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The Radioactive Springs of Istarske Toplice A Geochemical Study

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The warm sulphurous springs of Istarske Toplice issue on the foot of a fault scarp from Upper Cretaceous limestone. They are remarkably radioactive, particularly the spring uncovered in 1955 on a meadow west of the main spring. Its high radioactivity (218 m μ c/l) makes it the third strongest radioactive spring in Europe on record and is due to the secondary enrichment of uranium in the black mud deposited from the sulphurous water through which its water flows.

The southern rim of the North Istrian plateau which dominates the valley of the Mirna river is formed by a WSW-ENE fault. The plateau itself is covered by Middle Eocene deposits overlying uncomformably Upper Cretaceous limestone. Towards the northeast the Eocene cover of the plateau disappears and the limestone shows characteristic karst features. The fault can be followed through the gorge of the Mirna from Buzet to Istarske Toplice, where it is particularly visible (J. Poljak[1]), as the upthrown northwest side represents a fault scarp which is in places almost perpendicular. The scarp is formed by limestone of the Upper Cretaceous, while the Middle Eocene is represented mainly by Flysch. The river Mirna flows at Istarske Toplice near the foot of the scarp through Alluvial deposits, but on the left bank of the river there are outcrops of Flysch in the forest. There is also another subsequent fault running W-E (the fault of Gradinje). At the intersection of those two faults issue the thermal springs of Istarske Toplice (M. Salopek[2]).

In 1957 three shallow bore holes were sunk in the immediate neighborhood of the thermal springs (B. Raljević and M. Borić[3]). After passing through Alluvial sediments and a layer of almost black mud the bore holes reached the Upper Cretaceous limestone at depths of 24—26 meters. As there are outcrops of Flysch farther to the southwest in the valley which is only 20 meters above sea level and the rim of the plateau is about 200 meters above the plain, the displacement along the fault at Istarske Toplice would amount to about 250 m.

The drilling operations have also shown that at Istarske Toplice the fault runs through Cretaceous sediments almost to the surface. This explains the higher radioactivity of the thermal water flowing through the fault the more, as the lower part of the Upper Cretaceous consists of bituminous limestone[4].

The fault has been formed or at least reactivated during the Middle Eocene as the Flysch along the fault shows in places a phenomenon described by E. Beneo[5] from the Appennines and Sicily and called by him *»risedimentazione caotica«* (*argille scagliose*) as opposed to the normally stratified Flysch. Such alternations of stratified and chaotic Flysch are well exposed on the road that leads from Istarske Toplice over the rim to Zrenj. The phenomenon (*olistostroma*) is due to a submarine slide which occurred during the faulting and in places thoroughly mixed the deposits.

A good historical account of the place was given by B. Benussi[6]. Although there was a Roman settlement or military post on the cliff above the spring, no archeological remains have been found so far to show that the place was used in ancient times as a bath except, perhaps, locally, nor is there any mention of it in still existing classical literature. The first account of the thermal springs dates from 1600 when N. Manzuoli[7] mentions them and praises their powers in curing rheumatisms and diseases of the skin. G. F. Tommasini[8] also writes about the springs in 1650 but is less sure of their medical properties. During the French rule in Istria an army surgeon applied their water against skin diseases in soldiers with good results. This experience and also the effected cures of rheumatisms induced the marquess Gravisi to whose estates of Kostel (Pietrapelosa) the springs had belonged since 1440 to erect in 1817 a simple bathhouse and primitive quarters for the patients, which were replaced in 1840 by a more substantial building, while a new bathhouse was built in 1854. In 1858 the water was analyzed by K. v. Hauer (Table I A). Two years later Brigid found that the springs yielded 6 l/sec. of water. Gravisi sold the bath to A. Bertetich in 1875, who greatly improved the installations, added new buildings and had a new chemical analysis made by A. Briani and E. Huber in 1884 (Table I B). At that time there were three thermal springs which are still in existence. From 1918 to 1945 the owners were A. and E. Fachini.

TABLE I

1. Analysis by K. v. Hauer, 1858. (*Jahrb. geol. Reichsanstalt* 9 (1858) 689) (A).
2. Analysis by A. Briani and E. Huber, 1884. (P. Ghersa, *Le terme sulfuree di Santo Stefano in Istria.* Trieste 1884, p. 48) (B).
3. Analysis by M. Picotti and O. Casagrandi, 1932. (Unpublished analysis) (C).
4. Analysis by L. Dančević, 1947. (Unpublished analysis) (D).

	A	B	C	D
Na	23.14	18.68	22.40	24.10
K			0.360	
Ca	10.61	12.34	11.25	11.22
Mg	2.214	4.069	2.536	1.855
Cl	41.36	49.39	42.38	37.09
SO_4	13.31	9.106	9.740	11.42
CO_3	8.232	5.397	10.67	14.30
SiO_2	0.877	0.746	0.648	
Al_2O_3	0.236 (with Fe_2O_3)	0.266 (with Fe_2O_3)	0.020	
Fe_2O_3			0.020	0.017
	100.00	100.00	100.00	100.00
Salinity (in 1000 parts of water)	2.964	2.974	2.808	2.464
Total H_2S g/l	0.035	0.0251	0.0335	0.0212

ANALYSIS I

Chemical Analysis of the Water of the Main Spring
(1947)

Specific gravity, 1.00298 at $0^0/0^0C$
Temperature, 34.5^0C (94.1^0F)

The water contains in 1 kg.				In per cent of dry matter	
Ions	grams	milimols	milivals		
Cations				Na	20.98
Sodium ($Na^{\cdot}$)	0.7032	30.58	30.58	K	0.699
Potassium ($K^{\cdot}$)	0.02341	0.5988	0.5988	Ca	11.40
Calcium ($Ca^{\cdot\cdot}$)	0.3818	9.526	19.05	Mg	2.567
Magnesium ($Mg^{\cdot\cdot}$)	0.08593	3.533	7.066	Sr	0.011
Strontium ($Sr^{\cdot\cdot}$)	0.0003655	0.0042	0.0084	Ba	0.001
Barium ($Ba^{\cdot\cdot}$)	0.0000307	0.0002	0.0004	Mn	0.004
Manganese ($Mn^{\cdot\cdot}$)	0.0001316	0.0024	0.0048	Zn	0.002
Zinc ($Zn^{\cdot\cdot}$)	0.0000605	0.0009	0.0018	Pb	0.001
Lead ($Pb^{\cdot\cdot}$)	0.0000226	0.0001	0.0002	Sn	
Tin ($Sn^{\cdot\cdot}$)	0.0000053			Cu	
Copper ($Cu^{\cdot\cdot}$)	0.0000008		0.0001	Ni	
Nickel ($Ni^{\cdot\cdot}$)	0.0000033	0.0001	0.0002	Co	
Cobalt ($Co^{\cdot\cdot}$)	0.0000012			Cl	47.44
Anions			57.31	Br	0.133
Chloride (Cl')	1.588	44.79	44.79	I	0.001
Bromide (Br')	0.004468	0.0546	0.0546	SO_4	12.26
Iodide (I')	0.0000262	0.0002	0.0002	CO_3	3.514
Sulphate (SO_4'')	0.4105	4.273	8.546	SiO_2	0.938
Bicarbonate (HCO_3')	0.2392	3.920	3.920	Al_2O_3	0.014
Oxides in collodial solution			57.31	Fe_2O_3	0.035
Silicon dioxide (SiO_2)	0.03141	0.5230		TiO_2	
Aluminium oxide (Al_2O_3)	0.000464	0.0046			100.00
Ferric oxide (Fe_2O_3)	0.001173	0.0074			
Titanium dioxide (TiO_2)	0.0000079	0.0001		Salinity (in 1000 parts of water)	
Total sum of the items determined	3.470	97.82			
Bicarbonates calculated as carbonates	3.348				3.348
Total solids, dried at 180^0C	3.660				
Sulphate control					
Calculated	3.978				
Found	3.977				
Hydrogen sulphide (H_2S)	0.01531				

ANALYSIS II

Chemical Analysis of the Water of the Main Spring
(1953)

Specific gravity, 1.00250 at $0^0/0^0$C
Temperature, 30.5^0C (86.9^0F)

The water contains in 1 kg.			
Ions	grams	milimols	milivals
Cations			
Sodium ($Na^{\cdot}$)	0.5899	25.65	25.65
Potassium ($K^{\cdot}$)	0.0235	0.6011	0.6011
Calcium ($Ca^{\cdot\cdot}$)	0.4119	10.28	20.56
Magnesium ($Mg^{\cdot\cdot}$)	0.09422	3.874	7.748
Strontium ($Sr^{\cdot\cdot}$)	0.0004094	0.0047	0.0094
Barium ($Ba^{\cdot\cdot}$)	0.0000271	0.0002	0.0004
Manganese ($Mn^{\cdot\cdot}$)	0.0001423	0.0026	0.0052
Zinc ($Zn^{\cdot\cdot}$)	0.0000726	0.0011	0.0022
Lead ($Pb^{\cdot\cdot}$)	0.0000202	0.0001	0.0002
Tin ($Sn^{\cdot\cdot}$)	0.0000043		0.0001
Copper ($Cu^{\cdot\cdot}$)	0.0000007		
Nickel ($Ni^{\cdot\cdot}$)	0.0000026		0.0001
Cobalt ($Co^{\cdot\cdot}$)	0.0000011		
			54.58
Anions			
Chloride (Cl')	1.332	37.57	37.57
Bromide (Br')	0.003748	0.0469	0.0469
Iodide (I')	0.0000220	0.0002	0.0002
Sulphate (SO_4'')	0.3852	4.010	8.020
Bicarbonate (HCO_3')	0.5455	8.940	8.940
			54.58
Oxides in colloidal solution			
Silicon dioxide (SiO_2)	0.03598	0.5991	
Aluminium oxide (Al_2O_3)	0.000553	0.0054	
Ferric oxide (Fe_2O_3)	0.001398	0.0088	
Titanium dioxide (TiO_2)	0.0000067	0.0001	
Total sum of the items determined	3.425	91.59	
Bicarbonates calculated as carbonates	3.148		
Total solids, dried at 180^0C	3.166		
Sulphate control			
Calculated	3.779		
Found	3.716		
Hydrogen sulphide (H_2S)	0.0233		

In per cent of dry matter	
Na	18.74
K	0.747
Ca	13.08
Mg	2.993
Sr	0.013
Ba	0.001
Mn	0.004
Zn	0.002
Pb	0.001
Sn	
Cu	
Ni	
Co	
Cl	42.31
Br	0.119
I	0.001
SO_4	12.24
CO_3	8.522
SiO_2	1.143
Al_2O_3	0.018
Fe_2O_3	0.044
TiO_2	
	100.00

Salinity (in 1000 parts of water)

3.148

M. Picotti and O. Casagrandi made a new analysis of the main spring in 1932 (Table I C) and in 1933 M. Picotti[9] found the water highly radioactive (40 m μ c/l). During the last war the bathhouse and all the buildings were destroyed by fire. In June 1947 the main spring was partly repaired and in order to increase the temperature of the water all the colder inflows were excluded. The temperature rose from 32° to 34.5°C, but the amount of water fell to about one sixth and the radioactivity of the spring to less than a half (16.84 m μ c/l). At the same time L. Dančević made a new chemical analysis (Table I D). In November of the same year I visited the springs for the first time, determined the radioactivity and made a complete analysis (Analysis I). In 1953 attempts were made to reestablish the old conditions. The amount of water rose to 3 l/sec., the radioactivity reached the pre-war level, but the temperature fell to 30.5°C. A new analysis was also made (Analysis II). In 1955 the bathhouse was rebuilt provisionally and rooms for a limited number of patients prepared in the partly restored ruins.

The springs lie in the broad valley of the river Mirna not far from the place where it leaves the gorge at the foot of a 80 m. high perpendicular cliff at a latitude of 45°22′40″ N and a longitude of 13°52′50″ W. Its altitude is 20 m. (Cf. the Ordnance Sudvey map, Scale 1:75,000 [1.18 miles to the inch], Sheet No. 5852). There are three springs:

1. *Main spring.* It represents a basin in the floor of the bathhouse (1.55 × 2.55 m). On November 4, 1947 a few months after the repair of the basin, the temperature of the water was 34.5°C. At the same time a sample was taken for the chemical analysis of the water (Analysis I). Already on December 16, 1947 after a flood of the Mirna the temperature of the water amounted only to 33.4°C. When the former conditions of the spring were reestablished, the temperature on September 25, 1953 was 30.5°C. The same day a sample for a new chemical analysis of the water was obtained (Analysis II). The results of a series of determinations of hydrogen sulphide and of the radioactivity of the spring are shown in Table II.

The water of the spring is clear, with a strong odour of hydrogen sulphide and a salty taste.

According to the International Classification the main components of the water are sodium, calcium, chloride and sulphate. Total ionic concentration: $N/1000 = 114.6$; Na 30.6; Ca 19.1; Cl 44.8; SO_4 8.5. Reaction: Alcaline.

TABLE II

Hydrogen sulphide and radioactivity in the Main Spring

Analyst	Date	Temp. °C	H_2S g/liter	Radioactivity	
				Mache units	m μ c/l
M. Picotti and O. Casagrandi	1933	32	0.0355	110.0	40
S. Miholić	November 4, 1947	34.5	0.0151	47.33	16.84
	September 25 1953	30.5	0.0233	112.3	40.88
	April 12, 1955	31.8	0.0216	123.9	45.10
	June 21, 1955	32.2	0.0268	121.2	44.10
	November 7, 1956	32.6	0.0280	118.9	43.30
	April 19, 1957	31.6	0.0227	137.5	50.05

TABLE IV

The Strongest Radioactive Springs in Europe

Location	Radioactivity	
	Mache units	$m\mu c/l$
Lurisia, Italy	3150	1147
Jáchymov, Czechoslovakia	2250	819
Istarske Toplice	600.2	218.5
Valdemorilla, Spain	600	218
La Bourboule, France	436	159
Ischia, Italy	419.4	152.5
Gastein, Austria	385	140
Bagnères-de-Luchon, France	371.7	134.8
Chateldon, France	368	134
Vernet-les-Bains, France	313	114
Nerenčen, Bulgaria	303	110

in the vicinity after the Second World War. Taking this into account Table IV shows that Istarske Toplice are now on the third place among the most radioactive springs in Europe at present known.

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IZVOD

Radioaktivni izvori Istarskih Toplica
Geokemijska studija

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Istarske Toplice leže na križanju dvaju rasjeda ispod okomite vapnene stijene na desnoj obali rijeke Mirne 8 km jugozapadno od Buzeta. Okolni svijet upotrebljavao je izvore za liječenje od davnine, ali je tek početkom XIX. vijeka podignuto kupalište i nastamba za posjetioce. Lječilište je postepeno izgrađivano i postiglo je lijep uspjeh, ali je tokom posljednjeg rata potpuno izgorjelo. Postoje tri izvora: 1. *Glavni izvor* kaptiran kao zidani basen veličine 1,55 × 2,55 m. On je rekaptiran g. 1947. Pri tom se isključenjem hladnih pritoka nastojalo povisiti temperaturu vode. To je i pošlo za rukom. Temperatura je porasla od 32° na 34.5°C, ali je izdašnost vrela pala na jednu šestinu, a radioaktivnost na manje od polovice (Tabela II).

G. 1953. uspostavljeno je pređašnje stanje, pa se radioaktivnost opet vratila onakva, kakva je prije bila. Uspoređivanje analiza iz g. 1947. i 1953. pokazuje, da se termalna voda glavnog izvora sastoji iz dvije komponente: jedne, koja dolazi iz dubine, pa je toplija i bogatija na natriju, kloridima, sulfatima i teškim metalima i druge površinske, hladnije, jače radioaktivne i sa više kalcija, magnezija i hidrokarbonata. 2. *Izvor u spilji.* Pošto taj izvor leži više od glavnog izvora, javlja se u njem voda sada tek poslije obilnijih kiša. Svojom radioaktivnošću naliči na vodu iz glavnog izvora. 3. *Izvor na livadi.* Taj je izvor g. 1947. još postojao, ali je davao vrlo malo vode. Kasnije su ga poplave Mirne svojim muljem gotovo potpuno zatrpale. G. 1955. samo je travom obrasla udubina označavala mjesto, gdje se izvor nekoć nalazio. Te je godine ispitana cijela okolica Geigerovim brojačem, pa je baš na tom mjestu opaženo osobito intenzivno izbijanje. Nakon što je iskopano oko 20 m^3 zemlje, pojavili su se ostatci starog kupališta iz prve polovice XIX. vijeka i mali izvor visoke radioaktivnosti, koji po svojoj jakosti zauzimlje treće mjesto među poznatim radioaktivnim izvorima u Evropi (Tabela IV).

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