ISOTOPIC ANALYSIS OF GROUNDWATER AND CARBONATE SYSTEM IN THE SURDULICA GEOTHERMAL AQUIFER[1]

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ABSTRACT. We present here results of our investigation of the isotopic chemical composition of groundwater and carbonates in the Surdulica geothermal aquifer, Serbia. We considered the effects of carbonate dissolution and measured ^{13}C, ^{14}C, D, ^{18}O, ^{3}H, field pH, temperature, Na^+, Ca^{2+}, Mg^{2+}, HCO_3^- and other aqueous species from 30 springs and boreholes. Geothermal waters are supersaturated with calcite. Carbon isotope compositions vary with carbonate mineral dissolution. The δD and $\delta^{18}O$ of groundwater samples fit the meteoric water line, and indicate that groundwater is recharged mainly from higher altitudes and the cold season. Different groundwater residence times point out two mechanisms for their formation: fissure flow for young waters and standard diffusion processes for old ones.

INTRODUCTION

The Surdulica geothermal system is a major segment of the Serbia-Macedonian massif. The ~250 km^2 area is a potential source of geothermal energy and drinking water (~250 liter s^{-1}, 45–126°C). The largest hot springs are concentrated near the Bujanovac and Vranjska Spas (*ca.* 30 springs); this group of springs, which seems to discharge at locations of the main aquifer system reaching *ca.* 3000 m deep, has not yet been described. Also, relations between groundwater flow patterns and the physical structure of the aquifer have been poorly understood. Deep drilling has been limited to a few exploratory boreholes (up to 2000 m). Faults, particularly along the periphery of the South Morava valley, appear to be significant factors controlling the discharge from many of the parts of the Surdulica-Vranje-Bujanovac area. Several researchers have investigated geophysical and hydrological conditions (Žujović 1893; Dimitrijević *et al.* 1965; Babović *et al.* 1970; Anderson 1985; Popović 1990). Since 1986, we (Milovanović *et al.* 1989) have investigated the isotopic chemistry of the aquifer carbonate and groundwater circulation systems, range of residence times and the origin of the geothermal water. This study surveys carbon isotopic compositions of the system and groundwater ^{14}C ages and variations, and attempts to understand the processes upon which the isotopic values and their spatial distributions are based.

BASIC CHARACTERISTICS OF THE SURDULICA AQUIFER

The Vranje-Surdulica geothermal system is a narrow catchment area of the South Morava valley between Grdelica and Bujanovac (Fig. 1) in the Besna Kobila, Kukavica and Kozjak Mountains. The system is situated mostly in the Morava massif, consisting of Paleozoic gneiss, mica schists, amphibolites and greenstone (metagabbros, metadiabases, calc-schists, quartz and other chlorite schists) complexes. The Tertiary Surdulica system contains granitoids and dacite-andesite volcanics.

A large amount of CO$_2$ was introduced to the system during Tertiary magmatism, which could explain the strong carbonization of older rocks. This is apparent in metamorphic rocks from Boreholes 10 and 10.1 (drilled to 1603 m). Abundant sulfates in thermal waters (2–5 mmol liter^{-1}) and little sulfide suggest an anaerobic environment; thus, anaerobic decay with sulfate reduction

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[1] This paper was presented at the 14th International ^{14}C Conference, 20–24 May 1991, Tucson, Arizona.
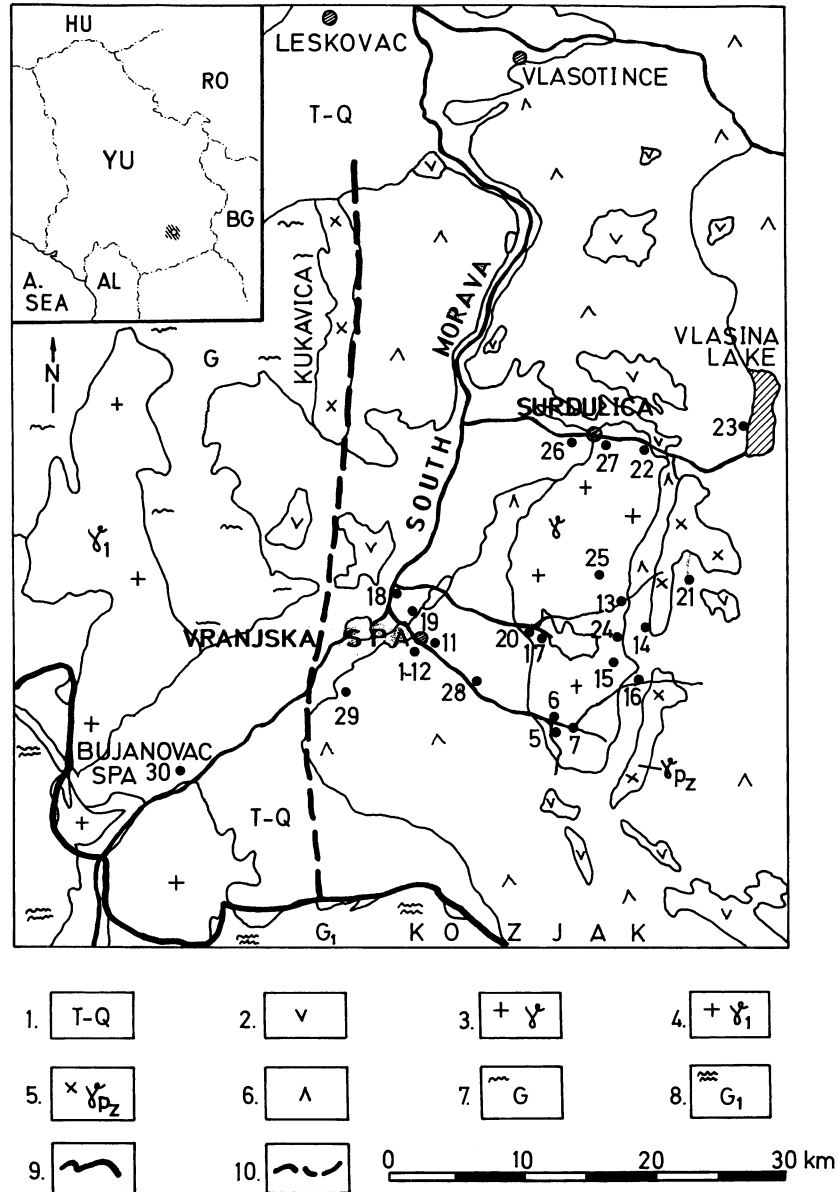[2] Geoinstitute, Rovinjska 12, 11000 Belgrade, Yugoslavia

Fig. 1. Geological map of the study area with sampling points: 1. Tertiary and Quaternary sediments; 2. Tertiary volcanic rocks; 3. Surdulica granitoid; 4. Bujanovac granitoid; 5. Kukavica granitoid; 6. green complex; 7. gneiss and mica schist (Morava massif); 8. gneiss (Pelagonia-Rhodope massif); 9. contact of these two massifs; 10. contact of gneiss and the green complex in the Morava massif

as a source of HCO_3^- can be ignored. However, the possibility that some modern CO_2 in thermo-mineral waters of this system has a mantle origin should not be excluded.

The study region lies between moderate continental and Mediterranean climates, with mean annual air temperature around 10.5°C. Runoff from Besna Kobila (1923 m asl) drains into the Aegean and Black Seas. The average annual precipitation ranges from 915 mm in the high areas to 655 mm

in the lower elevations, where most of the precipitation occurs from October to March. Stream flow is also highest during these months.

The system discharges to wells and springs about 150 liter s^{-1} of cold and nearly 100 liter s^{-1} of thermal waters (45–126°C). Relatively impermeable layers in the divided aquifer formation direct the subsurface flow to large springs (up to 80 liter s^{-1}), which discharge along many faults. The configuration and geological structure of the aquifer and D, ^{18}O, ^{13}C, ^{14}C isotopic data indicate that the Besna Kobila Mountain is a major recharge area. Natural thermal springs appear along the foothills of a schist massif at about 400 m asl, mostly near the Vranjska and the Bujanovac Spas.

The regional geothermal gradient is 1°C/25 m (Anderson 1985) with a local high gradient of up to 1°C/8 m. A plot of temperature *vs.* depth (Fig. 2) shows that even higher temperatures are found at some loci (here 2, 3, 4, 10). From this gradient, the maximal depth of circulation is *ca.* 2500 m. We also estimated the depth from which hot water discharges, based on silica and cation-ratio geothermometers (Henley *et al.* 1985), and concluded that two temperature regimes exist: for the Bujanovac Spa (sampling point 30, Table 1), with <700 m and temperature of 100°C, and for the Vranjska Spa, with up to 4000 m depth and temperature up to 200°C.
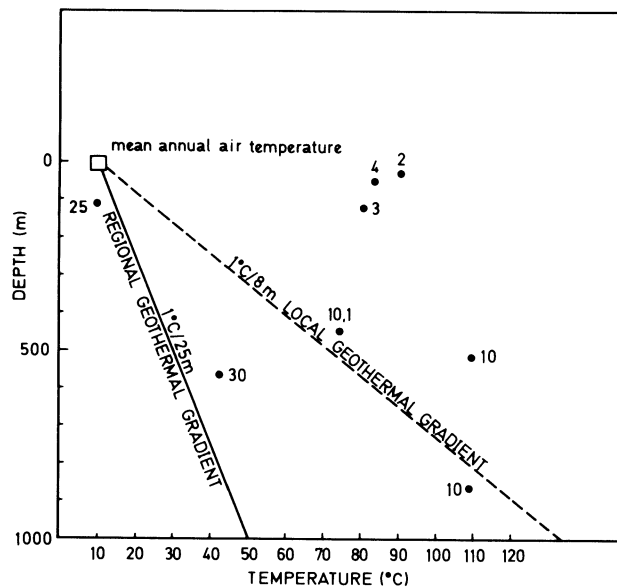

Fig. 2. Relation of water temperature to depth of discharge (all points represent boreholes, see Table 1)

SAMPLING AND ANALYSES

From 1986 to 1990, we measured ^{13}C, ^{14}C, ^{3}H, D and ^{18}O of groundwater, CO_2 gas and rocks at 30 sites. To define modern isotope input parameters, we collected samples from soil CO_2 and vegetation, and determined pH values, alkalinity and major ion chemistry in water samples.

We analyzed the ^{13}C and ^{18}O content in the CO_2 gas prepared from samples according to IAEA (1980), using a Micromass 602 mass spectrometer. We obtained deuterium data by reducing water with zinc at 460°C (Coleman *et al.* 1982). We report stable isotope data in δ values (‰) related to the V-SMOW standard for D, ^{18}O and for $δ^{13}C$ to PDB with 1 σ error of 2, 0.2 and 0.4‰, respectively. The $δ^{13}C$ value refers to the total dissolved carbon (TDC).

TABLE 1. Chemical Analyses of Waters from the Surdulica Aquifer (concentrations in mmol liter^{-1} unless otherwise indicated)

Sample	Sampling point	Collection date	Alt* (m)	Temp. °C	pH	Na⁺	K⁺	Ca²⁺	Mg²⁺	Sr²⁺	Mn²⁺	Zn²⁺	HCO₃⁻	CO₃	SO₄²⁻	F⁻	Cl⁻	SiO₂ (mg/liter)
Freshwater																		
Spring	14	10/20/86	1475	8.0	7.7	0.25	0.02	0.44	0.2	0.02	0.02	0.01	0.8		0.05	0.01	0.10	3
Capt. spring**	21	10/10/86	1300	7.5	7.5	0.15	0.01	0.45	0.3	0.02	0.01	0.01	1.0		0.05		0.05	5
Fountain	22	07/14/88	912	13.1	7.7	0.23	0.02	0.60	0.3	0.02	0.02	0.01	1.3		0.10		0.10	3
Capt. spring	5	07/12/88	700	17.6	6.8	0.24	0.05	0.60	0.4	0.01			1.2		0.10	0.01	0.05	9
River	6	12/28/88	687	4.4	7.3	0.13	0.02	0.60	0.2	0.01	0.01		1.0		0.10		0.10	5
River	28	10/01/87	430	6.3	7.6	0.46	0.05	0.74	0.4	0.02	0.01		1.4		0.20		0.20	
Transition and low-temperature thermal water																		
Mine water, d†=600	16	06/18/86	1310	11.2	7.3	0.20	0.01	0.30	0.2		0.01	0.01	0.5		0.10	0.02	0.10	7
B‡, d=112	25	07/12/88	1354	10.6	7.3	0.19	0.01	0.40	0.1		0.01	0.01	1.2		0.10	0.05	0.10	10
Tunnel, d=300	27	09/14/88	693	20.5	7.6	0.90	0.10	1.20	0.7	0.02	0.01		1.8		0.80	0.20	0.10	20
Capt. thermal spring	29	06/05/86	393	23.0	8.4	12.10	0.10	0.10	0.1			0.005	10.6	0.58	0.60	0.07	0.50	22
Capt. thermal spring	29	05/25/89	393	22.8	8.4	11.80	0.10	0.10	0.1				10.2	0.39	0.60	0.10	0.70	15
Capt. thermal spring	9	06/18/86	430	17.1	7.0	5.60	0.20	1.20	0.1				5.3		0.90	0.10	1.10	14
Capt. thermal spring	8	05/25/89	415	16.8	7.5	7.70	0.50	0.80	0.5				5.3		3.10	0.10	1.50	25
Hot thermal water																		
Capt. thermal spring	1	05/05/86	425	78.2	7.6	12.50	0.30	0.40	0.2				7.2		4.00	0.60	1.40	42
B, d=120	3	05/06/86	294	80.5	7.5	11.50	0.20	0.70	0.1				6.4		4.20	0.60	1.50	90
B, d=520	10	01/25/88	-105	79.4	8.2	13.50	0.30	0.50	0.4				9.8		3.20	0.20	1.50	39
B, d=1063	10	04/14/88	-648	111§	8.3	10.70	0.60	0.40	0.2				8.0		3.00	0.20	1.30	30
B, d=450	10.1	05/25/89	-33	67	7.5	12.80	0.40	0.30	0.2				8.1		3.10	0.50	1.70	88
B, d=535	30	07/12/88	-125	43	7.1	58.90	1.60	1.20	0.5	0.02			58.7		2.00		1.60	41
B, d=535	30	05/26/89	-125	42.2	7.1	57.30	1.50	1.02	0.6	0.02			56.5	0.38	1.70	0.13	1.70	51

*Alt = altitude of water horizon

**Capt. = captured

†d = depth (m)

‡B = borehole

§ = measured temperature at 1063 m depth = 126°C, flow = 27 liter s^{-1}

We measured ^{14}C activities using a Packard 3380 liquid scintillation spectrometer or gas proportional counting system (Srdoč, Breyer & Sliepčević 1971). ^{14}C values are expressed in percent modern carbon (pMC), with a measurement error of ± 3–25% (for hot waters); we measured tritium activity after electrolytic enrichment (Hut 1986).

RESULTS AND DISCUSSION

Water Chemistry and Isotopic Composition of Groundwater

Surdulica groundwaters are of $Na(Ca)-HCO_3(SO_4)$ type, with pH values ranging from 7.0–8.4 (Table 1). The partial pressure of CO_2 is within $10^{-0.3}$ to $10^{-2.9}$ atm (Table 2) and increases downgradient from cold to geothermal water (GTW). The cold springs and most low-temperature thermal waters are unsaturated with calcite. Ionic concentrations (especially those of Na^+, HCO_3^- and SO_4^{2-}) and groundwater temperature increase with depth. This is associated with considerable carbonization and pyritization of older rocks.

A plot of δD *vs.* $δ^{18}O$ of groundwater samples fits a local meteoric water line of δD = (7.3 ± 0.2) $δ^{18}O$ + (7 ± 2). Similarity between isotopic content of precipitation and GTW demonstrate their

TABLE 2. Isotopic Analyses and Chemical Data of Studied Waters

Sample	Sampling point	Log P_{CO_2}* (atm)	SI_c**	$δ^{13}C_{PDB}$ (‰)	^{14}C (pMC)	^3H (TU)	^3H, TU interval[†]
Freshwater							
Spring	14	−2.9	−1.0	−13.0	72	59	55–65
Capt. spring	21	−2.8	−1.2	−12.9	90	58	32–69
Fountain	22	−2.9	−0.7	−13.5	67	37	28–46
Capt. spring	5	−1.9	−1.0	−13.4	71.1	19	17–37
Capt. spring	5	−2.3	−1.4	−16.3	94.1	23	17–37
Capt. spring	11	−2.8	−0.2	−10.2	61.3	18	15–35
Transition and low-temperature thermal water							
Mine water	16	−2.9	−1.8	−12.7	39.7	14	11–45
B[‡], d[§] = 212	25	−2.5	−1.3	−10.7	38.7	38	38
Tunnel water	27	−2.7	0.1	−13.8		7	7
Thermal spring	29	−2.7	0.6	−7.8	26.9	12	5–18
Thermal spring	29	−2.5	0.5	−8.2	21.1	5	5–18
Thermal spring	9	−1.9	−0.1	−12.2	77.5	13	4.5–16
Thermal spring	8	−2.0	−0.1	−3.1	16.4	<2	
Hot thermal water							
Thermal spring	1	−1.7	0.9	−6.6	4.5	<2	
B, d = 120	3	−1.7	1.0	−3.7	6.0	<1	
B, CO_2 gas	3			−4.5			
B, d = 520	10	−2.2	1.8	−4.8	5.3	<0.9	
B, d = 867	10	−2.5	2.4	−1.8	5.4	<1.4	
B, d = 450	10.1	−1.6	0.9	−2.4	4.8	<3	
B, d = 535	30	−0.3	1.3	−0.9	3.3	<1	
B, d = 535	30	−0.4	1.2	−0.4	6.9	<2	

*Log P_{CO_2} = log $\dfrac{[H_2CO_3]}{K_{CO_2}}$; **$SI_c$ = log $\dfrac{\text{ion activity product}}{\text{equilibrium constant}}$

[†]Study period – 1986–1990; [‡]B = borehole; [§]d = depth (m)

meteoric origin. Distribution and seasonal variations of D and ^{18}O isotopes in the water indicate that GTW have been recharged predominantly from higher elevations (>500 m asl) and during colder seasons.

All of the water samples, except for a few old geothermal samples, contain tritium from 5 to 59 tritium units (TU; 1 TU = 0.118 Bq l^{-1}) (Table 2); this large interval is a result of different drainage rates throughout the system due to variable rock porosities. In rivers and shallow groundwater (freshwater, Table 2), ^{14}C concentrations are between 61.3 and 94.1 pMC, whereas $\delta^{13}C$ values range from –16.3 to –10.2‰ (Table 2). Transition- and low-temperature thermal water from deeper portions of the aquifer have lower ^{14}C (16.4–77.5 pMC) and higher ^{13}C (–13.8 to –3.1‰). The samples from hot thermal springs and boreholes had the lowest ^{14}C (3.3–6.9 pMC) and the highest $\delta^{13}C$ values (–6.6 to –0.4‰). The $\delta^{13}C$ value of the CO_2 gas analyzed from Borehole 3 is –4.5‰. The ^{13}C content of core samples from Boreholes 10, 10.1 and 26 (–8.4 to –1.1‰) are very similar to those in GTW from deep circulations. Samples taken from marble rocks ranged from $\delta^{13}C$ = +0.41 to +2.7‰.

Isotopic composition of dissolved carbonates formed during water interaction with rock matrix is plotted *vs.* the calcite saturation (Fig. 3). P_{CO_2} and $\delta^{13}C$ generally increase with calcite saturation, while ^{14}C decreases. To determine conditions of calcite mineral dissolution, we calculated the relation between HCO_3^- and ^{13}C content of water for systems open and closed to a CO_2 gas reservoir (Fig. 4). Under open-system conditions (Fig. 4A), cold waters gather between calcite saturation curves corresponding to initial values of ^{13}C content of soil gas, $\delta^{13}C_s$ = –24 to –20‰ at initial pH values, pH_i = 5–6. The isotopic composition of GTW is out of this range. This could be explained by significant dissolution of rocks and isotopic exchange between carbonate species in the aquifer. In Figure 4, we give the saturation curves for the supposed systems, assuming their initial parameters, $\delta^{13}C_s$ = –13‰ (mean value for freshwater), –8‰ (low thermal water, point 29) and pH_i = 5–7. Similar analysis derived for closed-system conditions (Fig. 4B) shows that cold groundwater recharge should have pH_i = 5–6 and $\delta^{13}C_s$ = –27 to –24‰, and P_{CO_2}s may range from $10^{-1.5}$ to $10^{-2.5}$. The ^{13}C content of the dissolved carbonate from rocks, $\delta^{13}C_r$, could be between –3.4‰ (mean for Borehole 10, Table 3) and +1.4 (mean for marble). Taking into account $\delta^{13}C_s$ = –13 and –8‰, and pH_i = 5–6, as initial parameters, we show that most measured ^{13}C values for warm waters are still out of the range of the saturation curves. These values are greater than for open-system conditions.

Age of Groundwater

As shown in Table 2, freshwaters contain considerable tritium, and to a certain degree, reduced concentration of ^{14}C. Thus, for an estimate of mean residence time (MRT), we used the finite-state, mixing-cells model (Yurtsever 1983). For most samples, this model gives 2 or 3 solutions for MRT and an adjustment factor Q (a parameter for non-decay ^{14}C loss induced by chemical interaction with carbonate rock). There may be two reasons for this: 1) the sampling was performed at the end of tritium-response curves of the groundwater system (1986–1990); 2) water takes fast and slow paths through the system. The analyzed water is a mixture of these two components. This assumption is validated by the fact that most of the studied waters cluster around Q = 0.7–0.75, which corresponds to a MRT of 100–700 yr (Table 4). On the other hand, tritium was detected in the same samples, which leads to 10–80-yr-old water, *i.e.*, young water. If waters with two very different MRTs exist simultaneously, we must assume two different mechanisms for their formation. In the case of fast water, it passes through fissures that conform to the geological structure of the aquifer, whereas a standard diffusion process is responsible for old water. We estimate the MRT at less than 80 yr for the fissured process and to 200–500 yr for the older waters. Isotopic
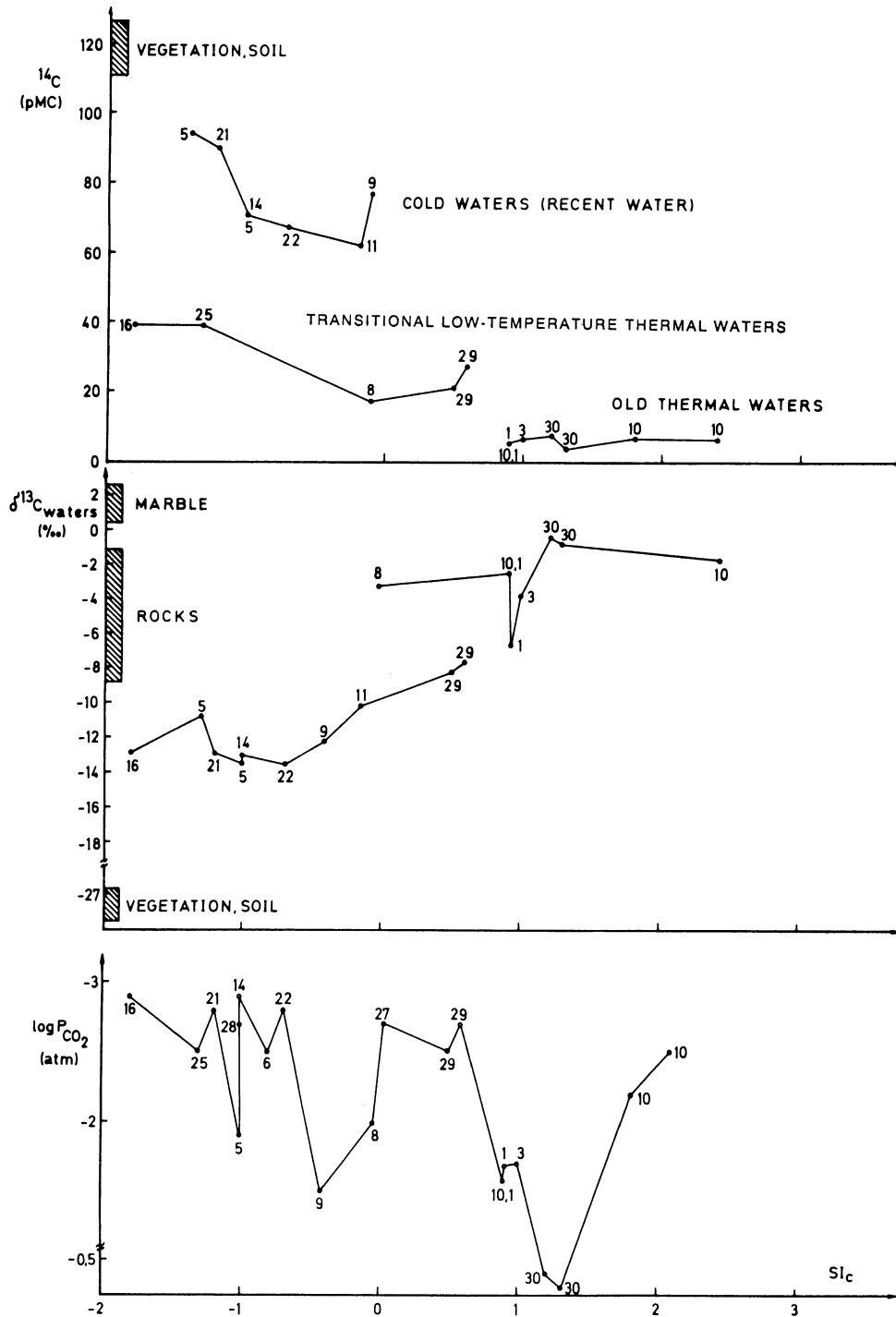
Fig. 3. Dependence of water ^{14}C, ^{13}C and P_{CO_2} on the saturation index of calcite

TABLE 3. $\delta^{13}C$ Data for Soil, Vegetation and Cores

Sample	Alt. (m asl)	Sampling point	Collection date	$\delta^{13}C$ (‰)	Description
Plant	700–1340	5–7, 20, 23	06/14/88 05/15/90	−28.5 −27.6	Beech, oak evergreen, broadleaf, grass
Soil	700–1340	5–7, 20, 23	06/14/88	−27.3	30 cm depth with roots
Peat	1200	23	06/14/88	−26.7	Outcrop
			Depth (m)		
Borehole	415	10	104–110 438–447 997–999	−3.4 −4.0 −2.9	Granodiorite* with pyrite encrustation
Borehole	417	10.1	423–425 435–446 447–450	−4.7 −1.3 −1.1	Amphibolite schist
Borehole	895	26	145–146 275–284 354–355 374–375	−5.7 −8.4 −4.9 −6.6	Silicified granodiorite with pyrite encrustation
Marble mine	1300	21		+0.4 +2.7 +1.1	Light sample Dark sample Random sample

*Undisturbed core samples from borehole

TABLE 4. Calculated Mean Residence Times (yr) of Surdulica Groundwaters Using A Finite-State Mixing-Cells Model

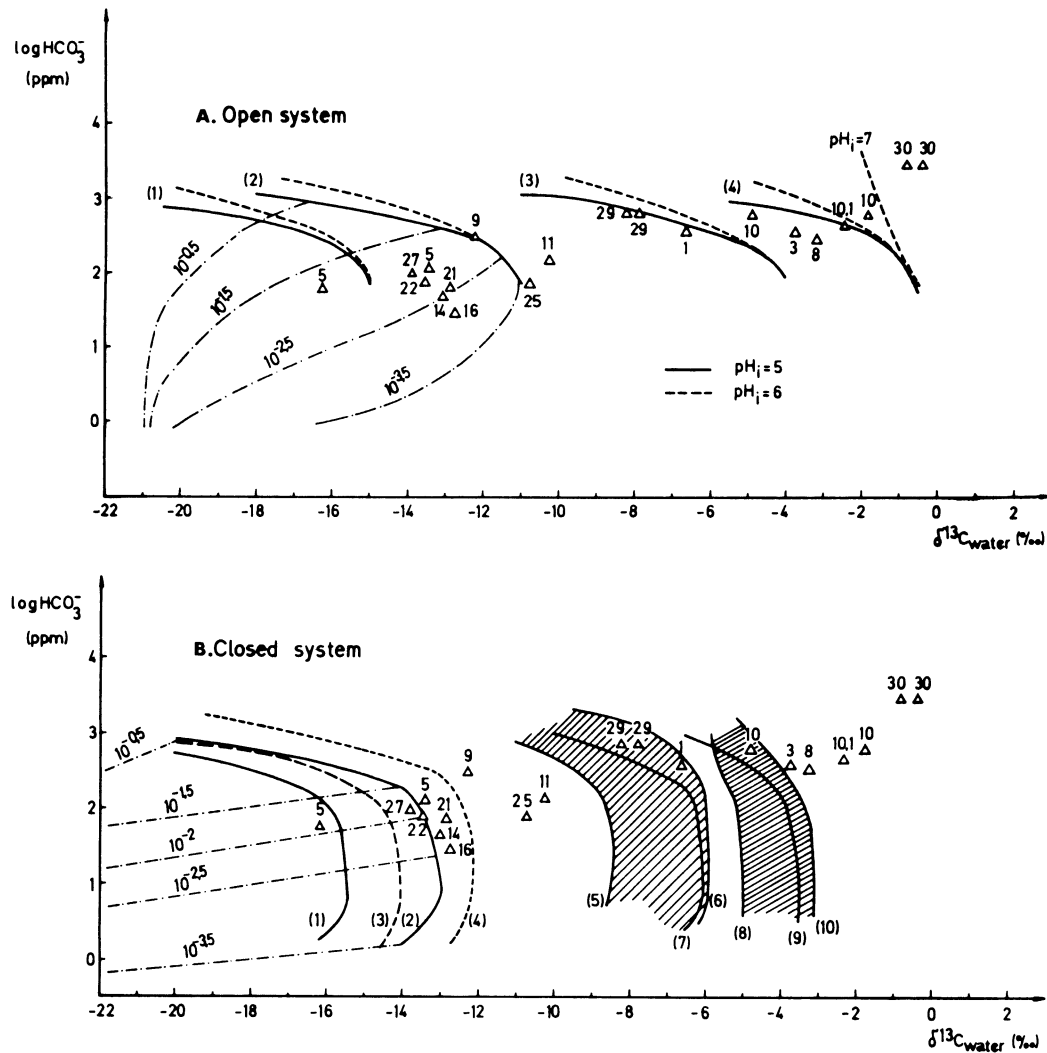| Sample | Q (Adjustment parameter for non-decay ^{14}C loss or dilution in the aquifer) | | | | | | | | ^3H components | |
	0.55	0.60	0.65	0.70	0.75	0.80	0.85	0.90	fast	slow
14	1–15	30–45	60–95	150–250	330–550	700–1000			10–25	
21				7–20	30–40	57–76	100–150	200–600	1–20	25–75
22	1–35	58–87	130–220	350–560	750–990				1–10	35–85
5	7–20	35–50	70–100	160–270	400–640	800–1000			1–10	50–150
5					5–30	40–50	65–90	100–350	1–10	50–150
11	0–95	150–270	420–720	900–1000					1–5	60–180
9		0–25	35–50	70–100	140–250	330–520	670–1000		<2	160–660
16										180–260
25										
29										150–700
29										150–700

Fig. 4. Relation between $\delta^{13}C$ and HCO_3^- for open and closed systems for various initial conditions (10, 30°C).
A. Open-system solution paths:
   (1) $\delta^{13}C_s = -24$; (2) $\delta^{13}C_s = -20‰$; (3) $\delta^{13}C_s = -13‰$; (4) $\delta^{13}C_s = -8‰$
B. Closed-system solution paths:
   (1) $\delta^{13}C_s = -27‰$, $\delta^{13}C_r = -3.4‰$, $pH_i = 5$; (2) $\delta^{13}C_s = -27‰$, $\delta^{13}C_r = +1.4‰$, $pH_i = 5$; (3) $\delta^{13}C_s = -24‰$, $\delta^{13}C_r = -3.4‰$,
   $pH_i = 5$; (4) $\delta^{13}C_s = -24‰$, $\delta^{13}C_r = +1.4‰$, $pH_i = 6$; (5) $\delta^{13}C_s = -13‰$, $\delta^{13}C_r = -3.4‰$, $pH_i=5$; 6) $\delta^{13}C_s=-13‰$, $\delta^{13}C_r$
   $= +1.4‰$, $pH_i = 5$; (7) $\delta^{13}C_s = -13‰$, $\delta^{13}C_r = +1.4‰$, $pH_i = 6$; (8) $\delta^{13}C_s = -8‰$, $\delta^{13}C_r = -3.4‰$, $pH_i = 6$; (9) $\delta^{13}C_s =$
   $-8‰$, $\delta^{13}C_r = +1.4‰$, $pH_i = 5$; (10) $\delta^{13}C_s = -8‰$, $\delta^{13}C_r = +1.4‰$, $pH_i = 6$. Subscripts, s and r, stand for soil and rock,
   respectively. - - - - = calcite saturation curves; —··— = calcite solution paths for various P_{CO_2} atm, $\triangle$ sample.

analyses indicate a complex carbon origin (biogenic CO_2 from the soil zone, carbonate species from carbonate mineral dissolution, CO_2 from the mantle); now, the question of age for these waters is open. Tritium-free waters suggest ages older than 100 yr. The low ^{14}C content (*ca.* 5 pMC) would infer waters *ca.* 20,000 yr old (hydrochemical age, Fontes 1979). Measured TDIC $\delta^{13}C$, > −6.6‰, indicates dilution by carbon of unknown origin. Other models (Fontes 1979) give unrealistic, even negative ages, and are not applicable to the Surdulica system. We believe that these waters are considerably younger than 20,000 yr because of high bicarbonate concentrations (up to 60 mmol

liter^{-1}) in the basin, which cannot be explained only by calcite and dolomite dissolution (m_{Ca} + m_{Mg} = 0.5–1.5 mmol liter^{-1}).

CONCLUSION

Geothermal waters are of meteoric origin, formed in recharge areas at higher elevations and during colder seasons. The results of tritium and ^{14}C measurements indicate fast (fissure) and slow (intergranular) flow paths through the system. Water composition is characterized by bicarbonate sodium (calcium) sulfates. The concentration of the main cations, anions and silica increases by a factor of almost ten, descending from the recharge area to the deep waters. Calcite saturation increases with depth, and GTWs are almost supersaturated.

It appears that cold water recharges under closed-system conditions, with initial parameters, $\delta^{13}C_s$ = –27+3‰, pH$_i$ = 5–6, reaching a value of –13‰ for $\delta^{13}C_s$ at the discharge. The concentrations of ^{13}C in GTW are significantly higher (up to 0‰), which indicate processes of intensive interaction between water and rocks, isotopic exchange, and a possible interior CO_2 source. The MRT for mixed waters calculated by finite-state mixing models is less than 80 yr for the fast component, and 200–500 yr for the older one. The age of geothermal waters based on isotopic analyses ranged from 100 to 20,000 yr.

ACKNOWLEDGMENTS

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