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The »Eye Water« of Srebrenica in Bosnia. A Geochemical Study

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Received June 27, 1957

The mineral waters around Srebrenica in Bosnia which all represent mine waters issuing from old mines have, as a rule, deposited near their orifices more or less extensive deposits of ochre. They all show a distinct radioactivity (2.911 — 7.02 mμ c/l.). Only one water, the »Eye Water«, so called because it is used by the peasants of the region as a cure for eye troubles, with a pH = 3 does not deposit any ochre and shows the lowest radioactivity (2.104 mμ c/l.). Besides 1312 p. p. m. of iron, the water contains 229 p. p. m. of aluminium and 13.12 p. p. m. of copper.

The East Bosnian Paleozoic, consisting of schists, sandstones, conglomerates and limestones[1] belonging mainly to the Carboniferous was intruded, possibly at the end of the Cretaceous, by extensive flows of andesite[2], which near Srebrenica gave rise to important deposits of sphalerite and of galena, the latter containing remarkable amounts of silver. It was mainly this silver that caused extensive mining operations probably already by the Illyrians in prehistoric times. In the first century A. D. the country became an important Roman mining center (Domavia) that lasted till the fourth century. During the 14th and 15th centuries Ragusan merchants exploited the mines with the help of Saxon miners. The consequence of all this was that the mountains around Srebrenica are honeycombed with stopes and addits, most of them inaccessible nowadays, but still letting through the acid mine waters formed by the oxidation of the sulphides.

One of those mine waters issuing in the town of Srebrenica itself and still extant to-day was mentioned in the 17th century by the Turkish traveller Evlia Chelebi[3]. He considered the water highly unwholesome and says that it causes goiter which is very likely, as arsenic is an antagonist to thyroxine. As practically all those waters contain arsenic in smaller or greater quantities, some of the waters have been used for medical purposes already very early.

Those mine waters are also radioactive and have deposited very extensive deposits of ochre in some places. They are therefore a very suitable material for the study of the accumulation of radioactive elements in deposits formed from mineral waters. One of them, however, does not deposit any ochre, owing to its great acidity (pH = 3) and can therefore be used for comparison. It is the so-called »Eye Water«. When fresh, the water is colourless, gets deep

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brown on standing in contact with the atmospheric air, but does not give any deposit.

In his previous publications the author has stressed first of all the accumulation of uranium in sinters. But while in the accumulations in schists belonging to the Carboniferous and the Cretaceous uranium is in equilibrium with the products of its radioactive decomposition, this is not always the case in recent deposits from mineral waters. Particularly in cases of calcareous sinters and ochres there is in general more radium present than it would correspond to the radioactive equilibrium. Only deposits from waters containing hydrogen suphide contain mainly uranium (often partly in organic binding).

In the existing literature, the stress lies mainly on the accumulation of radium which is precipitated together with barium as sulphate. The mechanism of this coprecipitation has been studied by H. Doerner and W. Hoskins[4], who found that in the presence of a large excess of barium over radium — a condition fulfilled in most mineral waters — sulphate ions will precipitate radium even though the solubility product of radium suphate is not exceeded. It was further investigated by B. E. Marques[5] and recently by L. Gordon and K. Rowley[6] who showed that the logarithmic distribution coefficient λ for Ba/Ra in precipitates is greater at 20^0 C ($\lambda = 1.69$) than at 90^0 C ($\lambda = 1.21$). Thus the precipitation of radium will be more complete in deposits formed from cold mineral waters. As the amount of unabsorbed uranium on ferric hydroxide ($1 — 2 \times 10^{-8}$) [7] exceeds the solubility product of barium sulphate (1.2×10^{-10}) it follows that sinters deposited from waters containing uranium and radium in radioactive equilibrium will in most cases contain more radium than it corresponds to this equilibrium.

One of the first to study the accumulation of radioactive substances in ochres deposited from springs was F. Heinrich[8]. Already he pointed out the compound nature of the radioactivity shown in the ochres. H. Schlundt[9] determined radiometrically the radioactivity of the calcareous sinters from Hot Springs, Arkansas and found $13.92 — 3751.0 \times 10^{-6}$ p. p. m. of Ra. In recent sinters of the Tamagawa Hot Springs E. Minami, N. Saito and I. Ishimori[10] found that the decomposition products of radon are not in equilibrium with radium, whereas in old sinters the equilibrium is almost reached. This agrees with the observations of the author who found in Varaždinske Toplice the ratio Ra/U much greater in recent sinters than in those which underlie the recently excavated ruins of the Roman bath. Á. Szabó[11] found in the mud from one of sulphurous springs in Băile Herculane 12.4×10^{-6} p. p. m. Ra, in a similar mud from Băile Someşeni 2.581×10^{-6} p. p. m. and in the ochre deposited from the thermal water of Geoagiu 3.1×10^{-6} p. p. m. Ra[13]. P. K. Kuroda[14] pointed out that since the radon of hot springs is greatly in excess of its parent element Ra^{226}, it must have entered the water shortly prior to the issue. The main supply source of radon is therefore the sinter deposit accumulated near the orifice. Y. Yokoyama[15] recently proposed a new method for the prospecting for uranium based upon the determination of Ra^{226} in mineral waters.

More stress has been laid on the determination of uranium in deposits from mineral waters in the United States. The procedure commonly employed is to determine the radioactivity of a sample radiometrically and express it

TABLE I

Chemical Analysis of the »Eye Water« near Srebrenica

Specific Gravity, 1.00691 at $0^0/0^0$ C
Temperature, 11.4^0 C (52.5^0 F)

The water contains in 1 kg				In per cent of dry matter	
Ions	grams	milimols	milivals		
Cations				H	0.031
Hydrogen ($H^{\cdot}$)	0.00167	1.657	1.657	Na	0.150
Sodium ($Na^{\cdot}$)	0.008262	0.3593	0.3593	K	0.012
Potassium ($K^{\cdot}$)	0.0006738	0.0172	0.0172	Ca	0.338
Calcium ($Ca^{\cdot\cdot}$)	0.01877	0.4683	0.9366	Mg	0.188
Magnesium ($Mg^{\cdot\cdot}$)	0.01044	0.4293	0.8586	Al	4.108
Aluminium ($Al^{\cdot\cdot\cdot}$)	0.2280	8.651	25.953	Fe	24.67
Iron ($Fe^{\cdot\cdot}$)	1.369	24.51	49.02	Mn	0.049
Manganese ($Mn^{\cdot\cdot}$)	0.00269	0.0490	0.0980	Zn	0.008
Zinc ($Zn^{\cdot\cdot}$)	0.00045	0.0068	0.0136	Pb	0.001
Lead ($Pb^{\cdot\cdot}$)	0.00005	0.0003	0.0006	Cu	0.236
Copper ($Cu^{\cdot\cdot}$)	0.01312	0.2065	0.4130	Ni	
Nickel ($Ni^{\cdot\cdot}$)	0.000004			Cl	0.022
			79.33	SO_4	68.34
Anions				$HAsO_4$	0.004
Chloride (Cl')	0.001231	0.0347	0.0347	SiO_2	1.838
Sulphate (SO'')	3.809	39.65	79.29		
Hydroarsenate ($HAsO_4''$)	0.000215	0.0015	0.0030		
Oxides in colloidal solution			79.33		100.00
Silicon dioxide (SiO_2)	0.1020	1.698		Salinity (in 1000 parts of water)	
Total sum of the items determined	5.566	77.74			
Sulphate control:					5.566
Calculated	2.674				
Found	2.684				

as uranium (eU) and then to determine uranium fluorimetrically (U). The difference between eU and U is assumed to be due to radium in excess to the radioactive equilibrium. Thus it was found that the calcareous sinter on the Allen property, Kern County, California contains 0.75 percent eU and 0.008 percent U, the limonitic deposits from the hot springs on the Stokes and Stowell properties, Plumas County, California contain 0.66 percent eU and 0.001 percent U[16], while the calcareous sinter at the Jemes Springs, Sandoval County, New Mexico contains 0.006 percent eU and 0.002 percent U[17].

If we now compare the composition of the »Eye Water« with that of Veliki Guber[18], which deposited the greatest amount of ochre, estimated in 1887 at 20000 tons[19], we can notice at a first glance a substantial difference in their chemical composition. While in the Guber spring zinc predominates among the heavy metals (7.123 p. p. m.), the »Eye Water« is particularly rich in copper (13.12 p. p.m.). The Guber spring shows a relation Co $>$ Ni (0.03549 p. p. m. Co and 0.01915 p. p. m. Ni), which is characteristic of pyrite of sedimentary origin[20], while the »Eye Water« contains only traces of Ni (0.004

p. p. m.) and no Co. Contrary to the observation made in Germany by H. Moenke[21] that waters with the lowest *p*H value show the greatest content in arsenic, the »Eye Water« contains a much smaller amount of that element (0.215 p. p. m. $HAsO_4$) as compared with the Guber spring (8.049 p. p. m. $HAsO_4$).

One thing can, however, be inferred from the investigations and that is: The increased radioactivity of the Guber spring is obviously in connection with the extensive ochre deposits around its orifice. And in accordance with the results obtained elsewhere, the factor of enrichment among all the investigated springs around Srebrenica is greatest in the spring of Veliki Guber (3.04 times). Similar conditions have been found in other places. In Višegradska Banja[22] and in Fojnica[23], where the sinter deposits have been particularly extensive, there is also an enrichment of radon in the water (7.27 and 4.95 times respectively).

The spring »Eye Water« issues from an old mine in the gorge on the left bank of the brook Crvena rijeka (Red River) at a latitude of 44°6′16″ N and a longitude of 19°19′10″ E. Its altitude is 550 meters. (Cf. the Ordnance Survey map Scale 1 : 75.000 [1.18 miles to the inch], Sheet No. 6362). The spring gives 0.033 liters per second.

EXPERIMENTAL

The spring was investigated on September 5, 1954. The temperature of the water was 11.4° C, its reaction *p*H = 3 and it showed a radioactivity of 2.104 mμ c/l.

The water is clear, odorless and colourless with a strong astringent taste.

According to the International Classification the main components of the water are iron, aluminium, sulphate. Total ionic concentration: *N*/1000 = 158.7; Fe 49.0; Al 26.0; SO_4 79.3. Reaction: Acid, *p*H = 3.

The chemical composition of the water is shown by the analysis in Table I (p. 31).

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IZVOD

»Očna voda« kod Srebrenice. Geokemijska studija

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U uskoj dolini Crvene rijeke, u neposrednoj blizini Velikoga Gubera, izvire na lijevoj obali potoka, mineralno vrelo. Vrelo je slabo i daje samo 0.033 litre vode na sekundu, ali sadrži 1.369 g željeza, 0.2280 g aluminija i 0.01369 g bakra u kg. Po sadržaju željeza to je jedno od najjačih vrela u Evropi (Samo Lévico, Acqua forte s 1.886 g Fe i Lausick, Herrmannsquelle s 1.539 g Fe u kg sadrže više željeza), a po sadržaju aluminija dolazi na drugo mjesto samo Ronneby, Ekholtz-källan s 0.2390 g Al u kg je neznatno jači). Radioaktivitet iznosi 5.782 Macheove jedinice = 2.104 nC/l.

Ispitivanje je izvršeno 5. rujna 1954., a analiza vode prikazana je u tablici I na str. 31.

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Primljeno 27. lipnja 1957.

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