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The Acidulated Water of Kiseljak in Bosnia. A Geochemical Study

S. Miholić

*Institute of Balneology and Climatology of the Yugoslav Academy of Sciences
and Arts, Zagreb, Croatia, Yugoslavia*

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Along a fault that stretches NW of Sarajevo a number of mineral waters is situated one of which, the spring at Kiseljak, has been investigated in detail. Its heavy metal content, with tin predominating, points to a Variscan metallization. Its radioactivity, very low as expected theoretically, originates from Triassic strata. All results tally very well with the results obtained by investigations of other mineral springs in the region.

The region NW of Sarajevo is dissected by two systems of faults of which only the fault of Busovača interest us here and along which the strata to the SW have been uplifted in the Quaternary and form now the Vranica mountain. Along this fault a number of mineral waters issue (Ilidža, Blažuj, Kiseljak, Bjelalovac, Fojnica, Klokoti and Busovača). The fault itself, however, is very old and goes back to at least the Late Paleozoic (Carboniferous) judging from the prevalence of tin among the heavy metals contained in the mineral waters¹. The axis of the Vranica mountain is arched and has a culmination point at Bijela Gromila (2071 m). Therefore all along the fault the mountainous country shows towards the NW older and older strata, Middle and Late Triassic near Ilidža, Early Triassic near Kiseljak and Kreševo, and Late Paleozoic (Carboniferous and Permian) near Fojnica. The Paleozoic continues till Jajce where it again disappears under the Triassic.

As has been said, the mineral waters along the fault contain tin as the most characteristic heavy metal (Ilidža, 0.0217 p. p. m., Kiseljak 0.04355 p. p. m.). Moreover I. Jurković² found cassiterite near Klisac S of Fojnica. This would all point to a Variscan mineralization of the fault.

If the heavy metals point to conditions prevailing in the deeper underground, radioactivity shows the character of the strata nearer the surface. Given the short half-life of radon, the radioactivity of a water depends primarily on the subsurface formations. Here a remarkable fact has been observed. As pointed out by Table I only waters issuing from carboniferous sediments show a higher radioactivity, while those from Triassic and Oligocene are very low in it. It has already been shown that bituminous deposits belonging to particular geologic formations (Late Precambrian, Carboniferous and Cretaceous) are richer in uranium and that this is probably due to its accumulation by organisms that flourished in those periods³.

TABLE I

	Geologic formation of subsurface strata	Temperature °C	pH	Radioactivity	
				Mache-units	m μ C/1
Ilidža	Triassic	55.3	8	0.6249	0.2269
Kiseljak	Triassic	12.2	8	0.278	0.101
Fojnica	Carboniferous	30.4	7	9.281	3.378
Klokoti (gas)	Carboniferous	17.8	6	10.26	3.74
Busovača	Oligocene	12.8	9	0.6702	0.2497

Besides, we find in Fojnica a very good example of secondary enrichment of uranium in the calcareous sinter deposited by the water. Here the uranium has been precipitated with the iron. A proportional increase of radioactivity of the water on its course through the sinter from 10.26 to 48.96 Mache units takes place, as has been shown elsewhere⁴.

The spring at Kiseljak is an acidulated water, known as such already in the XVIIth century and the most important of its kind in Bosnia. The question therefore arises as to the source of its carbon dioxide. There are several possibilities: 1st, the carbon dioxide is juvenile and comes from a great depth; 2nd, the carbon dioxide is derived from carbonates either by the reaction $\text{CaCO}_3 + \text{SiO}_2 = \text{CaSiO}_3 + \text{CO}_2$ which starts in the katazone at temperatures above 500°C, corresponding to a depth of about 1500 meters, and yields wollastonite, or by the similar reaction $2\text{CaMg}(\text{CO}_3)_2 + \text{SiO}_2 = \text{Mg}_2\text{SiO}_4 + 2\text{CaSO}_3 + 2\text{CO}_2$ which yields forsterite⁵. Or else the carbon dioxide is liberated nearer the surface from carbonates by sulphuric acid derived from the oxidation of pyrite which on oxidation yields ferrosulphate and sulphuric acid and 3rd through the decay of organic matter.

Up to a few years ago we had no means to determine which of those three modes is the source of the carbon dioxide of a particular spring. Now a study of the isotopic composition of the involved carbon could tell us its origin. Of the two stable carbon isotopes ¹²C and ¹³C living organisms prefer the lighter isotope and deposit the heavier isotope in their shells and bones. Therefore the juvenile carbon dioxide shows a medium ratio ¹²C/¹³C of 90 - 91, the carbon dioxide derived from carbonates a lower ratio of 88 - 89, and the one from decaying organic matter a higher of 92 - 93⁶. It has not yet been possible to determine the ratios of the carbon isotopes for the carbon dioxide from the mineral water in Kiseljak for lack of the necessary equipment, but the possibility now exists to determine the way it has been formed.

The spring lies in a well wooded hilly country in the valley of the Lepe-nica river at a latitude of 43°56'41" N and a longitude of 18°4'39" W. Its altitude is 476 m. (Cf. the Ordnance Survey map, Scale 1 : 75,000 [1.18 miles to the inch], Sheet No. 6460). The water flows from an artesian well 27 meters deep and rises 2.15 meters above the floor. The yield is 1 liter per second. A wooden structure protects the well.

EXPERIMENTAL

The investigations were made on August 19, 1954. The temperature of the water was 12.2°C, its reaction pH = 8, it contained 1.918 gram of free carbon dioxide per liter and showed a radioactivity of 0.278 Mache units = 0.101 $\mu\text{C}/\text{l}$.

The water is clear, gets slightly turbid after 1-2 hours, is odourless and colourless with a slightly saline and acid taste.

The heavy metals were determined polarographically as follows:

Determination of copper and lead. The polarograph* was calibrated with a standard containing 1 mg of Cu and 1 mg of Pb in 10 ccm a 0.3 M solution of potassium-sodium tartrate. With the sensitivity of the apparatus of 11 a step of 31.7 mm was obtained at - 0.21 V for Cu, and one of 25.9 mm at - 0.67 V for Pb. With the sensitivity of 13 the step for Cu was 21.1 mm and 13.5 mm for Pb. The sample was polarographed under the same conditions and gave with the sensitivity of 11 a 59.9 mm step for Cu and a 5.8 mm step for Pb corresponding to 1.577 mg

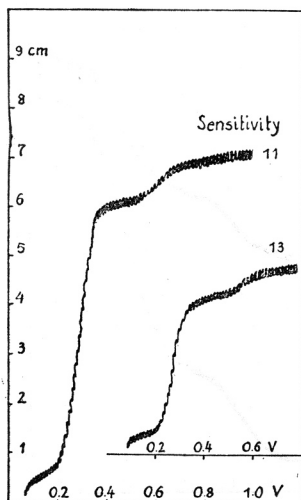


Fig. 1.

Fig. 1. Determination of copper and lead.

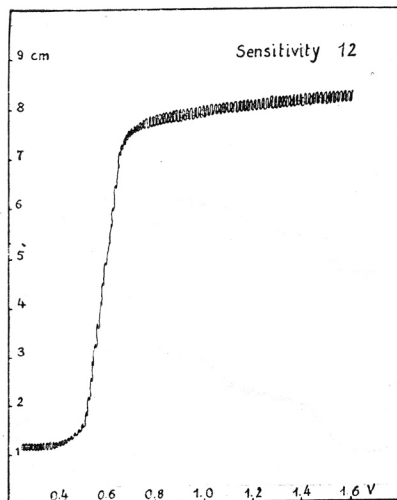


Fig. 2.

Fig. 2. Determination of tin.

of Cu and 0.2239 mg of Pb in 40155.5 g of water. With the sensitivity 13 the steps were 24.3 mm for Cu and 3.2 mm for Pb corresponding to 1.152 mg of Cu and 0.2370 mg of Pb in 40155.5 g of water (Fig. 1). The mean value is 1.365 mg Cu and 0.2305 mg in 40155.5 g of water or 0.03399 mg of Cu and 0.005001 mg Pb in 1000 g of water.

Determination of tin. In former analyses of mineral waters tin has been determined, as a rule, gravimetrically. This time even tin was determined polarographically⁷. The thiostannate obtained by treating the sulphides with $(\text{NH}_4)_2\text{S}$ was decomposed by acetic acid, the obtained precipitate of tin sulphide filtered, dissolved in nitric acid, the solution evaporated in a glass dish, then evaporated several times with *Aqua regia* to dryness to destroy organic substances and finally dissolved in 10 ccm of 1N hydrochloric acid which contained 0.01 per cent of gelatin as a suppressor. Only the cathode step has been used in the determination of tin. The polarograph was calibrated with a standard containing 1 mg of Sn in 10 ccm

* A Heyrovsky-Shikata model manufactured by Československá zbrojovka, Brno.

1 N hydrochloric acid + 0.01 per cent of gelatin as suppressor. With the sensitivity of the apparatus of 12 a step of 37.5 mm was obtained at -0.47 V, while the sample gave under the same conditions steps of 66.3, 64.6 and 65.8 mm (Fig. 2). The mean value is 65.6 mm corresponding to 1.749 mg of Sn in 40155.5 g of water or 0.04355 mg in 1000 g of water.

Determination of nickel and cobalt. The polarograph was calibrated with a standard containing 1 mg of Ni and 1 mg of Co in 10 ccm of 1 M ammonia and 1 M ammonium chloride + 0.005 per cent of gelatin as suppressor. With the sensitivity of the apparatus of 15 a step of 9.8 mm was obtained at -1.13 V for Ni, and one of 11.0 m at -1.32 V for Co. With the sensitivity of 16 the step for Ni was 6.8 and 7.3 mm for Co. The sample was polarographed under the same conditions and gave with the sensitivity of 15 a 8.5 mm step for Ni and a 6.0 mm step for Co corresponding to 0.8673 mg of Ni and 0.5455 mg of Co in 40155.5 g of water. With the sensitivity 16 the steps were 5.8 and 6.0 mm (mean value 5.9 mm) for Ni and 4.5 and 4.2 mm (mean value 4.4 mm) for Co corresponding to 0.8676 mg of Ni and 0.6027 mg of Co in 40155.5 g of water (Fig. 3). The mean value

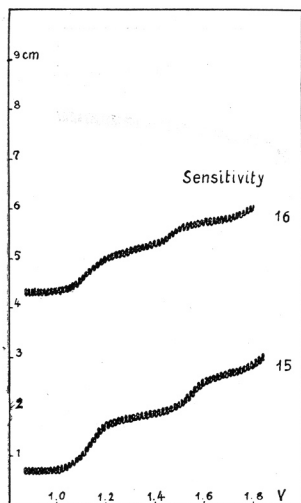


Fig. 3.

Fig. 3. Determination of nickel and cobalt.

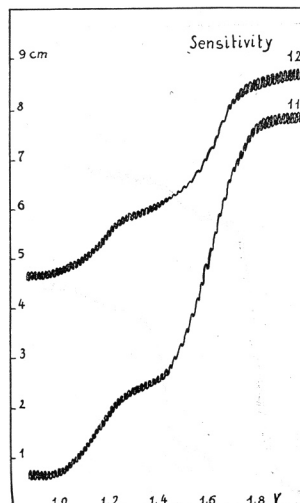


Fig. 4.

Fig. 4. Determination of zinc and manganese.

of all determinations is 0.8675 mg of Ni and 0.5471 mg Co in 40155.5 g of water or 0.02160 mg Ni and 0.01430 mg Co in 1000 g of water.

Determination of zinc and manganese. The polarograph was calibrated with a standard containing 1 mg of Zn and 1 mg of Mn in a mixture of 10 ccm water and 10 ccm of a saturated solution of potassium chloride. With the sensitivity of the apparatus of 11 a step of 19.3 mm was obtained at -1.06 V for Zn and one of 22.5 mm at -1.53 V for Mn. With the sensitivity of 12 the step for Zn was 13.0 mm and 16.5 mm for Mn. The sample was polarographed under the same conditions and gave with the sensitivity of 11 a 14.4 mm step for Zn and a 45.5 mm step for Mn corresponding to 0.7461 mg of Zn and 2.022 mg of Mn in 40155.5 g of water. With the sensitivity of 12 the steps were 10.0 mm for Zn and 31.3 mm for Mn corresponding to 0.7692 mg of Zn and 1.897 mg of Mn in 40155.5 g of water (Fig. 4). The mean value of the determinations is 0.7577 mg of Zn and 1.960 mg of Mn in 40155.5 g of water or 0.01887 mg Zn and 0.04881 mg in 1000 g of water.

The chemical composition of the water is shown by the analysis in Table II.

According to the International Classification the main components of the water are, calcium, sodium, hydrocarbonate, sulphate. Total ionic concentration: $N/1000 = 155.0$; Ca 40.7; Na 21.9; HCO_3 51.3; SO_4 21.9. Reaction: Alkaline, $pH = 8$.

The heavy metals found in the mineral water point out that the fault is very old going probably down to the Precambrian and that it was very active during the Paleozoic (Caledonian and particularly Variscan orogeny). From the small amounts of zinc and lead found in the water, however, one can infer that the fault was relatively inactive during the Mezozoic and

TABLE II
Chemical analysis of the Acidulated Water in Kiseljak

Specific gravity, 1.00487 at 0°/0°C Temperature, 12.2° C (54.0° F)				
The water contains in 1 kg			In per cent of dry matter	
Ions	grams	milimols		milivals
Cations				
Sodium (Na')	0.5024	21.85	21.85	Na 11.72
Potassium (K')	0.02755	0.7047	0.7047	K 0.643
Lithium (Li')	0.000519	0.0748	0.0748	Li 0.012
Calcium (Ca'')	0.8158	20.35	40.70	Ca 19.04
Magnesium (Mg'')	0.1722	7.073	14.146	Mg 4.014
Strontium (Sr'')	0.001475	0.0168	0.0336	Sr 0.034
Barium (Ba'')	0.0000297	0.0002	0.0004	Ba 0.001
Manganese (Mn'')	0.0000488	0.0009	0.0018	Mn 0.001
Zinc (Zn'')	0.0000189	0.0003	0.0006	Zn
Lead (Pb'')	0.0000050			Pb
Tin (Sn'')	0.0000436	0.0004	0.0008	Sn 0.001
Copper (Cu'')	0.0000340	0.0005	0.0010	Cu 0.001
Nickel (Ni'')	0.0000216	0.0004	0.0008	Ni 0.001
Cobalt (Co'')	0.0000143	0.0002	0.0004	Co
Anions				Cl 3.580
Chloride (Cl')	0.1534	4.326	77.51	SO ₄ 24.52
Sulphate (SO ₄ '')	1.051	10.94	4.326	CO ₃ 35.93
Bicarbonate (HCO ₃ '')	3.203	51.30	21.88	SiO ₂ 0.321
Oxides in colloidal solution			51.30	Al ₂ O ₃ 0.028
Silicon dioxide (SiO ₂)	0.01376	0.2291	77.51	Fe ₂ O ₃ 0.154
Aluminium oxide (Al ₂ O ₃)	0.00120	0.0118		100.00
Ferric oxide (Fe ₂ O ₃)	0.00658	0.0412		Salinity (in 1000 parts of water)
Total sum of items determined	5.949	116.9		4.285
Bicarbonates calculat- ed as carbonates	4.285			
Total solids, dried at 180° C	4.197			
Sulphate control				
Calculated	5.265			
Found	5.152			
Free Carbon dioxide (CO ₂)	1.918			

Tertiary when the present mountains in Bosnia were formed. Its activity in the Quaternary could not be followed geochemically.

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REFERENCES

1. S. Miholić, *Econ. Geol.* **42** (1947) 713.
2. L. Marić, *Neues Jahrb. Mineral. Geol. Abhand.* **87** (1954) 1.
3. S. Miholić, *Econ. Geol.* **47** (1952) 543.
4. S. Miholić, *Geološki Vjesnik* **7/9** (1956) 231.
5. V. M. Goldschmidt, *Geochemistry*, Oxford 1954. p. 238.
6. K. Rankama, *Isotope Geology*, London 1954. p. 191.
7. J. M. Kolthoff and James J. Lingane, *Polarography*. 2nd ed. Vol. 2. New York 1952. p. 523.

IZVOD

Mineralna voda Kiseljak. Geokemijska studija

S. Miholić

Područje sjeveroistočno od Sarajeva presijecaju dvije rasjeline, koje konvergiraju prema jugoistoku. Sjevernu od njih prati niz mineralnih voda (Ilidža, Blažuj, Kiseljak, Bjelalovac, Fojnica, Klokoti i Busovača). Duž te rasjeline digao se u kvarteru teren prema jugozapadu i tvori danas planinu Vranicu, koja u Bijeloj Gromili doseže visinu od 2071 m. Posljedica je toga, da se duž rasjeline prema jugozapadu javljaju sve stariji slojevi: srednji i gornji trias kod Ilidže, donji trias kod Kiseljaka i Kreševa i gornji paleozoik (karbon i perm) kod Fojnice i Klokota. Paleozoik seže do Jajca, gdje opet pada pod trias.

U mineralnim vodama, koje izviru duž rasjeline preteže kositar (Ilidža 0.0217 mg/kg, Kiseljak 0.04355 mg/kg), a znatan je i sadržaj na niklju, kobaltu, te bakru. Sve to upućuje na variscičku metalizaciju. Rasjelina je prema tome mnogo starija od kvartera, pa je vjerojatno postojala već u arhaiku, a bila je naročito aktivna u paleozoiku, osobito u karbonu, dok je za vrijeme alpskog boranja, kad je nastalo sadanje gorje u Bosni, bila relativno inaktivna.

Dok sadržaj na teškim metalima u mineralnim vodama daje mogućnost, da si stvorimo neki sud o odnosima, koji vladaju u većim dubinama zemlje, to nam njihov radioaktivitet pruža putokaze o prilikama u površnim slojevima. Kako se vidi iz Tabele I, vode koje izviru iz karbona pokazuju znatno veći radioaktivitet od onih, koje izviru iz triasa i oligocena. Tako ta određivanja potvrđuju zaključke stvorene pri ispitivanju mineralnih voda u Hrvatskoj i Makedoniji.

Ispitivanja na vrelu izvršena su 19. kolovoza 1954. Temperatura vode bila je 12.2°C, pH = 8, ona je sadržavala 1.918 g slobodnog ugljikovog dioksida u litri i pokazivala radioaktivitet od 0.278 Mache-ovih jedinica = 0.101 nC/l.

Voda je bistra, poslije 1-2 sata malo se zamuti, bez mirisa je i boje, okusa slabo slana i kisela.

Analiza vode prikazana je u Tabeli II.