Genesis of thermal groundwater of Lelic karst massif in Western Serbia

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ABSTRACT: The territory of Lelic karst is located in Western Serbia (Europe), in the region of the Inner Dinarides open zone. Lelic karst occupies about 280 km^2, and with its more than 200 geomorphologic, geological and hydorgeologic features, this area is seen as a highly interesting one from the hydrogeologic point of view. The main aquifers are tectonically deformed Middle Triassic limestones.

The main characteristics of this karst massif are very strong springs with cold water occurring on the tectonic contact between limestone and Neogene sediments, and thermal water tapped by wells in the zone of covered karst. The temperature of thermal water ranges from 20 to 30 ^{0}C, mineralization is about 500 mg/l, and these waters are of HCO_3-Ca, Mg type.

The aim of this paper is to explore the conditions and processes which lead to the forming of chemical and physical characteristics of these waters, by means of genetic coefficients, as well as a complete chemical and isotopic analysis. Taking into consideration that the concentration of main ions of this water is the same, this paper is focusing on specific components (Sr, SiO_2, …) and their balance in the in-depth zone of circulation.

The genesis of groundwater is significant from both theoretical and scientific aspects, as well as from that of its practical and sustainable use.

1. INTRODUCTION

Serbia is very rich in thermal, mineral, and thermo mineral water occurrences. There are about 250 of them on its territory. A significant portion of thermal waters on the territory of Serbia formed in limestones, the most significant aquifers being Triassic limestones. The study area (Fig. 1) belongs to the Inner Dinarides region in Western Serbia.

Fig. 1 Geographical position of the study area

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The thermal groundwaters of Lelic karst formed within Middle Triassic limestones. These waters occur on the contact of carbonate rocks and Neogene sediments, while thermal waters are tapped by wells in the region of covered karst as well.

To write this paper, the data of previous investigations have been collected and reinterpreted. Then the field research followed with the aim of mapping and sampling of thermal groundwaters for chemical analyses. After completing chemical analyses, the conditions and processes resulting in physical and chemical features of Lelic karst thermal waters were interpreted comprehensively.

2. GEOLOGICAL-HYDROGEOLOGICAL FEATURES OF THE TERRAIN

Geological features

The study area belongs to the zone of the Inner Dinarides of Western Serbia (Fig.1). Triassic limestones and Neogene sediments are of the greatest significance (Fig. 2) from the point of view of forming and discharging of thermal ground waters. This is the reason for their detailed description while the remaining mapped units will be only mentioned.

The oldest rocks in the study area are Upper Paleozoic (Pz_2) quartz sandstones and marbles.

Triassic limestones occupy the largest portion in the region. The Lower Triassic (T_1) is represented by sandstones, limestones and slates. The thickness of these sediments is locally up to 200 m (Mojsilovic, et al 1965). Dolomites and dolomitic limestones of Anisian (T_2^1), normally overlie Lower Triassic sediments. Sedimentological-petrographic features of dolomites show high percentage of MgO (Mojsilovic, et al, 1965), about (25.13%), which is very significant from the aspect of the forming of mineral water chemical composition, if it is known that the thermal waters of covered karst are with equal Mg and Ca ion concentrations. The limestones of the **Middle and Upper Triassic ($T_{2,3}$)** are represented by massive limestones being the most significant aquifer of groundwaters on the whole territory of Lelic karst. The total thickness of Triassic limestones is about 300m (Mojsilovic et al, 1965). Volcanic activity in the Triassic was shown by the outbreak of porphyrite and pyroclastite in the Valjevo region.

Jurassic sediments are related to the unstable zone situated in the southern part of the study area. The most widespread are diabase-chert formations. Deep and vein equivalents of peridotite magma are stated in the study area. The thickness of Jurassic sediments is about 250 m (Mojsilovic, et al, 1965).

Upper Cretaceous series, represented by massive and stratified in thick beds limestones, marls and conglomerates, transgress Jurassic sediments. Flysh sediments represented by mica sandstones, siltstones, and conglomerates (Filipovic et al, 1971) belong to the Upper Cretaceous as well.

Neogene sediments are represented by conglomerates, marls, clays and sands. Taking into account their insulating properties, from the point of view of heat transfer, these sediments are significant as geothermal aquiclude.

Quaternary sediments are represented by alluvial and terrace deposits in the valleys of large rivers and are comprised of gravels, sands, and clays, their total thickness being about 50m.

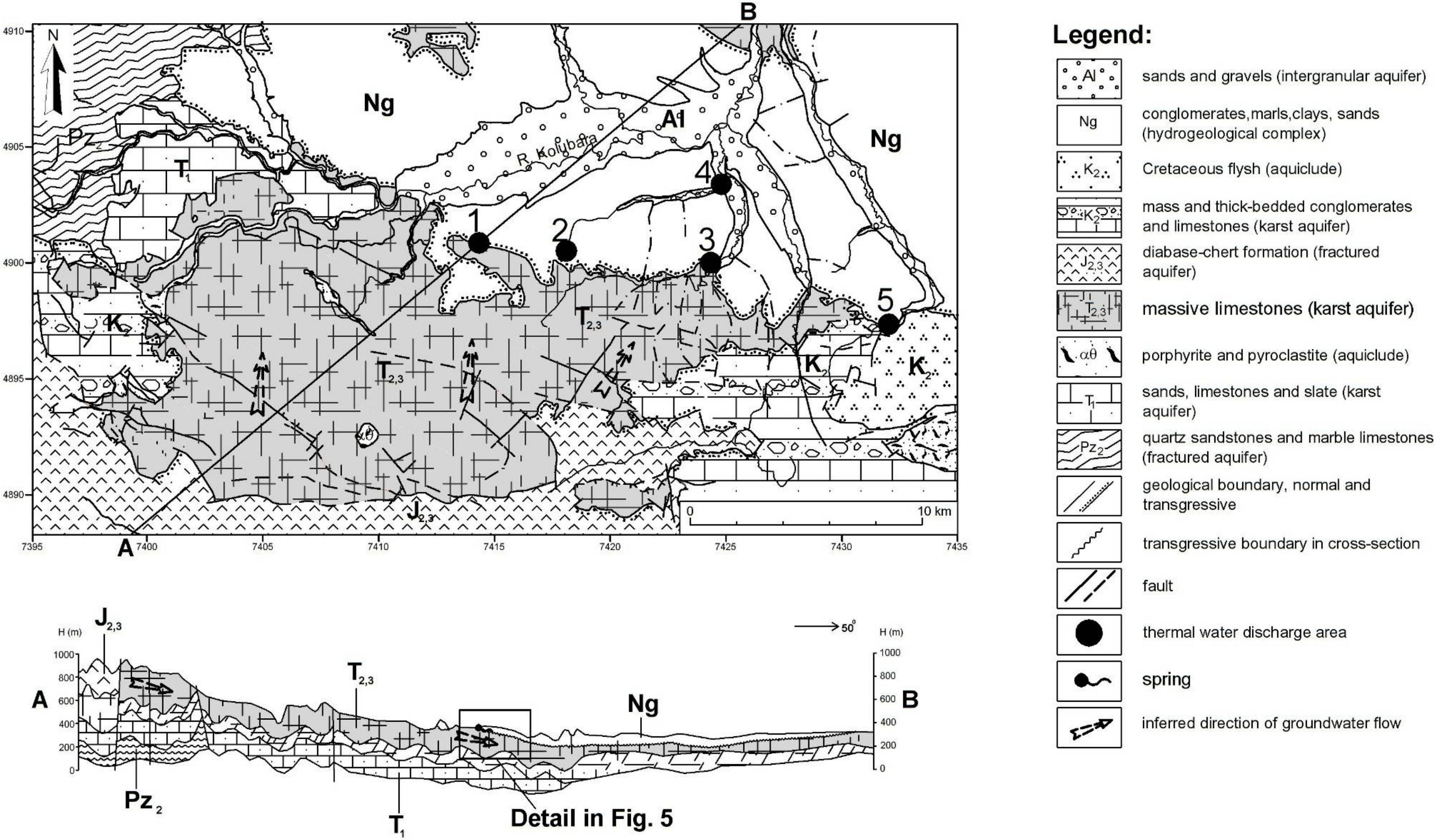

Fig. 2 Schematic geological-hydrogeological map of Lelic karst with inferred cross-section A-B

Hydrogeological features

Depending on the structural type of porosity and the water permeability of rock masses, the following aquifer types are sorted out (Fig. 2):

- An intergranular aquifer formed within gravels and sands of alluvial deposits of the Kolubara river and its tributaries.
- A karst aquifer of higher yield (shaded part in the hydrogeological map, fig. 2) formed within Triassic limestones ($T_{2,3}$) being the main collector in the study area. The surface of the uncovered karst collector is about 280 km^2, while the surface of the collector covered by Neogene sediments is estimated to be about 150 km^2 . The zone of covered Triassic limestones is at the same time a thermal groundwater aquifer. The collector is pronouncedly karstified and cavernous porosity prevails. The thickness of the aquifer is unknown, but it has been confirmed by drilling to be more than 300 m.The depth of karstification has not been confirmed, but on the basis of test drilling it can be concluded that it is deeper than 250 m. The karst type of an aquifer also formed within Cretaceous limestones and dolomites, as well as within Triassic limestones but with considerably lower water-bearing capacities.
- A fractured aquifer formed within the rocks of Paleozoic age as well as in the rocks of diabase-chert formation of Jurassic age.
- The hydrogeological complex of Neogene sediments is formed of rocks where in vertical profile rocks alternate with the function of aquifer and aquiclude, however this complex, as a whole, has the function of aquiclude and represents hydrogeological barrier to groundwater movement of a karst aquifer. These sediments are significant because of their function of hydrogeothermal barrier as well, being a necessary condition for thermal groundwater occurrence in the study area.

3. CONDITIONS OF LELIC KARST THERMAL GROUNDWATER DISCHARGE

The region of Lelic karst abounds in cold and thermal water occurrences. The outflow of these waters is related to the carbonate rock contact as aquifer and Neogene sediments, as an aquiclude. Thermal waters are drained by four springs, and also by wells which tap these waters in the zone of covered karst. The conditions of thermal groundwater outflow will be described in the further text.

The thermal spring in the village of Petnica (zone 1 in Fig. 2) is of an ascending type and it is predisposed by a fault. The spring flow is about 10 l/s, while the water temperature amounts 23 ^{o}C. The spring is characterized by a stable temperature regime. There are three more wells in this area which tap thermal waters of Triassic limestones with the water temperature ranging from 20 to 30.5 ^{o}C.

The thermal spring in the village of Paune (zone 2 in Fig. 2) is situated at the contact of Triassic limestones and Neogene sediments which represent a hydrogeological barrier. The spring occurs at the spot where Neogene sediments are eroded and Triassic limestones wedge out on the surface of the terrain. The spring flow is about 2 l/s, while the water temperature amounts 21 ^{o}C.

In the village of Kljuc(zone 3 in Fig. 2) there occurs thermal water outflow through two springs; one spring with the temperature of 21 ^{o}C is of the ascending type predisposed by a fault and with the spring flow of about 1 l/s, the other spring is of a subthermal type with the spring flow of about 100 l/s and with the temperature of about 16 °C (Protic, 1995). There is a well in this area tapping thermal waters with the temperature of 21°C.

Thermal waters in Mionica (zone 4 in Fig. 2), thermal waters are tapped by wells, a single spring flow of each amounting about 10 l/s. The temperature of these waters ranges from 27 do 30 °C.

Thermal water at Banja Vrujci spa (zone 5 in Fig. 2) occurs as a seepage spring in the alluvial plain of the river Toplica. The total spring flow is estimated to be about 100 l/s, and the temperature of the water 27 °C. In this case the aquiclude is comprised of flysh deposit, while the thermal water outflow occurs at the spot where flysh deposits are eroded and Triassic limestones are at the surface of the terrain. There are a few wells in this area tapping thermal water with the temperature of about 31 °C.

4.GENESIS OF THERMAL GROUNDWATERS OF LELIC KARST

The forming of thermal groundwaters requires the existence of a half open hydrogeological structure, namely the hydrogeological collector to be protected from quick water exchange, for intensive water exchange would result in cooling of adjacent rock masses.

During Anisian volcanic activity occurred resulting in the occurring of porphyirite and pyroclastite at the surface of the terrain in the region of Lelic karst.Volcanic activity occurred in the study area during Neogene, as well. These rocks are vein equivalents of a deeper granitoid pluton which probably represents a source of heat in the geothermal system. In the floor of Triassic limestones, there are Paleozoic rocks which are, at the same time, the heat transferors, as well.

The average value of the terrestrial heat flow density on the territory of Lelic karst amounts 106 mW/m^2, which is above the average of continental part of Europe, where the value of the terrestrial heat flow amounts 60 mW/m^2 (M. Milivojevic, 1989).

The karst aquifer of thermal groundwaters is recharged by infiltration of atmospheric precipitation in the area of uncovered part of the karst collector and on account of surface streams where they directly overlie limestone rocks.

The conditions of forming of thermal groundwater physico-chemical features

The temperature of thermal waters of uncovered karst amounts about 21 °C, while the temperature of covered karst ranges from 21 °C to 30.5 °C.

The results of the research of the chemical composition of Lelic karst waters are shown in Table 1. There it can be seen that the waters in the thermal springs (Petnica, Paune, Kljuc, Banja Vrujci) are of hydrocarbonate–calcium type, while the thermal waters tapped by wells are of hydrocarbonate-calcium-magnesite type.

All described thermal groundwater occurrences are of HCO_3-Ca,(Mg) type, except the thermal waters occurring in Mionica (zone 4 in Fig. 2). These waters originate, by one part out of the aquifer situated in marl-clay deposits of Neogene age. Sodium ions comprise one of the basic components of the chemical composition of clay minerals. The origin of sodium ions can be explained by the process of cation exchange Ca^{2+} from Na^+ out of rocks, and as a result of this exchange in solution, i.e. water equivalent quantity of Na^+, appears instead of Ca^{2+}, according to the following scheme (N. Dimitrijevic, 1988):

$$Ca^{2+} + 2HCO_3^- + Na\ (rock) \leftrightarrow Ca^{2+}\ (rock) + Na^+ + 2HCO_3$$

It can be seen in Table 1 that as we move away from the contact of Triassic limestones and Neogene sediments Cl ion concentration decreases, while Na and SO_4 ion concentration increases.

Table 1. The survey of the chemical composition of thermal groundwater occurrences on the territory of Lelic karst

sort of occurrence	depth of the well	Q (l/s)	depression	**T (°C)**	pH	M (mg/l)	Ca (mg/l)	Mg (mg/l)	Na (mg/l)	HCO_3 (mg/l)	Cl (mg/l)	SO_4 (mg/l)
Kljuc												
Well raj-1	202	1,5	75	13,4	7,1	340,0	125,0	4,9	2,4	335,0	20,6	5,0
Well raj-2	203	2,3	112	13,5	7,4	352,0	113,6	9,6	1,5	390,0	3,5	2,1
Well raj-3	109	5,5	32,5	18,2	7,2	346,0	101,7	10,2	2,2	354,0	3,7	4,8
Well raj-4	149	11,0	Free outflow	21,0	6,8	303,0	52,0	30,1	18,0	348,0	0,5	14,2
Petnica												
Well pt-4	250	16,2	35	20,0	7,0	365,0	101,4	19,6	3,6	383,7	11,9	9,7
Well pt-3	350	11,9	25,22	22,0	7,0	364,0	98,0	22,2	4,1	378,0	5,8	9,2
Spring	-	5,0	-	23,0	7,6	323,3	90,1	26,1	1,3	390,4	7,0	1,8
Well pt-2	500	7,0	Free outflow	30,5	7,4	323,8	68,1	35,3	11,0	394,1	2,8	12,0
Paune												
Spring	-	2,0	-	21,0	7,0	500,0	90,0	18,3	4,6	353,0	11,0	5,0
Banja Vrujci												
Seepage spring	-	100,0	-	26,0	7,4	460,0	76,0	14,6	16,8	292,8	35,0	12,0
Well B-2	270	25	Free outflow	31,0	7,2	383,0	78,0	15,0	37,0	390,0	9,0	15,0
Well BV-1	449	31,0	Free outflow	27,0	7,2	314,6	56,9	29,2	24,6	335,5	8,0	8,9
Mionica												
Well IEBL	180	12,0	Free outflow	28,7	7,7	351	34,4	17,0	74,9	421,0	0,9	15,7

The dependence of Ca and Mg ion concentration exchange on water temperature, and the depth of circulation of thermal groundwaters tapped by these wells, was confirmed by further analysis. The relationships of rCa/rMg for the waters formed in the region of Petnica and Kljuc (zones 1 and 3 in Fig 2) are shown in Table 2. The exchange of hydrochemical coefficient rCa/rMg (r-meq) in the region of Kljuc and Petnica is shown in Fig 3. It can be seen in these diagrams that with increasing temperature ratio of rCa/rMg decreases. This is typical for waters formed in dolomites and dolomitic limestones. The dolomites and dolomitic limestones are in the floor of Triassic limestones, thus it can be concluded that they are the major collectors, from where, waters tapped by wells, recharge (Fig. 5).

Table 2. The Survey of the chemical composition of waters in the vicinity of Kljuc and Petnica and hydrochemical coefficient rCa/rMg (r-meq)

The name of the occurrence	T (°C)	rCa	rMg	rNa	$rHCO_3$	rCl	rSO_4	rCa/rMg
Kljuc								
Well raj-2	13,5	5.68	0.79	0.065	6.39	0.1	0.04	7.2
Well raj-3	18,2	5.085	0.84	0.095	5.8	0.1	0.1	6
Well raj-4	21,0	2.6	2.475	0.78	5.7	0	0.295	1.05
Petnica								
Well pt-4	20,0	5.06	1.61	0.15	6.29	0.33	0.2	3.1
Well pt-3	22,0	4.89	1.82	0.17	6.18	0.16	0.19	2.7
Spring	23,0	4.49	2.14	0.05	6.4	0.19	0.04	2.09
Well pt-2	30,5	3.39	2.9	0.47	6.46	0.08	0.24	1.17

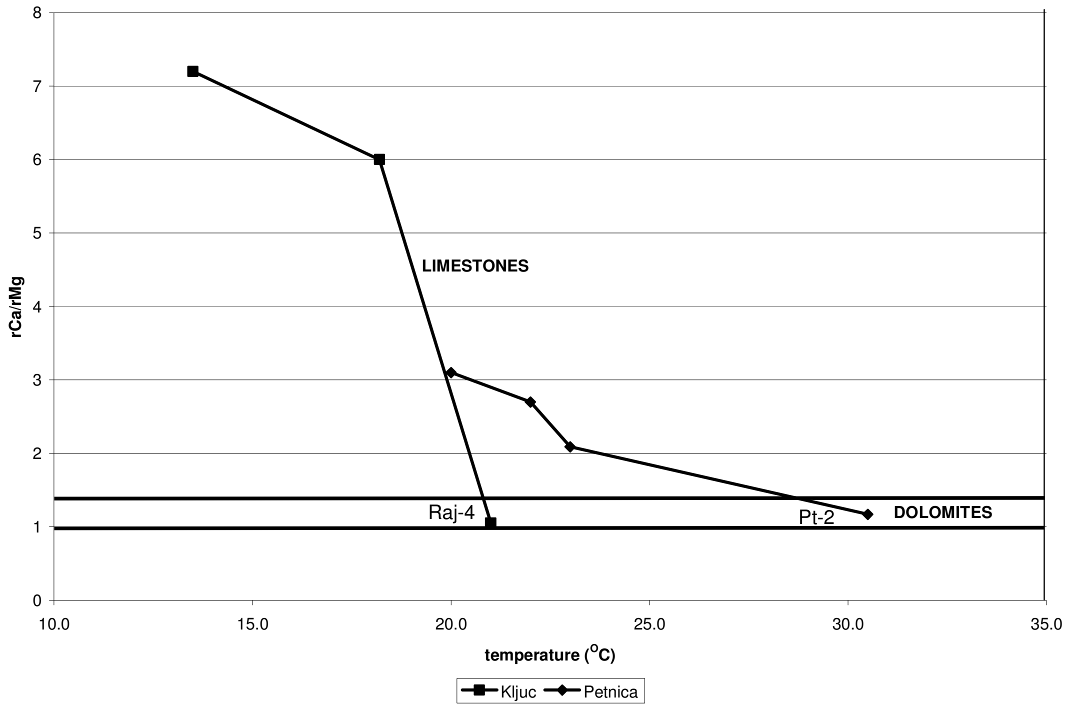

Fig. 3 Graph of dependence of rCa/rMg on temperature

Considering specific components in the study area, the increased content of strontium in thermal waters of Banja Vrujci spa should be emphasised. Sr occurs in nature in the form of two minerals: strontianite ($SrCO_3$) and celestine ($SrSO_4$), which often accompany limestones. In the region of Banja Vrujci spa also, on the surface of the terrain there are occurrences of pyroclastite, which are flowing equivalents of granitoid pluton, thus it is supposed that increased content of Sr is related to these rocks, as well. Having in mind that the radius of Sr^{2+} is approximately equal to the radius of C^{2+} ion (Mason, 1958), it has probably resulted in ion exchange between these two ions, thus it can be the reason for the increased strontium concentration.

Isotope composition of thermal groundwater on the teritory of Lelic karst

The most reliable index of the origin and age of ground waters is their isotope composition. The content of stable and radioactive isotopes in thermal waters of Lelic karst is shown in Table 3.

Table 3. The survey of the content of stable and radioactive isotopes in thermal groundwaters on the territory of Lelic karst (M. Milivojevic, 1989)

Locality	Water			
	Radioactive isotopes	^3H (T.U.)	Stable isotopes	
	^{14}C (year)		^{18}O (%SMOW)	^2H (%SMOW)
Petnica	12.000±200	-	-10,42	-81
Mionica	30.000	4,1±1,6	-11,55	-80
Banja Vrujci	7.700±150	6,5±1,4	-11,46	-89

To determine the origin of thermal waters the stable isotopes $\delta^{18}O$ and δ^2H, were used, and their content is given in the $\delta^{18}O$-δ^2H diagram (Fig.4). It can be seen in the diagram that analysed waters of Lelic karst are of meteorite origin. This shows that the aquifer formed within Triassic limestones is recharged in the area of uncovered karst. The moving of $\delta^{18}O$ is not significant, so it can be considered that the temperature in the collector was not high enough to cause the change of $\delta^{18}O$ between rocks and water. It can also be concluded that waters in the region of Mionica and Petnica formed in one aquifer (Triassic limestones and dolomites), while thermal waters in Vrujci formed in the aquifer of Cretaceous limestones.

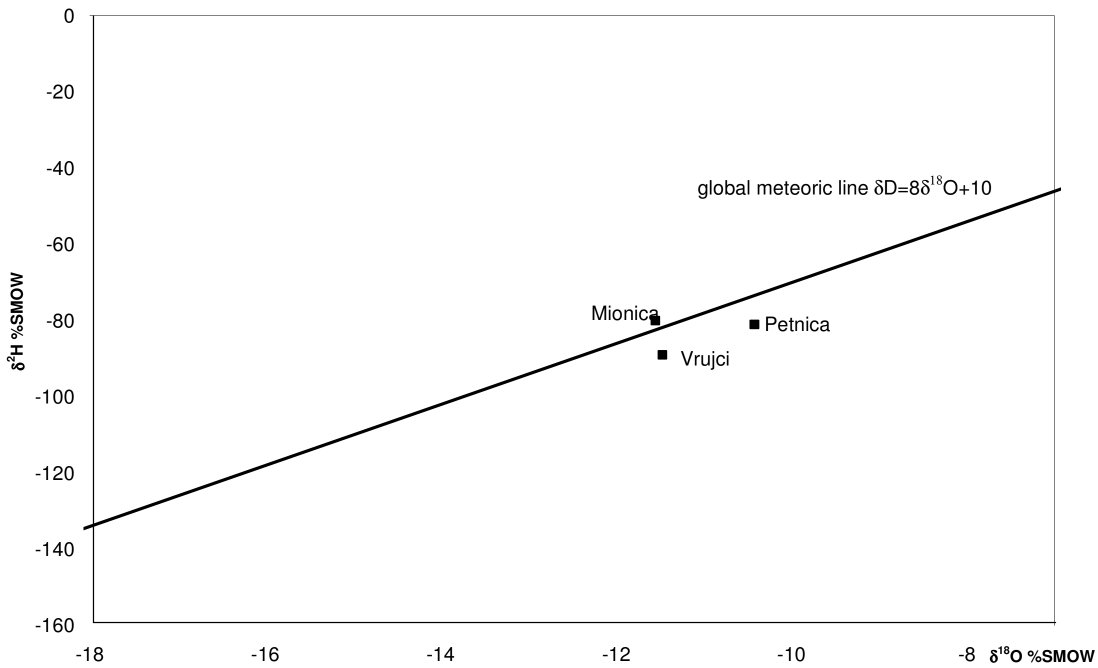

Fig. 4 Diagram of stable isotope content of Lelic karst thermal groundwaters

On the basis of ^3H content ranging from 4.1 to 6.5 TU, it can be concluded that these waters formed in the period before the year1952 and after the year 1952 (E. Mazor, 1991).

The age of thermal waters of covered karst on the basis of radioactive isotope of carbon ^{14}C ranges from 7.700 to 30.000 years (Milivojevic, 1989). The age of water thermal spring in Petnica is about 780 years (Komatina, 2001), which point out at privileged directions of moving along the fault by which the thermal water outflow is predisposed to the quicker circulation of ground waters, as well.

It should be pointed out that given data are relatively old and that all thermal water occurrences of Lelic karst have not been analysed. By designing complete isotope analyses of all thermal waters on the territory of Lelic karst the data concerning the age of these waters woul be obtained, as well as those concerning the depth of circulation and recharge area.

On the basis of all given data schematic model of chemical composition of Lelic karst thermal waters forming is shown using the example of Petnica (zone 1 in Fig 2):

a) Infiltration of precipitation,
b) Circulation through limestones and dolomites,
c) Heating of these waters because of heating flow,
d) Outflow of these waters at the contact of limestones and Neogene sediments predisposed by the fault,
e) Exploitation of these waters by wells in the zone of covered karst.

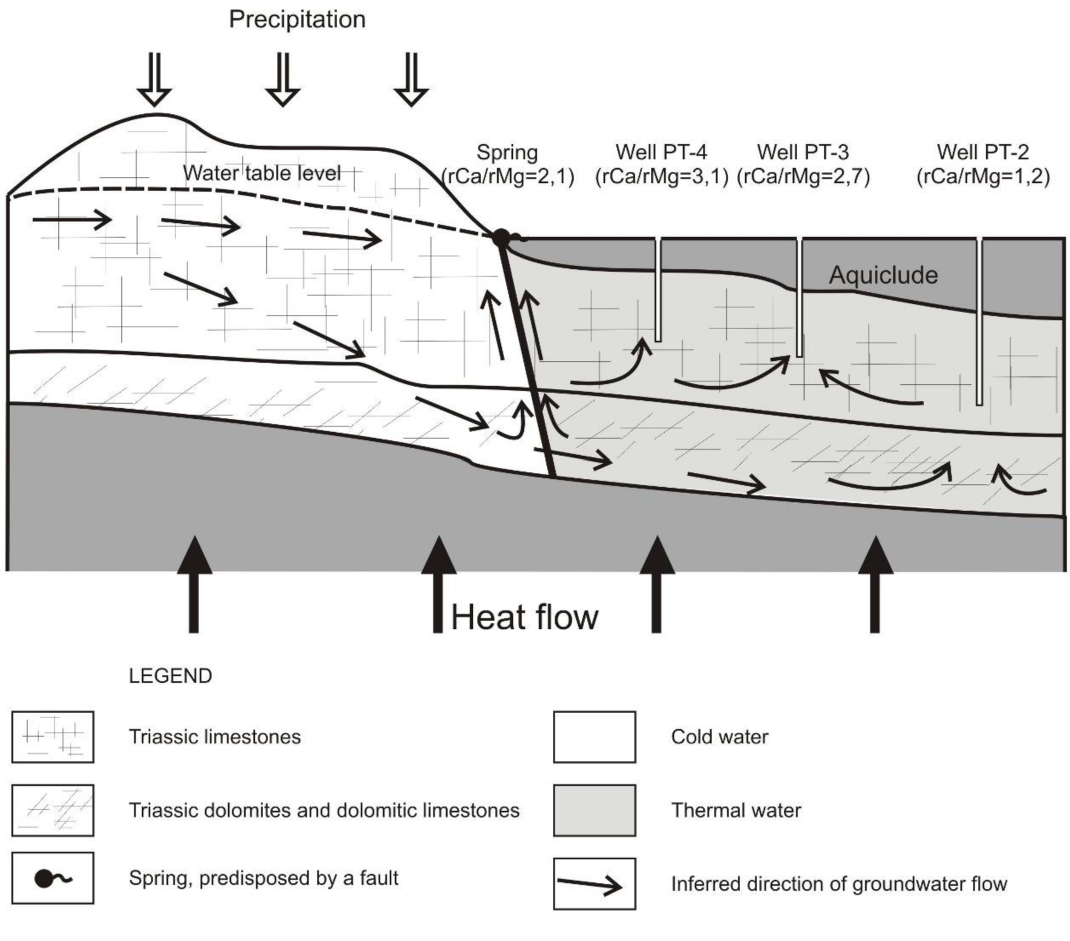

Fig. 5 Scheme of conditions for forming of Lelic karst thermal waters

5. CONCLUSION

Lelic karst is situated in Westerm Serbia in the region of the Inner Dinarides open zone. Triassic limestones are the major thermal water collector. The aim of this paper is to explain the origin of thermal waters formed in the region of Lelic karst.The temperature of thermal groundwaters ranges from 21 to 30 ^{o}C, the water ion content being HCO_3-Ca,(Mg).

Using the analysis of chemical content components it was concluded that thermal waters in the zone of covered karst formed in dolomites and dolomitic limestones, while thermal waters discharging at the contact of limestones and Neogene sediments are purely carbonated. This is shown by the ratio of rCa/rMg, which ranges from 3 to 7,2 in the zone of uncovered karst, while, in the zone of covered karst it ranges from 1 to 1.2.

On the basis of isotope analyses, it has been confirmed that the waters are of meteor origin and that the relative age of the waters is from 7.700 to 30.000 years (Milivojevic, 1989).

Further research should be focussed on investigating the thickness of Triassic limestones and their distribution in the region of covered karst. It is also necessary to carry out isotope analyses of all thermal waters. The regime monitoring of temperature and chemical content is necessary, as well, to confirm the previous hypotheses. To confirm the origin of increased concentrations of Sr, additional sedimentological-petrological analyses should be carried out as well as a detailed prospection of the terrain.

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