CARBOGASEOUS MINERAL WATER IN SERBIA AND BiH AS INDICATOR OF DEEP HYDROGEOTHERMAL RESOURCES

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ABSTRACT

Continuous and abundant CO_2 seepage at the sources and springs of geothermal water, the geological composition, hydrogeological and geothermal properties of earth's crust in the upper sections, where this phenomenon takes place indicate that CO_2 has been generated continuously during geological processes. In our opinion this is due to thermolysis, that is the process of carbonate rock decomposition by heat in geothermal aquifers and in the presence of geothermal water. Therefore, abundant seepage of CO_2 may be a clear indicator of deep hidden reservoirs of geothermal waters, which are composed of carbonate rocks (limestone, marble, dolomite, calcschist), or to be more specific the indicator of hidden hydrogeothermal resources in deep geothermal reservoirs.

1. INTRODUCTION

In the territory of former Yugoslavia there are more than fifty localities with geothermal water springs, which rich with CO_2. Of this number more than thirty springs are situated in the territory of Serbia and B&H. Many of these spring have been known ever since ancient times.

Apart from geothermal water rich in CO_2, there are several localities in which the seepage of pure CO_2 (dry gas) takes place. There are three such localities in B&H and one in Serbia. At the localities in B&H the seepage of dry CO_2 is utilized for the production of dry ice, i.e. liquid carbon dioxide, which will be used in food industry and the industry of soft and carbonated drinks. The construction of such a factory for the production of fluid carbon dioxide is also planned in Serbia.

Geothermal carbogaseous water is usually used to produce bottled mineral water. In Serbia there are five and in B&H there are three factories that produce mineral water. In addition to the production of CO_2 and bottled mineral water, the geothermal resources are in most localities used for and touristic and balneological purposes, for town heating either directly or by heat pumps.

This paper presents the results of isotopic tests and other geothermal explorations that indicate the presence of deep hydrogeothermal aquifers in two different sections, of which on is situated in the south of Serbia and the other in the central part of B&H.

2. GEOTECTONIC POSITION OF AREAS WITH SPRINGS OF GEOTHERMAL CARBOGASEOUS CARBONIC-ACID WATERS

In Serbia and in B&H the geotectonic position of the springs of geothermal carbogaseous waters is located at Inner Dinaric Formations. The Inner Dinaric Formations are the northern section of the Dinaric Formations, which represent the largest geotectonic unit at the Balkan Peninsula. The latest interpretations that deal with the tectonics of the Balkan Peninsula, which result from the "global tectonics" theory, suggest that Earth's crust in the territory of Serbia and B&H consists of terranes.

The terranes located in the central and western section of Balkan Peninsula are the result of subduction that took place during the Jurassic period [8]. According to these authors the Inner Dinaric Formations consist of the following terranes: The Dinaric Ophiolite Belt terrane (DOBT), The Central Bosnian Mts. terrane (CMBT), The Jadar Block terrane (JBT), The Drina-Ivanjica terrane (DIT); The Vardar Zone composite terrane (VZCT); The Serbian-Macedonian composite terrane (SMCT) and The Dalmatian-Herzegovinian composie terrane. The distribution of the terranes is given in Figure 1.

The occurrence of carbogaseous water springs in the territory of Serbia is located southwards of Belgrade and follows the general direction north-south (Figure 1). This area spreads further to the south over the territory of Macedonia and reaches the north of Greece. Leaving the territory of Serbia the line of geothermal carbogaseous water occurrence abruptly turns to the west towards B&H (Figure 2). The main group of springs of geothermal carbonic-acid waters in B&H is situated in the central part, near Sarajevo (Blazuj, Fojnica, Busovaca, Klokoti). The second group of springs is located in the vicinity of Doboj, Maglaj, Zepce, Tesanj, Teslic and in Slatina near Banja Luka.

3. GEOLOGICAL OVERVIEW

The Serbian-Macedonian composite terrane is situated between the Dinarides in the west and the Carpatho-Balkanides in the east (Figure 1). Geologic age of rocks in this terrane is Precambrian. The evidence of superposition was used to separate two complexes: lower or older and upper or Vlasina complex. The lower complex of the Serbian-Macedonian Massif is highly heterogeneous in lithology and three series are differentiated (Figure 2). The body that contains thermal water lies in the lower and middle series, composed of fractured gneisses, marbles, and quartzites. There is no geological evidence of the extent of these bodies to the south. The only evidence of the likely extent of both series to south of Prokuplje is the occurrence of travertine at Sijarinska banja.

In B&H within the area of DOBT and CMBT terranes, Mesozoic rocks occupy a vast territory. The rocks belonging to each of the three periods are found: Triassic, Jurassic and Cretaceous rocks. Triassic rocks occupy the smallest territory, while the Jurassic and Cretaceous rocks are prevailing.

In Inner Dinaric Formations, Triassic rocks extend horizontally over a vast territory and have a large thickness. Minor occurrences of Triassic rocks at the surface and data obtained from deep boreholes indicate that Triassic rocks are situated mainly underneath Jurassic formations, partly underneath Cretaceous rocks and to some extent underneath Neogene rocks. The thickness of early Triassic rocks is rather small. However, the overlaying rock complex has a significant thickness and is composed of mid and late Triassic rocks consisting of karstified limestone and dolomite with thickness amounting to 1,5 km to the maximum. Triassic rocks are crucial for geothermal potentiality since they represent the best possible aquifers of cold and geothermal waters in the areas of Pannonia Basin and Dinaric Formations, or to be more specific in the territory of Serbia, B&H, Croatia, Hungary, Romania, Slovakia and Poland.

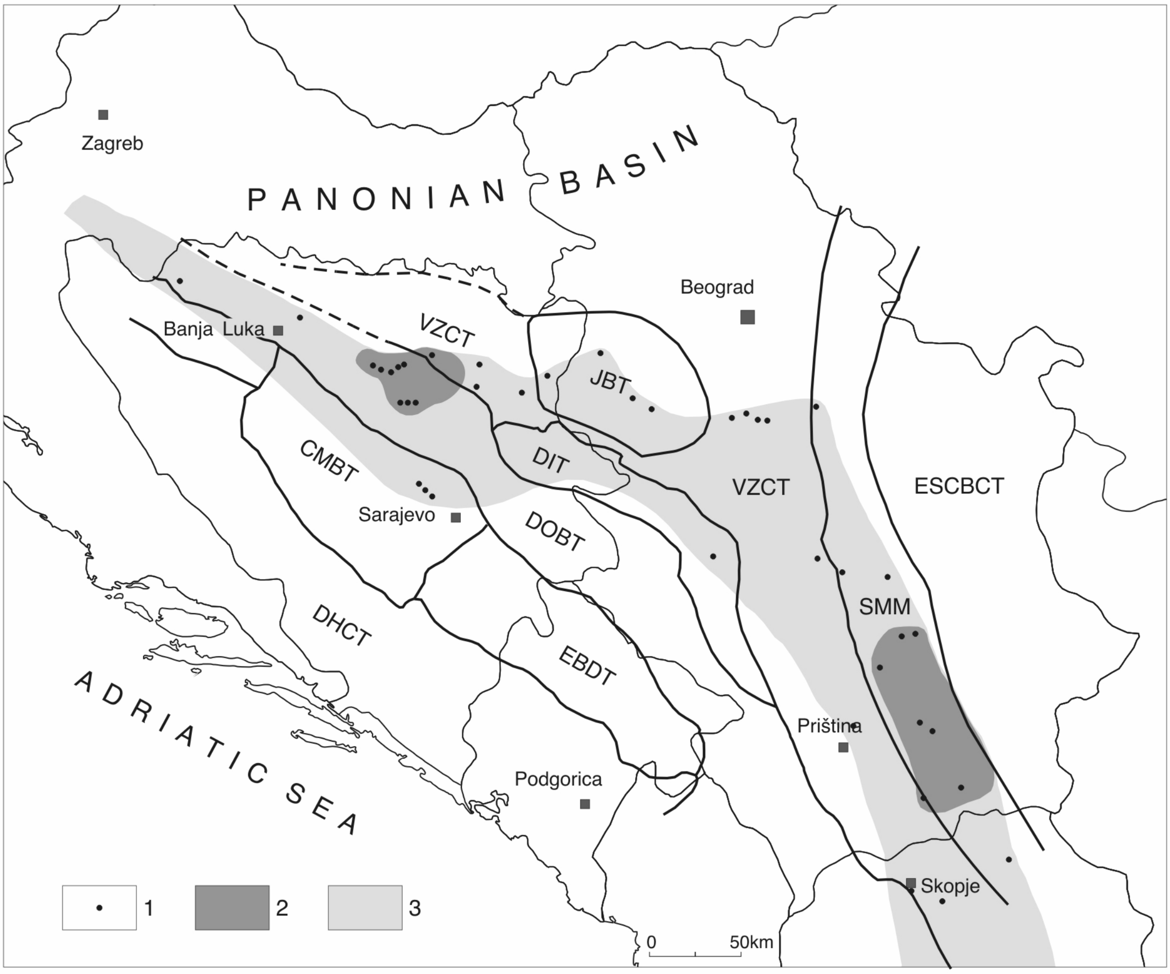

Figure 1. Geotectonic units of the central part of Balkan Peninsula (terranes, explanation in text) with locations of carbogaseous springs. (1-carbogaseous spring; 2-exploratory area; 3-zone with occurances of carbogaseous spring).

Jurassic rocks spread over a large area at the surface and lay over the Triassic rock formations. They consist of the well-known "diabase-hornfels" (DHF) formed during the subduction of Dinaric Formations under the Pannonia Basin. This formation consists of ophiolite melange (sandstone, claystone, fornfels, olistolith, serpentinite, periidotite, gabbro, amphibolite, diabase, dolerite, spilite). The mean thickness of DHF is about 1 km (Figure 3).

Flysch formations represent the oldest Cretaceous rocks, formed during early Createaceous period and their thickness ranges from 1,8 to 2,3 km. Early Cretaceous flysch spreads over a vast area and mainly consists of limestone and marl. Its thickness ranges from 0,4 to 0,6 km (Figure 3).

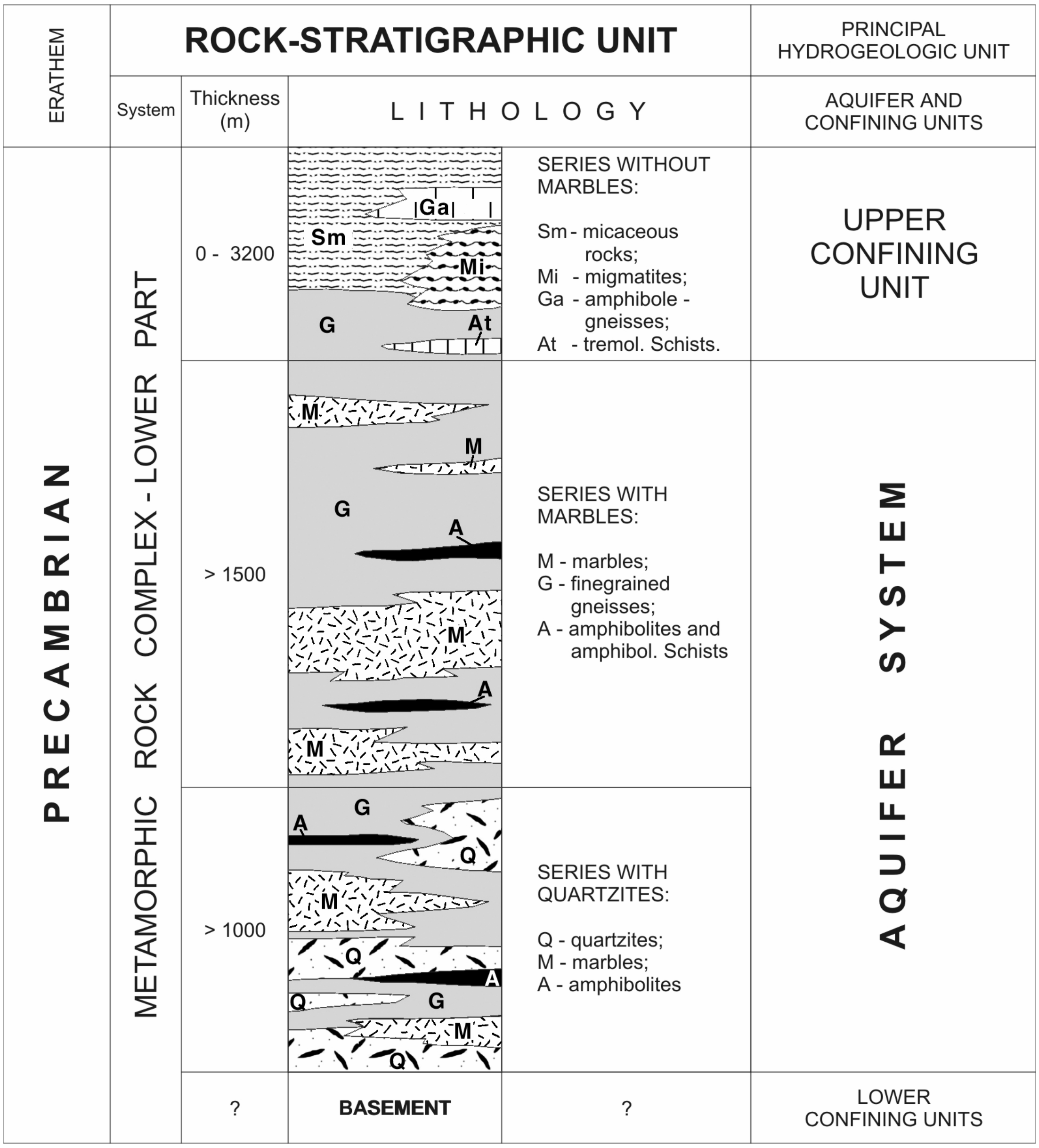

Figure 2. Lithostratigraphical column of the lower part of the Serbian-Macedonian Massif in Southern Serbia showing the position of aquifers with carbogaseous water

4. DISCUSSION

The studied occurrences of carbogaseous thermal water from area of South Serbia (SMM-terrane) according to isotopic investigations have meteoric origin and show a considerable oxygen shift to the right of the precipitation line. The shift from Craig's line is the greatest (about 2 %) for Tulare springs, the next greatest (about 1.4 %) for Sijarinska Banja, Bujanovacka Banja and Suva Cesma, and 1.2 % for Vica spring water. The shifts, in our opinion, ought to be higher due to the temperature, but the reason they are not is the high CO_2 which reduces the shift of $\delta^{18}O$ [6]. The study of free gases in aquifers of hydrogeothermal systems is as important as the study of the origin of water containing them. Gases are formed in aquifers of a hydrogeothermal system, or are formed elsewhere and moved into the aquifers.

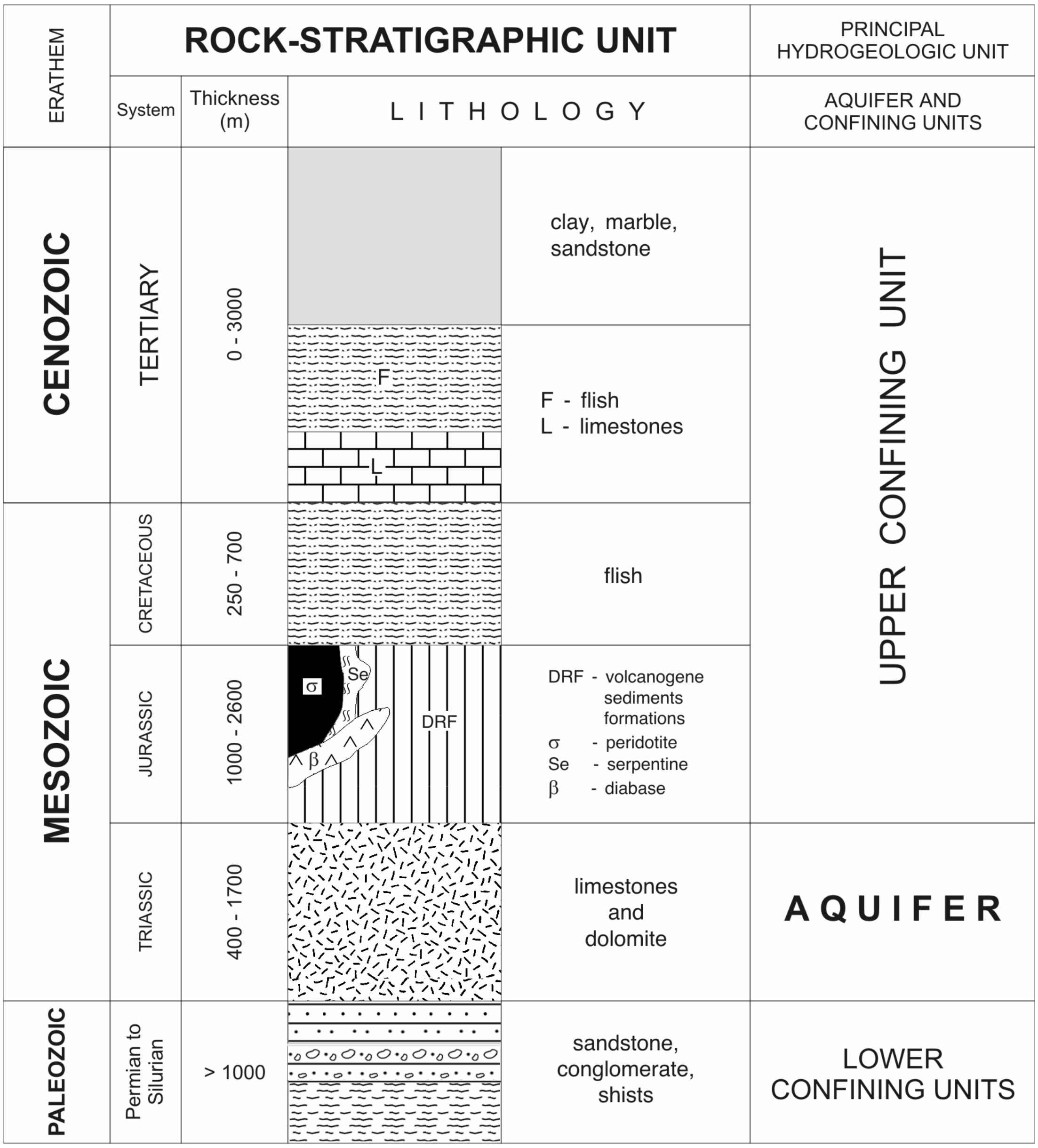

Figure 3. Lithostratigraphical column of the lower part of the Doboj sourroundings in Central Bosnia showing the position of aquifers with carbogaseous water

The origin of gas is very important, because it indicates specific chemical reactions and geothermal processes in the aquifer or the entire hydrogeothermal system. That is why data on the genesis of gases can be helpful in assessments of geothermal resources. In the given case, it is CO_2 gas, identified in all the mentioned geothermal springs in Serbia and BiH.

The main isotope for identification of CO_2 origin is ^{13}C. According to many authors, its content in free CO_2 of magmatic derivation varies from -4 to -8 %o PDB. Craig (1963) reports that about 80 % of carbon in water and free gas of Steamboat Springs and Lassen Park (U.S.A.) thermal springs contains $\delta^{13}C$ of -8 %o PDB of the likely magmatic origin. Taylor (1967) states that most of CO_2 samples analyzed in U.S.A. and New Zealand have $\delta^{13}C$ from -4.0 to -8.5 %o PDB. Endogenic CO_2 in carbogaseous springs of the Central Massif in France derives from the depth of the crust and have $\delta^{13}C$ between -6 and -7.5 ‰ PDB. Allard & Javoy (1975) analyzed CO_2 from Erta Ale volcano in Ethiopia and found average $\delta^{13}C$ of -7 ‰ PDB. The origin of CO_2 in hot geothermal springs of Italy was studied in detail by Panichi & Tongiorgi (1976), and Hulston & McCabe and Layon (1974) reported carbon isotopes in CO_2 and CH_4 of Weirakei hydrogeothermal reservoir of New Zealand. Masiouneuve & Risler (1979), on the basis of the mentioned and their data on Sabalan volcano in Iran, for CO_2 occurrences in Menderes tectonic trough of Turkey, and for occurrences of carbonated springs located in the "carbogaseous" perialpine belt of West Europe, proposed the hypothesis that a homogeneous reservoir of ascending CO_2 was in the upper mantle.

Carbon dioxide formed during the thermic decomposition of carbonate rocks has $\delta^{13}C$ higher than -4 ‰ PDB. This was stated by Craig (1963), who analyzed carbon from CO_2 in thermal springs of the Yellowstone Park. Concerning the hydrogeothermal system of Salton Sea, Muffler & White (1968) gave the interpretation that decomposition of carbonate rocks begins at a temperature of 300 ^{o}C. Isotopic content of $\delta^{13}C$ from CO_2 is from -1 to -5 ‰ PDB in Yellowstone, from -1 to -2 ‰ PDB in Monte Amiata of Italy, from -1 to -5 ‰ PDB in Larderello, -3.5 ‰ PDB in Salton Sea, and from -3.0 to -4.5 ‰ PDB in Weirakei. As $?^{13}C$ content in limestones of marine derivation is from +3 to -4 ‰ PDB [4], the above values of $\delta^{13}C$ in different hydrogeothermal high-temperature systems indicate the likely CO_2 derivation from magmatic assimilation or from geothermaly decomposed limestones. Isotope $\delta^{13}C$ contents of less than -8 ‰ PDB have been found in many hydrogeo-thermal systems and indicate the biogenic or exogenic derivation of CO_2.

Our data of $\delta^{13}C$ amounts in free CO_2 from the studied springs are given in Figure 4. It shows areas of $\delta^{13}C$ values based on the mentioned reference data which represent recognized intervals for identification of its genesis. The figure shows that $\delta^{13}C$ in free CO_2 from thermal waters of Suva Cesma at Prokuplje and Sijarinska Banja corresponds in content to $\delta^{13}C$ in free CO_2 derived from thermic decomposition of carbonate rock, i.e. marble. This suggests a large thickness of rocks with saturated marble or the depth of these rocks where temperatures are from 100 ^{o}C to 300 ^{o}C or higher. In other words, it means that marbles of Prokuplje and Suva Cesma extend to Sijarinska Banja and farther to the south, and to the east and the west. This raises the question: is CO_2 being formed in saturated or dry marbles, or, is CO_2 being formed in saturated marbles at the temperatures prevailing at present Kissin & Pakhomov (1967) consider that CO_2 can be produced by hydrolysis of carbonate rocks at temperatures higher than 100 ^{o}C. A similar opinion is shared by Panichi & Tongiorgi (1976). According to them, carbonate rocks are hydrolysed at temperatures of 100-300 ^{o}C. As the hydrogeothermometric average temperatures of water in each studied occurrence are 100 ^{o}C or higher (Suva Cesma 100-110 ^{o}C; Vica 110 ^{o}C; Kursumlijska Banja >120 ^{o}C; Sijarinska Banja 120-130 ^{o}C; Tulare 100 ^{o}C; Vranjska Banja 120-130 ^{o}C; and Bujanovacka Banja 125-135 ^{o}C), it may be inferred that the temperature condition has been fulfilled and that CO_2 is formed in saturated marbles throughout its extent. The evidence of the continuous production of CO_2 in marble is its abundant steady flow at the mentioned springs, and the concomitant effects. Large amounts of CO_2 in thermomineral waters indicate its thermogenic hydrolytic derivation.

The values of $\delta^{13}C$ from CO_2 of Kursumlijska Banja, Vranjska Banja and Bujanovacka Banja springs are in the boundary area of magmatic $\delta^{13}C$ from geothermally decomposed and hydrolysed carbonate rocks (Figure 3), which at the first glance suggests a mixture of CO_2 of different derivations. However, the local geology and statements by the mentioned authors gave grounds for the assumption of the thermic-hydrolytic decomposition of marbles and production of CO_2.

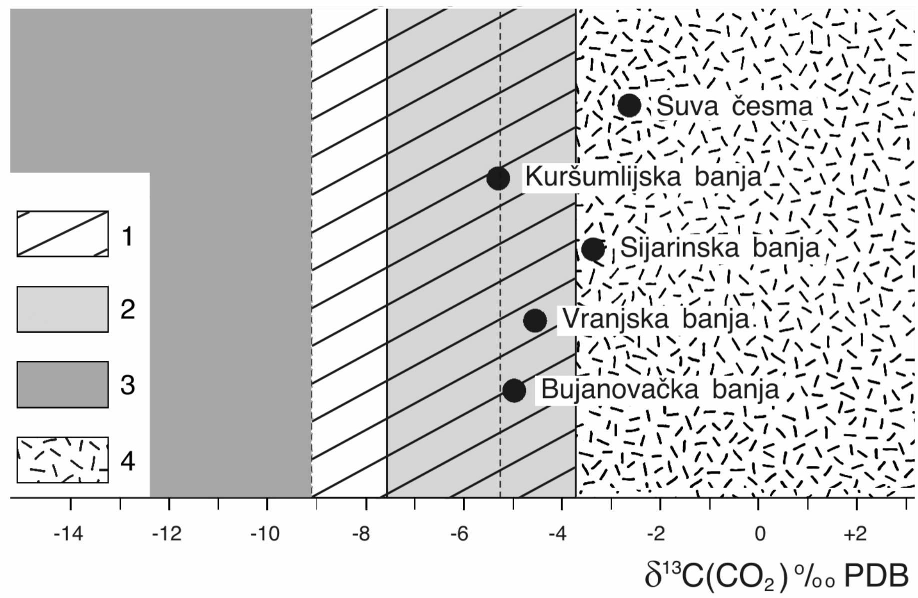

Figure 4 Isotope $\delta^{13}C$ content and genesis of free CO_2 in water of the studied thermomineral springs (Milivojevic, 1989)
(1-Endogenic-magmatic CO_2 (Fournier et al., 1891; 2-Endogenic-magmatic CO_2 (Blavoux et al., 1982; 3-organic and sedimentary CO_2; 4-CO_2 produced by geothermally decomposed and hydrolyzed carbonate rocks)

The geological structure and the geothermal features of the terrain, the chemical and isotopic composition of the springs with carbonic-acid geothermal waters in Central Bosnia [16], indicate with great certainty that the high content of carbon dioxide is the result of thermolysis, which decomposed the Triassic limestone that lays at great depths (2-4 km), Figure 3. These limestone formations represent the geothermal reservoir of the large hydrogeothermal system that belongs to Inner Dinaric Formations. This reservoir occupies the area of approximately 20,000 km^2 and the temperature of its geothermal water amounts to 160 ^oC [15]. The hydro-geothermal system that belongs to Dinaric Formations is situated in the southern periphery of Pannoni Basin. This system extends from Belgrade at the east to Sisak at the west and from River Sava at the north to the cities of Banja Luka and Sarajevo at the south.

5. CONCLUSION

The analysis of $\delta^{13}C$ in free CO_2 gas contained in geothermal springs of the southern part of Serbian-Macedonian Massif gave the first exact information on the aquifer extent and the metamorphic complex of this geotectonic unit. The aquifer contains fractured gneisses, marbles and quartzites covering an area of about 1700 km^2. Its depth is undefined, but hydrogeothermometers and the geothermal character suggest a depth greater than 2000 metres.

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