to these data this spa belongs to the most radioactive spas in Macedonia, but also in the ranks of most radioactive spas in Europe.

Thermomineral water according to chemical composition belongs to the NaCl type water (Mirčovski et al., 2016).

# ASSESSMENT OF THE TEMPERATURE OF THE THERMOMINERAL WATER IN PRIMARY COLLECTOR

The assessment of the temperature of thermomineral water in the primary collector is performed using chemical hydrogeothermometers, which are based on the assumption that the temperature of the thermal water in the primary collector is established chemical balance of thermomineral water between fluid, gas and minerals.

Determination the temperature in the primary collector has worked for the thermomineral water from the well B-1 from the spa Kežovica and well B-2 from the site L'dži located above the source, according to chemical analyses made in Geological Institute in Ljubljana in 1977 (Božović et al., 1977; Koteski, 1987; Mirčovski et al., 2001, 2016) (Table 1).

From Table 1 it can be seen that the temperature, mineralization and the content of Ca, Mg, Na, K, Li and SiO<sub>2</sub> which is performed by assessing the temperature of thermal water from the wells B-1 and B-2 in the primary collector, is relatively uniform, with small deviations in some of the analyses. The stable content of these parameters for a longer period of time indicates that in the primary collector is established chemical equilibrium between thermal water and surrounding geological environment. The application of chemical hydrogeothermometers in such cases gives the opportunity for a more realistic assessment of the temperature of thermal water in the primary collector.

To determine the temperature in the primary collector is used hydrogeothermometer on: SiO<sub>2</sub> (Fournier, 1973; Arnorsson, 1983), chalcedony (Fournier, 1973), Ca–Mg (Giggenbach, 1983), Na–K (Arnorsson, 1983), K–Na (Giggenbach, 1983) and Na-Li (Fouliac & Michard, 1981). The results are shown in Table 2.

From Table 2 can be seen that all results obtained for temperatures of thermomineral water in the primary collector is higher than those measured in wells B-1 and B-2, except for two temperature values which are smaller and are determined by the Ca–Mg hydrogeothermometer.

Quartz hydrogeothermometer for Kežovica gives temperatures ranging from 112 to 128 °C and for L'dži slightly lower temperatures ranging from 102 to 115 °C. Hydrogeothermometer of chalcedony for Kežovica provides a temperature of 94– 101 °C and for L'dži 84–88 °C.

# Table 1

Chemical analyses of the thermomineral water (mg/l)

	Geological	Institute in	Kotevski		Mirčovs	ki et. al.	Mirčovski et al.	
	Ljubljana, 1977		1987		2001		2016	
	B-1 Kežovica	B-2 L'dži	B-1 Kežovica	B-2 L'dži	B-1 Kežovica	B-2 L'dži	B-1 Kežovica	B-2 L'dži
Cl	468	370	511.2	538	_	-	567.258	596.471
HCO <sub>3</sub>	171	202	195.2	169.0	_	-	148.0	157.0
$NO_2$	0.01	0.01	_	_	_	_	0.006	0.002
$NO_3$	0.6	<0.5	_	_	_	_	0.469	0.726
$SO_4$	174	155	162.4	164.4			162.938	148.965
F	16.8	11.3	-	_	_	-	_	-
$CO_3$	_	-	15.5	12.0	-	_	_	-
J	0.28	0.32	_	_	-	-	—	-
$K^+$	21	14.5	11.6	10.5	11.76	13.52	13.225	12.838
Na <sup>+</sup>	440	343	407.60	472.8	491.79	579.4	493.671	498.925
$\mathrm{NH_4}^+$	0.05	0.05	-	-	-	_	<0.01	< 0.01
Ca <sup>2+</sup>	14.8	28.8	15	18.2	12.37	15.89	14.494	14.494
Mg <sup>2+</sup>	0.9	5.9	33		0.508	0.610	0.527	0.596
Fe	0.06	< 0.01	0.15	0.02	0.0099	0.0099	0.0107	0.098
Mn	<0.01	< 0.01	-	_	0.0140	0.0093	0.0082	0.00996
Al	0.020	0.045	-	_	< 0.01	< 0.01	< 0.01	0.0152
As	0.13	0.07	_	_	0.1667	0.1859	0.237	0.252
Ва	<2	< 0.05	-	_	0.0053	0.0074	0.0017	0.0047
Cr	< 0.01	< 0.0.15	-	_	< 0.001	< 0.001	0.0043	0.006
Cu	0.0003	0.014	_	_	0.0024	0.0045	0.0069	0.0078
Мо	< 0.20	< 0.01	-	_	0.0203	0.0179	0.0153	0.0145
Pb	0.0041	0.0014	_	_	0.0068	0.0131	< 0.001	< 0.001
Ti	< 0.01	< 0.01	_	_	< 0.001	< 0.001	0.065	0.069
Zn	0.011	0.012	_	_	0.0014	0.0014	<0.01	0.619
V	0.015	0.01	_	_	0.0051	0.0027	0.0018	0.0019
Р	-	_	_	_	0.002	0.0021	<0.01	< 0.01
Sr	-	_	_	_	0.2818	0.3801	0.285	0.285
Se	-	_	_	_	0.0315	0.0137	0.0210	0.022
Ni	_	_	_	_	0.0130	0.0161	< 0.001	< 0.001
W	_	_	_	_	0.1419	0.1904	_	_
Li	-	_	_	_	0.2443	0.1975	0.147	0.151
Со	_	_	_	_	< 0.001	< 0.001	< 0.001	< 0.001
Cd	-	_	_	_	< 0.001	< 0.0025	< 0.001	< 0.001
Sb	_	_	_	_	0.0068	0.0034	0.0018	0.018
Ag	-	_	_	_	0.0017	0.0019	< 0.001	< 0.001
В	_	_	_	_	_	_	9.85	10.384
Sn	_	_	_	_	_	_	< 0.001	< 0.001
Be	_	_	_	_	_	_	< 0.001	< 0.001
Ti	_	_	_	_	_	_	0.065	0.069
Bi	_	_	_	_	_	_	< 0.001	< 0.001
SiO <sub>2</sub>	86	65.6	75.5	63.5	_	_	-	-
Mineralization	1350	1129	1450	1310	_	_	1537	1585
pH	7.9	7.9	-	-	_	_	8.2	8.2
T °C	58	53	62	50	_	_	58	52
$CO_2$	_	_	3.2		_	_	_	_
	<u> </u>				<u> </u>		<u>I</u>	

	No	Quartz Fournier 1973	Quartz Arnorsson 1983	Chalcedone Fournier 1973	Ca–Mg Giggenbach 1983	Na–K Arnorsson 1983	K–Na Giggenbach 1983	Na–Li Fouliac & Michard 1981
Geological Institute in Ljubljana 1977 Kežovica B–1	58	125 – 128	119 – 124	101	90	130	179	_
Geological Institute in Ljubljana 1977 L'dži B–2	53	114 – 115	105 - 113	86 - 88	57	122	171	-
Koteski 1987 Kežovica B–1	62	120 - 122	112–119	94 –95	33	116	148	_
Koteski 1987 L'dži IB–2	50	112 – 113	102 – 111	84 - 86	_	80	134	_
Mirčovski et al. 2001 Kežovica B–1	_	-	-	_	82	84	44,9	103
Mirčovski et al. 2001 L'dži B–2	_	-	-	-	81	83	-	86
Mirčovski et al. 2016 Kežovica B–1	58	-	-	_	85	91	145	79
Mirčovski et al. 2016 L'dži B–2	52	_	-	-	82	112	143	79

Table 2

Assessment temperatures in the primary collector  $(T^{\circ}C)$ 

Ca–Mg hydrogeothermometer given lower temperatures than quartz and chalcedone hydrogeothermometer and they range from 33 to 90 °C. According Na–K hydrogeothermometer obtained temperatures ranging from 80 to 130 °C, and they are similar to the temperatures which are obtained by hydrogeothermometer of quartz and chalcedony.

K–Na hydrogeothermometer gave unrealistically high temperatures ranging from 134 to 179  $^{\circ}$ C.

Na-Li hydrogeothermometer gives temperatures ranging from 79 to 103 °C. These temperatures are similar to temperatures obtained by hydrogeothermometer of quartz, chalcedone and Na–K.

As assessed temperatures on thermominaral water in the primary collector can take average temperatures obtained by hydrogeothermometers of quartz, chalcedone, Na–K and Na–Li that are ranging from 90 to 120 °C. The estimated temperatures in the primary collector are in accordance with the temperatures given by Georgieva (1995) on the hydrogeothermal system of Kežovica–L'dži, which are move in the range of 100 to 115 °C.

## CONCLUSION

According to the structural type of porosity which occurs in rocks that are present within the wider environment of the investigated field can be distinguished: boundary type of aquifer, fissure type of aquifers and waterless rocks.

Boundary type of aquifer is formed in incoherent rocks from the Quaternary age in which it is present intergranular porosity. There are represented by alluvial and diluvial sediments.

Fissure type of aquifers was formed in the Štip granites of Jurassic age which in this area is represented by adamelit, biotite and biotite granites, which has developed a fissure type of porosity.

The group of waterless rocks are categorized Paleocene flysch sediments and they are built from the sandstones, marls, conglomerates, clay and limestone. Thermomineral water from the geothermal system of the spa Kežovica and source L'dži is appear at the intersection of the Lakavica fault which extends northwest-southeast and is located between the granites and Eocene sediments and cross fault that goes along the Bregalnica river with direction of stretches east-northeast-westsouthwest.

These waters originate from fractured type of aquifer formed in tectonic cracked of the Štip granites which has subartesian character. As assessed temperatures on thermomineral water in the primary collector can take average temperatures obtained by hydrogeothermometers of silicon, chalcedony, Na–K and Na–Li that are ranging from 90 to 120 °C.

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#### Резиме

### ХИДРОГЕОЛОШКИ КАРАКТЕРИСТИКИ И ПРОЦЕНА НА ТЕМПЕРАТУРАТА ВО ПРИМАРНИОТ КОЛЕКТОР НА ТЕРМОМИНЕРАЛНАТА ВОДА ОД ХИДРОГЕОТЕРМАЛНИОТ СИСТЕМ НА БАЊАТА КЕЖОВИЦА И Л'ЏИ – ШТИП

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Во овој труд се презентирани хидрогеолошките карактеристики на пошироката околина на хидрогеотермалниот систем на бањата Кежовица и Л'џи, а врз основа на хемискиот состав на термоминералната вода анализиран во периодот од 1977 до 2016 година. Со помош на хидрогеотермометри е направена процена на температурите во примарниот колектор од кој потекнува оваа вода.

Според структурниот тип на порозноста која се јавува во карпите кои се присутни во пошироката околина на истражуваниот терен се издвоени: збиен тип на водоносници, пукнатински тип на водоносници и водонепропусни карпи. Според хидродинамичките карактеристики на нивото на водата се присутни водоносници со слободно ниво и субартески водоносници. Термоминералната вода од хидрогеотермалниот систем Кежовица и Л'џи потекнува од пукнатински тип на водоносница со субартески притисок, формирана во тектонски испуканите штипски гранити.

Со помош на хидрогеотермометрите на силициум, калцедон, Na–K и Na–Li, е направена процена на температурата во примарниот колектор на термоминералната вода, која се движи од 90 до 120 °C.