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The Thermal Waters of Višegrad in Bosnia

A Geochemical Study

S. Miholić

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

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Of the thermal waters of Višegrad in Bosnia one source (Sokolović' Bath) issues from a fault about 10 meters above the valley floor, while the water from the second source (Caid's Bath) passes extensive calcareous sinter deposits and issues at the left bank of a brook. Its water has lost part of its calcium und iron in the sinter, but on the other hand its radioactivity has increased 7,27-fold due to secondary accumulation of uranium in the sinter. The mechanism of this accumulation is discussed.

The problem of secondary enrichment of uranium through adsorption of uranium by suitable materials from very dilute solutions has recently received considerable attention. Some commercially important uranium deposits are considered by some authors as produced by secondary enrichment.

There is for instance the case of the uraninite deposits of the Colorado plateau[1] where the uranium ions from descending solutions, perhaps originating in the overlying marine sediments of Cretaceous age, have been adsorbed by and are partly replacing plant material contained in Jurassic and Triassic strata. In places the Cretaceous rocks have been later eroded away. They consist either of fluvial sandstones and conglomerates or of black carbonaceous shales deposited in a lagoonal environment (Mancos shale[2]). H. A. Tourtelot[3] has described Late Cretaceous black organic-rich shales in which scales and bones of fish are abundant and which cover vast expanses to the Northeast of the Colorado plateau in places containing as much as 0.03 percent uranium.

Another important deposit is represented by the Precambrian Witwatersrand ores, now considered the world's largest single source of uranium, where the uranium is in close connection with carbonaceous matter and with gold. Their genesis is still one of the most controversial topics in modern geochemical literature. While the uranium is considered by some as primary and syngenetic[4], it is viewed by others as secondary and epigenetic[5]. Very similar deposits of uranium that might become even more important have been discovered recently in Canada, where Upper Precambrian (Huronian) conglomerates on the Blind River, Ontario contain uranium and also some gold[6].

Still another instance is the sometimes remarkable content of uranium in subbituminous coal and in lignite which contain up to 0.01 percent uranium. Experiments by G. W. Moore[7] have shown an almost 100 percent irreversible retention of uranium in subbituminous coal from percolating diluted solutions. As shown by I. A. Breger et al.[8] the uranium is held in the coal as an organo-uranium compound or complex that is soluble at a pH of less than 2.18. Most of the coals now being mined for uranium in the United States are in beds of Cretaceous age[9]. The highest uranium contents of a given layer of coal is usually at the top which, as a rule, underlies bituminous shale. This would point to enrichment by descending solutions.

Sediments from mineral waters sometimes also show an enrichment of uranium. A number of instances has been found in Yugoslavia (Lešće, Fojnica, Višegrad, Srebrenica, Istarske Toplice) and similar phenomena have been observed in other countries too. In the thermal springs of Gastein (Austria) F. Scheminzky and E. Müller[10] found a remarkable accumulation of uranium in the sinter, but owing to the geological conditions and the low concentration of calcium (20.0 p. p. m.) and iron (0.06 p. p. m.) in the thermal water, the sinter formations are rather restricted. In the United States up to 0.008 percent uranium is present in the calcareous sinter on the Allen property situated along Erskine Creek, Kern County, California while limonitic deposits from hot springs on the Stokes and Stowell properties, about 13.7 kilometers Northwest of Quincy, Plumas County, California contain up to 0.001 percent uranium (G. W. Walker, T. G. Lovering and H. G. Stephens[11]). The calcareous sinter formed along the Jemez River at the Jemez Springs (70^{0}C), Sandoval County, New Mexico contains up to 0.002 percent uranium, while a similar sinter around Caseman well 17.1 kilometers North of San Ysidro, also in Sandoval County shows a slight radioactivity. The radioactivity is, however, in all those cases in excess of the amount due to uranium in equilibrium with its daughter products and is caused mainly by radium precipitated in the sinters (G. T. Lovering[12]).

Several cases of secondary enrichment of uranium are here possible[13] : 1. Deposits formed under oxidizing conditions from slightly alcaline solutions (calcareous sinters), 2. Deposits formed under oxidizing conditions from slightly acid solutions (ocher deposits) and 3. Deposits formed under reducing conditions in presence of hydrogen sulphide and/or organic matter. The first case interests us here.

The mechanism of adsorption of uranium ions on ferric oxide hydrate in slightly alcaline solution has been studied in detail by T. G. Lovering[14] and later by P. B. Barton Jr.[15] who showed that results obtained by experiment agree with those predicted by the Freundlich equation and concluded that the uranium is adsorbed on the ferric oxide hydrate. The gelationus hydrosol after aging and partial dehydration yields goethite ($Fe_2O_3 \cdot H_2O$) in a way not yet elucidated, in spite of the number of samples examined[16], but in which either humic substances[17] or colloidal silica[18] may have played their part, and eventually hematite which is the stable form above 130^{0}C, while the adsorbed uranium is expelled and forms secondary uranium minerals. This mechanism probably accounts for the common association of hematite with uranium in veins[19]. P. B. Barton Jr.[15] found in the limonites of the Goodsprings District, Nevada up to 0.090 percent uranium, while the pyrometasomatic magnetite-hematite deposit at the Prince Mine, New Mexico contains, according to G. Walker and F. W. Osterwald[20] up to 0.031 per cent uranium.

Analogous absorption phenomena on limonite, goethite and hematite have been pointed out by C. F. Davidson[21] for thorium.

Although no commercially important deposit of uranium due to secondary enrichment that could be ascribed to recent hydrothermal activity has been found as yet, investigation of enrichment of uranium in hydrothermal deposits is likely to offer some hints for a better understanding of the mechanism of such an accumulation.

The spa of Višegrad lies in the gorge of the brook Banja 4.5 kilometers NNE of Višegrad at a latitude of 43°49′12″ N and a longitude of 19°18′20″ E. Its altitude is 414 meters (Cf. the Ordnance Survey map Scale 1 : 75.000 [1.18 miles to the inch], Sheet No. 6462). The water issues from serpentine, but as calcium predominates in it and as it has formed an extensive calcareous sinter terrace, the material of which has yielded an excellent building stone for centuries, it is more probable that it flows from the Upper Cretaceous limestone which covers great areas in the vicinity of the spa. There are two springs: 1. *Sokolović' Bath* on a slope about 10 meters above the bottom of the valley.

TABLE I.

Chemical Analysis of the Water of Sokolović' Bath

Specific gravity, 1.00053 at 0°/0°C
Temperature, 34.2°C (93.6°F)

The water contains in 1 kg				In percent of dry matter	
Ions	grams	milimols	milivals		
Cations				Na	5.032
Sodium ($Na^{\cdot}$)	0.01406	0.6114	0.6114	K	0.698
Potassium ($K^{\cdot}$)	0.001950	0.0499	0.0499	Ca	25.45
Calcium ($Ca^{\cdot\cdot}$)	0.07111	1.774	3.548	Mg	2.599
Magnesium ($Mg^{\cdot\cdot}$)	0.007262	0.2986	0.5972	Cl	1.879
				SO_4	5.841
Anions			4.807	CO_3	46.39
Chloride (Cl')	0.005251	0.1481	0.1481	SiO_2	8.955
Sulphate (SO_4'')	0.01632	0.1699	0.3398	Al_2O_3	0.287
Bicarbonate (HCO_3')	0.2635	4.319	4.319	Fe_2O_3	2.866
			4.807		100.00
Oxides in colloidal solution					
Silicon dioxide (SiO_2)	0.02502	0.4166		Salinity (in 1000 parts of water)	
Aluminium oxide (Al_2O_3)	0.000801	0.0079			
Ferric oxide (Fe_2O_3)	0.008008	0.0502			0.2794
Total sum of items determined	0.4133	7.846			
Bicarbonates calculted as carbonates	0.2794				
Total solids, dried at 180°C	0.2797				
Sulphate control					
Calculated	0.3590				
Found	0.3614				

A bathhouse was built above the spring in the XVIth century by the Grand Vizir Mehmed Sokolović and is still in use. It contains a square basin, 2,5×3 meters, covered by a cupola. The water issues through a channel from the bedrock and falls into the basin. The spring gives 0.417 liters per second.
2. *Caid's Bath* on the left bank of the brook, where a bathhouse was built some 30 years ago. It contains a square basin, 2.5×2.5 meters, under a vault. The water flows through the sinter terrace, issues from a channel, falls into the basin and gives 0.863 liters of water per second. By flowing through the sinter, the water has increased its radioactivity by a factor of 7.27 as a result of the accumulation of uranium in the sinter. This is the highest factor of enrichment so far found. In all other instances the factor is lower (Lešće 1.18, Fojnica 4.95, Srebrenica 3.04, Istarske Toplice 5.05).

TABLE II.
Chemical Analysis of the Water of Caid's Bath

Specific gravity, 1.00072 at 0°/0°C
Temperature, 33.7°C (92.7°F)

The water contains in 1 kg				In percent of dry matter	
Ions	grams	milimols	milivals		
Cations				Na	6.066
Sodium ($Na^{\cdot}$)	0.01804	0.7845	0.7845	K	0.950
Potassium ($K^{\cdot}$)	0.002824	0.0722	0.0722	Ca	18.69
Calcium ($Ca^{\cdot\cdot}$)	0.05559	1.387	2.774	Mg	6.604
Magnesium ($Mg^{\cdot\cdot}$)	0.01964	0.8076	1.6152	Cl	1.832
			5.246	SO_4	4.933
Anions				CO_3	48.42
Chloride (Cl')	0.005448	0.1537	0.1537	SiO_2	10.16
Sulphate (SO_4'')	0.01467	0.1527	0.3054	Al_2O_3	1.077
Bicarbonate (HCO_3')	0.2921	4.787	4.787	Fe_2O_3	0.269
Oxides in colloidal solution			5.246		100.00
Silicon dioxide (SiO_2)	0.03023	0.5033		Salinitiy (in 1000 parts of water)	
Aluminium oxide (Al_2O_3)	0.003203	0.0314			
Ferric oxide (Fe_2O_3)	0.000801	0.0050			0.2974
Total sum of items determined	0.4425	8.684			
Bicarbonates calculated as carbonates	0.2974				
Total solids, dried at 180°C	0.2831				
Sulphate control					
Calculated	0.3823				
Found	0.3610				

EXPERIMENTAL

The two springs of the Višegrad spa were investigated on September 25, 1955.

1. *Sokolović' Bath*. The temperature of the water was 34.2°C, ist reaction pH=9, and it showed a radioactivity of 6.951 Mache units = 2.530 mμ C/l.

The water is clear, odourless and colourless.

According to the International Classification the main components of the water are, calcium, hydrocarbonate. Total ionic concentration: $N/1000 = 9.6$; Ca 3.5; HCO_3 4.2. Reaction: Alcaline, $pH = 9$.

The chemical composition of the water is shown by the analysis in Table I (p. 41).

2. *Caid's Bath.* The temperature of the water was 33.7°C, its reaction $pH = 9$, and it showed a radioactivity of 50.50 Mache units = 18.38 mμ C/l.

The water is clear, odourless and colourless.

According to the International Classification the main components of the water are calcium, hydrocarbonate. Total ionic concentration: $N/1000 = 10.4$; Ca 2.8; HCO_3 4.8. Reaction: Alkaline, $pH = 9$.

The chemical composition of the water is shown by the analysis in Table II (p. 42).

A comparison of the two analyses shows that the water has lost both calcium and iron by flowing through the sinter. Both losses are much greater than those found under similar conditions in Fojnica[22]. There is, however, an increase of sodium, chlorine, magnesium and silica. The increase in sodium and chlorine could be accounted for by the fact that the immediate surroundings of the spa have been much denser settled in former days than they are at present and that the increase in sodium chloride is due to organic refuse that seeped into the sinter. The increase in magnesium and silica might be due to the influence of the subsoil consisting of serpentine. As already pointed out there is a very important increase in radioactivity due to the secondary enrichment of uranium in the sinter.

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REFERENCES

1. A. Rosenzweig, J. W. Gruner and L. Gardiner, *Econ. Geol.* **49** (1954) 351.
2. Y. W. Isachsen, T. W. Mitcham and H. B. Wood, *Econ. Geol.* **50** (1955) 127.
3. H. A. Tourtelot, *Bull. Am. Assoc. Petroleum geol.* **40** (1956) 62.
4. S. Miholić, *Econ. Geol.* **49** (1954) 537.
5. C. F. Davidson, *Mining Mag.* (London) **88** (1953) 73.
6. J. D. Bateman, *Econ. Geol.* **50** (1955) 361.
7. G. W. Moore, *Econ. Geol.* **49** (1954) 652.
8. I. A. Breger, M. Deul and S. Rubinstein, *Econ. Geol.* **50** (1955) 206.
9. V. E. McKelvey, D. L. Everhart and R. M. Garrels, *Econ. Geol. 50th Anniversary Vol.* **1955,** 464.
10. F. Scheminzky and E. Müller, *Bad Gasteiner Badeblatt, No.* **5/7** (1955) Sep.
11. G. W. Walker, T. G. Lovering and H. G. Stephens, *California Div. Mines Special Rept.* **49** (1956) 3.
12. T. G. Lovering, *U. S. Geol. Survey Bull.* **1009** (1956) 315.
13. S. Miholić, *Memorias del Congresso geológico internacional.* México 1956 (in press).
14. T. G. Lovering, *Econ. Geol.* **50** (1955) 186.
15. P. B. Barton Jr., *Econ. Geol.* **51** (1956) 178.
16. R. C. Mackenzie, *Problems of Clay and Laterite Genesis. A Symposium.* New York 1952. p. 65.
17. R. C. Mackenzie, *Annales edafol. y fisiol. vegetal* (Madrid) **13** (1954) 111.
18. M. Muñoz Taboadela, *J. Soil Sci.* **4** (1953) 48.
19. V. E. Kelvey, D. L. Everhart and R. M. Garrels, *Loc. cit.*
20. G. W. Walker and F. W. Osterwald, *Econ. Geol.* **51** (1956) 213.
21. C. F. Davidson, *Mining Mag.* (London) **94** (1956) 197.
22. S. Miholić, *Geološki Vjesnik* **7/9** (1956) 231.

IZVOD

Termalne vode kod Višegrada. Geokemijska studija

S. Miholić

U uskoj dolini potoka Banje, 4,5 kilometra NNE od Višegrada izvire termalno vrelo na obronku, desetak metara nad potočnim koritom. U XVI. vijeku sagrađeno je nad izvorom kupalište (*Sokolovićeva banja*). U okolini tog izvora istaložile su se velike naslage vapnene sedre, koja je u nizu stoljeća služila kao izvrstan građevni materijal. Jedan dio termalne vode teče međutim kroz naslage sedre i izlazi kod samog potoka na njegovoj lijevoj obali. Početkom XX. vijeka podignuto je kupalište i nad ovim vrelom *(Kadijina banja)*. Oba vrela daju zajedno 1.28 litru vode na sekundu. Prolazeći kroz naslage sedre termalna se voda hladi (od 34.2^{0}C na 33.7^{0}C), gubi dio svojega kalcija (od 0.07111 na 0.05559 grama u kilogramu) i željeza (od 0.0080 na 0.0008 grama u kilogramu), koji su se istaložili u sedri. Radioaktivitet je međutim porastao — zbog sekundarne akumulacije urana u sedri — 7.27-struko (od 6.951 na 50.50 Macheovih jedinica, što je dosad najveći porast), pa stvara tako radioaktivno termalno vrelo po jakosti drugo u Jugoslaviji, a prvo u Bosni.

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BALNEOLOŠKO-KLIMATOLOŠKI INSTITUT
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ZAGREB

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