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Cross-section through Western Carpathians – digitized drawing by Professor D. ANDRUSOV, 1929

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POSSIBLE WAYS TO EXTRACT CHEMICAL ELEMENTS FROM GROUNDWATERS IN SLOVAKIA

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Cross-section through Western Carpathians – digitized drawing by Professor D. ANDRUSOV, 1929

Possibilities of extracting the mineral content of groundwaters - I.

The first study aimed at identifying the association of potential elements suitable for extraction from groundwaters in Slovakia was prepared by hydrogeochemists of the State Geological Institute Dionýz Štur - **Dušan Bodiš & Kamil Lopašovský** (1996).

Dr. Dušan Bodiš

In the study, they state that it is only of an introductory nature and, in case of interest, it must be elaborated in more detail from the point of view of the category of conditions. From the mentioned categories, they determined 4 basic levels, which are decisive in extracting elements from groundwater.

Cross-section through Western Carpathians – digitized drawing by Professor D. ANDRUSOV, 1929

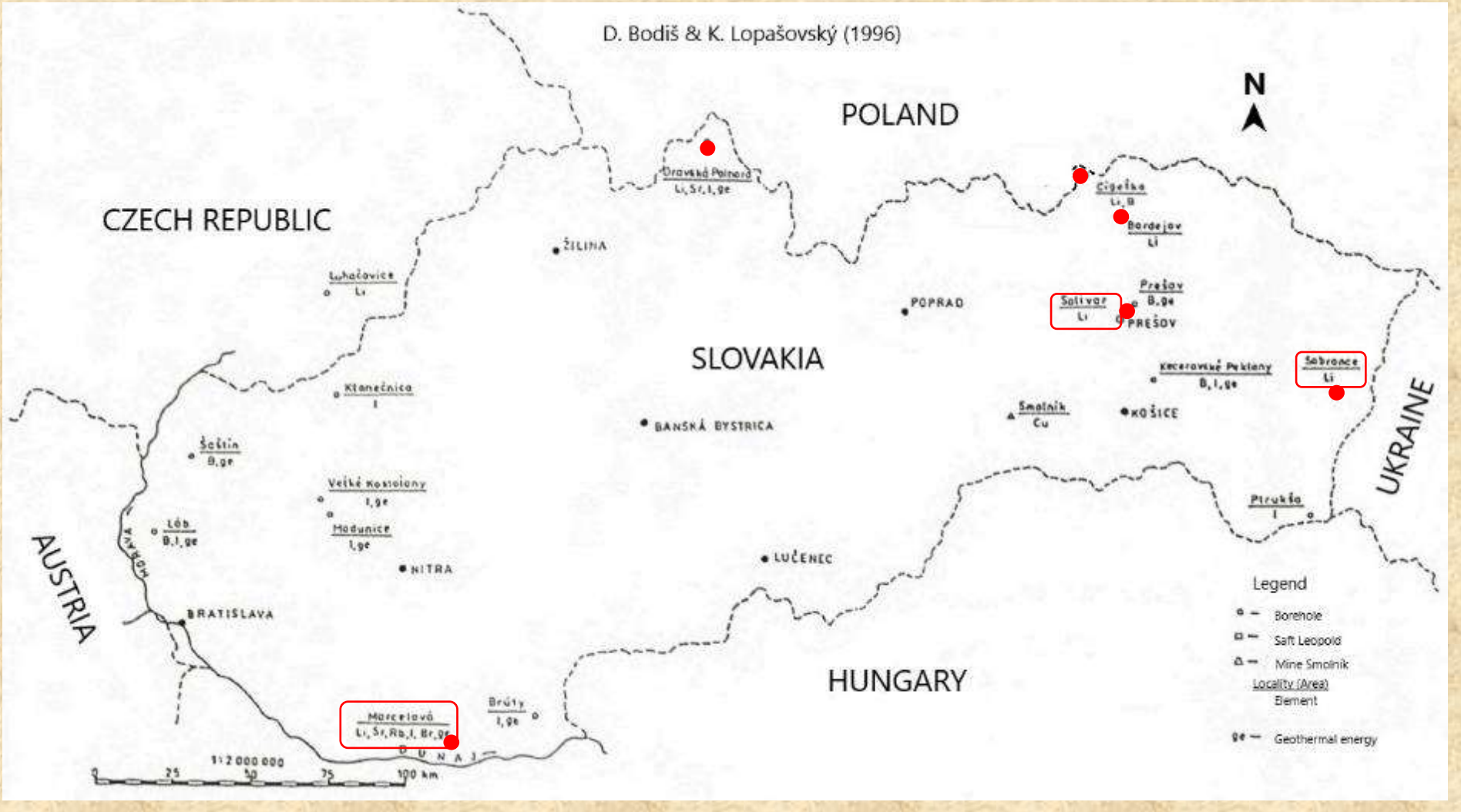
Possibilities of extracting the mineral content of groundwaters - II.

From the geochemical perspective of their extraction, the ability to concentrate individual elements in groundwater, whether from the rocks of the earth's crust or ocean water, currently or in the past during marine transgressions, results, while they could be preserved in **hydrogeologically closed structures**.

The content ratio of elements in groundwater and rocks (Table 1) roughly documents the ability of individual elements to concentrate in groundwaters. The elements with the highest value of this ratio also benefit from the waters to the greatest extent. From the point of view of the exploitation of these elements, their maximum concentration, or even concentration as such, only one of the factors. It only points to the potential possibility of their extraction from groundwater.

In the conditions of the Western Carpathians in Slovakia (Figure 1), based on existing knowledge, the following elements are potential for extraction from groundwater: **lithium (>10 mg.l^{-1}), strontium (>200 mg.l^{-1}), iodine (> 18 mg.l^{-1}), bromine (> 130 mg.l^{-1}), boron (> 130 mg.l^{-1}) and copper (> 100 mg.l^{-1})**.

Figure 1 Schematic map potential sources of extracting elements from groundwater



Cross-section through Western Carpathians – digitized drawing by Professor D. ANDRUSOV, 1929

Possibilities of extracting the mineral content of groundwaters - III.

An overview of the content of elements in the rocks of the earth's crust, in ocean water (average composition of ocean water) and from the maximum content of elements in groundwater results in very interesting conclusions for the **geochemical perspective** of their extraction from groundwater (Table 1).

Table 1

Element	Mean content in rocks	Max. content in groundwaters	Content in ocean water	Groundwater/ rock
	(ppm)	($mg.l^{-1}$)	($mg.l^{-1}$)	
Li	32	700	0,2	21,9
Na	25 000	160 000	10 500	6,4
K	25 000	60 000	380	2,4
Rb	150	960	0,12	6,4
Cs	3,7	25	0,0005	6,75
Mg	18 700	110 000	1 350	5,9
Ca	29 600	205 000	400	6.9
Sr	340	10 000	8	29,4
Cu	47	46 500	0,003	989,4
U	47	100	0,003	40
B	12	23 000	4,6	1916
Cl	170	400 000	19 000	2 353
Br	2,1	17 500	65	8 333
I	0,4	1 400	0,06	3 500
As	1,7	905	0,003	532,4
W	1,3	56	0,0001	43

By the geochemical perspective we mean the ability the concentration of individual elements in groundwater from the rocks of the earth's crust or ocean water in the present or in the past during marine transgressions, which caused their preservation in **hydrogeologically closed structures** until today.

Cross-section through Western Carpathians – digitized drawing by Professor D. ANDRUSOV, 1929

Possibilities of extracting the mineral content of groundwaters - IV.

The categories of conditions for extracting potential elements from groundwaters were defined in the following points:

- - groundwater reserves,
- - technological possibilities of obtaining them,
- - complexity of extracting elements (exploitation of several elements with the simultaneous use of geothermal energy and gases).
- - the world economy and the price of individual elements,
- - comparing the price of an element when it is extracted from rocks and groundwaters,
- - costs associated with environmental impact extraction of elements from groundwaters (waste disposal products).

Basic levels decisive in the extraction of elements from groundwater

- physicochemical and geochemical properties of elements
- technology • economy • ecology

Cross-section through Western Carpathians – digitized drawing by Professor D. ANDRUSOV, 1929

Groundwaters of the Western Carpathians potentially from the point of view extracting - Li.

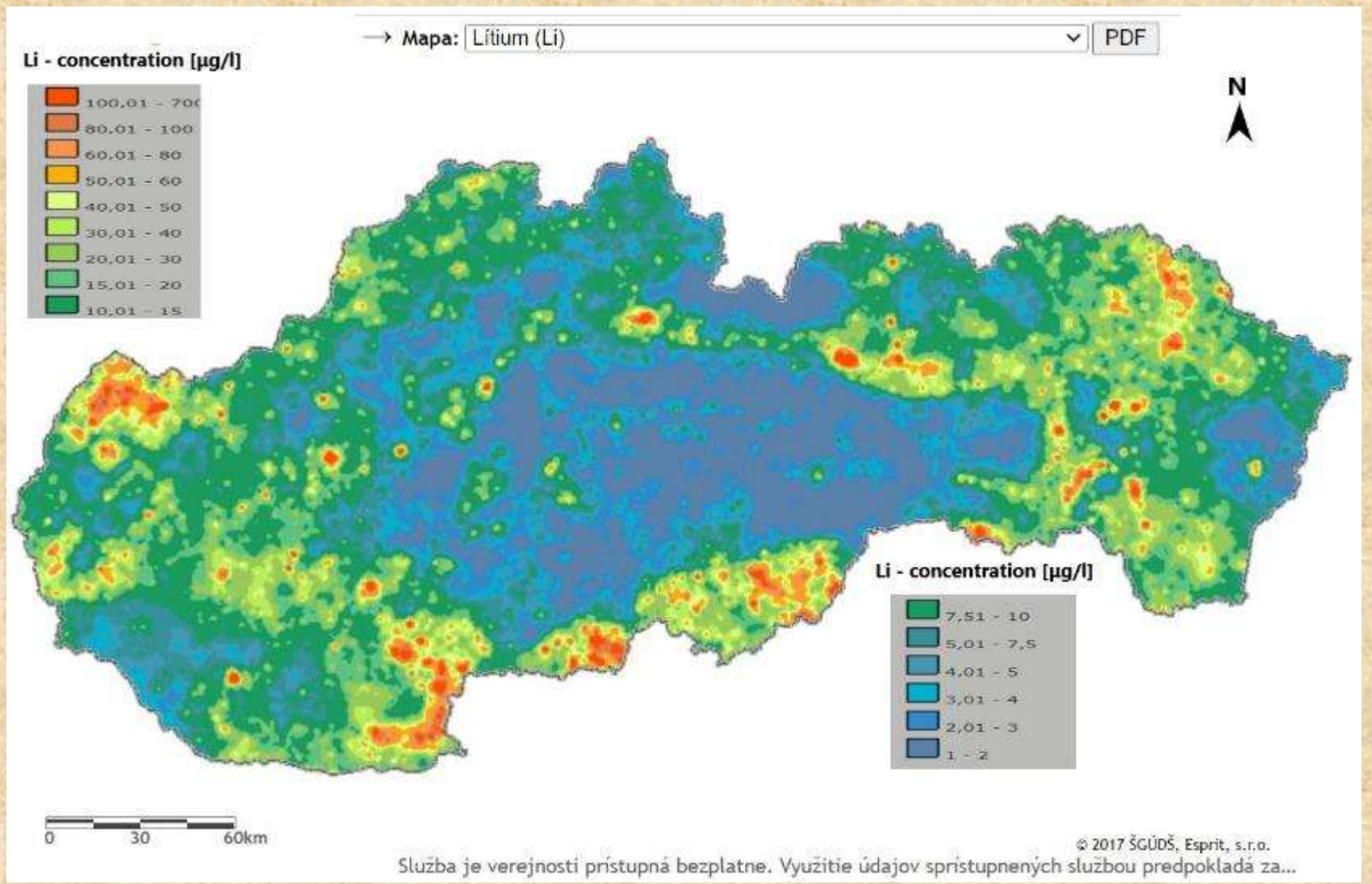
The subject of the study was the following types of groundwater (Li – grounwater: 1 – 700 μg.l^{-1}):

a) mineral waters of the Western Carpathians (> 10 mg.l^{-1}, Twater < 20 °C) – Cigeľka, Bardejov.

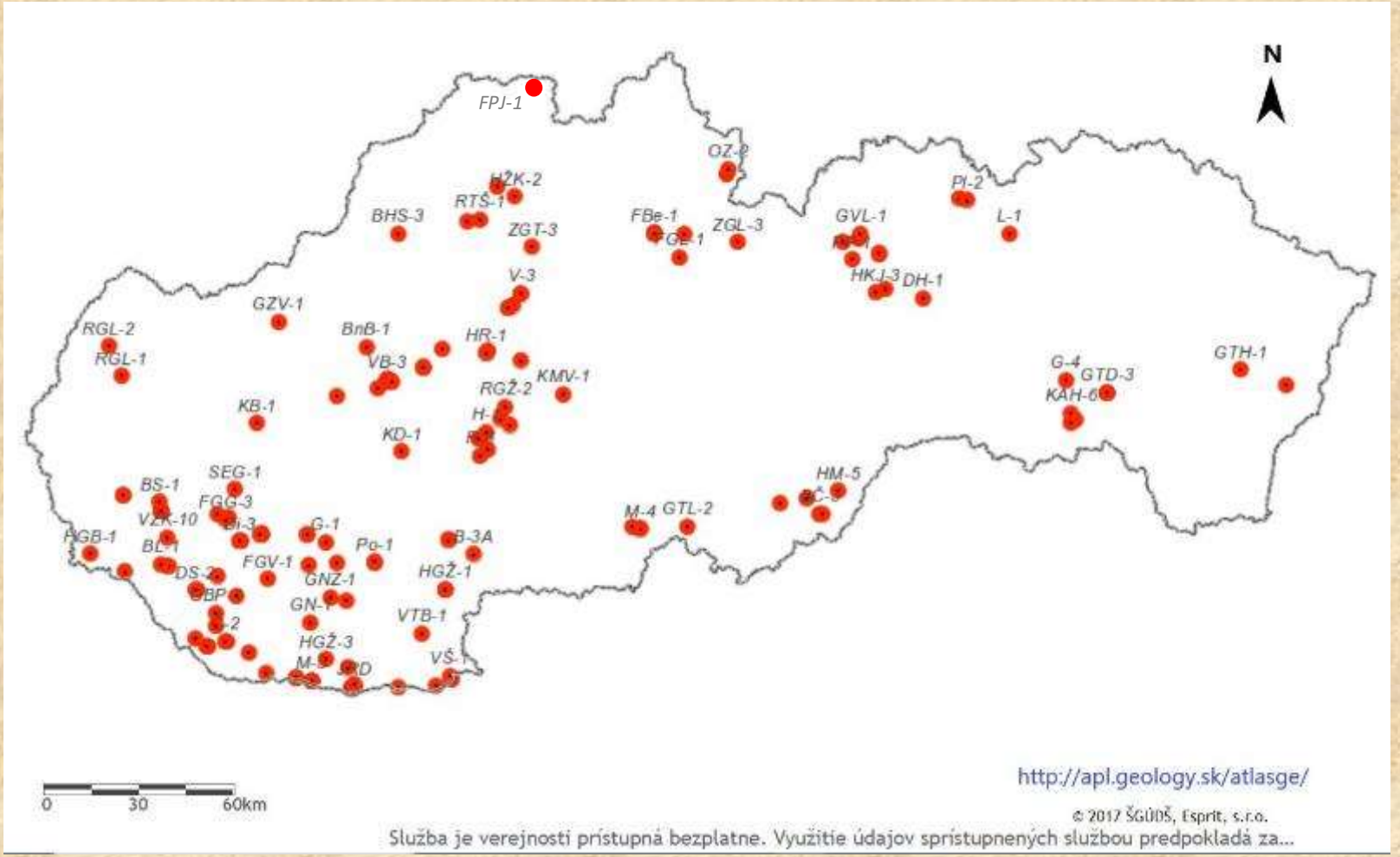
b) geothermal waters bound to Mesozoic carbonates and Neogene of the Western Carpathians (> 10 mg.l^{-1}, Twater > 20 °C) – Sobrance, Oravská Polhora, Marcelová,

c) secondary brine obtained during salt extraction in Prešov – Solivar (> 320 mg.l^{-1}).

Geochemical Atlas of Slovakia, part I: Groundwater



Schematic map potential sources of extracting elements from geothermal waters



Cross-section through Western Carpathians – digitized drawing by Professor D. ANDRUSOV, 1929

Groundwaters of the Western Carpathians potentially from the point of view extracting – mineral waters with Li.

Mineral waters of the Western Carpathians in Slovakia:

Cigeľka:
TDS: 30 $g.l^{-1}$
Twater: 7 – 12 °C
Na-HCO3-Cl
Source of healing water

Bardejov:
TDS: 10 $g.l^{-1}$
Twater: 10 – 15 °C
Source of healing water

Cross-section through Western Carpathians – digitized drawing by Professor D. ANDRUSOV, 1929

Groundwaters of the Western Carpathians potentially from the point of view extracting – geothermal waters with Li.

Geothermal waters - Mesozoic carbonates, Paleogene and Neogene sediments of the Western Carpathians (Li > 10 mg.l^{-1}, Twater > 20 °C):

<u>Sobrance (N/Mz)</u>
TDS: 10 g.l^{-1}
Twater: 33 °C
Li = **10** mg.l^{-1}, Na-Cl,
Sources of healing water

<u>Oravská Polhora – FPJ-1 (Pg),</u>
TDS: 20 g.l^{-1}, Twater: 18 –35 °C, Li = **31** mg.l^{-1}
Na-Cl, Depth = 2417 m

Sources of healing water

<u>Marcelová (Mz)</u>,
TDS: 90 g.l^{-1}
Twater: 65 °C
Li = **51** mg.l^{-1}, Na-Cl
Borehole with depth
1620 m is closed of cementation.

Cross-section through Western Carpathians – digitized drawing by Professor D. ANDRUSOV, 1929

Groundwaters of the Western Carpathians potentially from the point of view extracting – geothermal waters with Li.

lokalita: SOBRANCE
dátum odberu: 16. X. 1968

zdroj: prameň Hlavný
množstvo vzorky: 22,750 l

Fyzikálne a chemické vlastnosti

teplota °C	pH	zH	Ra, 10^{-10} Ci/l	Rn, 10^{-10} Ci/l	org. C mg/l
15,5	6,7	11,7	22,0	69,0	–

CO_2 mg/l	H_2S mg/l	HBO_2 mg/l	o-SiO_2 mg/l	celk. miner. mg/l
700,0	40 (1969)	24,95	30,40	9466,79

Iónové zloženie

katióny	mg/l	mval/l	mval %	anióny	mg/l	mval/l	mval %
Li^{1+}	10,40	1,498	0,46	Cl^{1-}	4010,17	131,219	39,84
Na^{1+}	2590,00	112,609	34,57	Br^{1-}	1,56	0,019	0,00
K^{1+}	220,00	5,626	1,73	J^{1-}	0,85	0,007	0,00
NH_4^{1+}	0,50	0,028	0,01	F^{1-}	3,46	0,182	0,06
Mg^{2+}	194,56	16,000	4,91	NO_2^{1-}	0,00	0,000	0,00
Ca^{2+}	527,05	26,300	8,08	NO_3^{1-}	0,35	0,006	0,00
Sr^{2+}	33,33	0,760	0,23	SO_4^{2-}	556,70	11,556	3,51
Ba^{2+}	–	–	–	HPO_4^{2-}	13,52	0,282	0,09
Mn^{2+}	0,00	0,000	0,00	HCO_3^{1-}	1305,40	21,400	6,50
Fe^{2+}	0,84	0,030	0,01	CO_3^{2-}	0,00	0,000	0,00
Al^{3+}	0,10	0,011	0,00	OH^{1-}	0,00	0,000	0,00
súčet	3576,78	162,862	50,00	súčet	5890,01	164,671	50,00

Stopové prvky (10^{-6} g/l)

As	0,0	Ni	< 5	Cu	4,00	Pb	2,00
Mo	nedá sa stanoviť	Co	0,0	Zn	11,60	U	0,1
Cr	0,0	Ti	< 20	spektrochemicky dokázaná prítomnosť Rb, Ag, Ba, Mn			

Plyny (obj. %)

	CO_2	H_2S	O_2	N_2	He	H_2	Ar	CH_4	celk. množstvo plynov ml/l
1	88,37	3,37	0,082	4,08	0,000085	–	0,085	0,021	358,4
2	–	–	1,9	95,00	0,002	–	2,00	0,50	14,8
3	–	–	–	–	–	–	–	–	–

Hydrochemické faktory a klasifikácia

$S_1(Cl)$	73,54	$S_2(SO_4)$	7,12	A_1	13,16	Mg/Ca	0,61	Sr/Ca 10^4	29,00	SO_4/M	0,035
$S_2(SO_4)$	0,00	S_3	0,00	A_2	0,02	Na/K	20,01	HCO_3/Cl	0,16	Cl/Br	906,30
$S_3(Cl)$	6,16	A_3	0,00	$S_{80:1}$	8,08	Ca/Na	0,23	Cl/Na	1,16		

základný typ nátrium-chloridový $S_1(Cl)$

Plynové faktory a klasifikácia

spontánny plyn			nekyslý plyn		
He / Ar	–	Ar . 10^4 / N_2 . 1,19	–	$K^{N_2}_{O_2}$	50,0	Ar . 10^4 / N_2 . 2,5	84,2

silno sírovodíková, stredne uhličitá, dusíková voda

Horniny

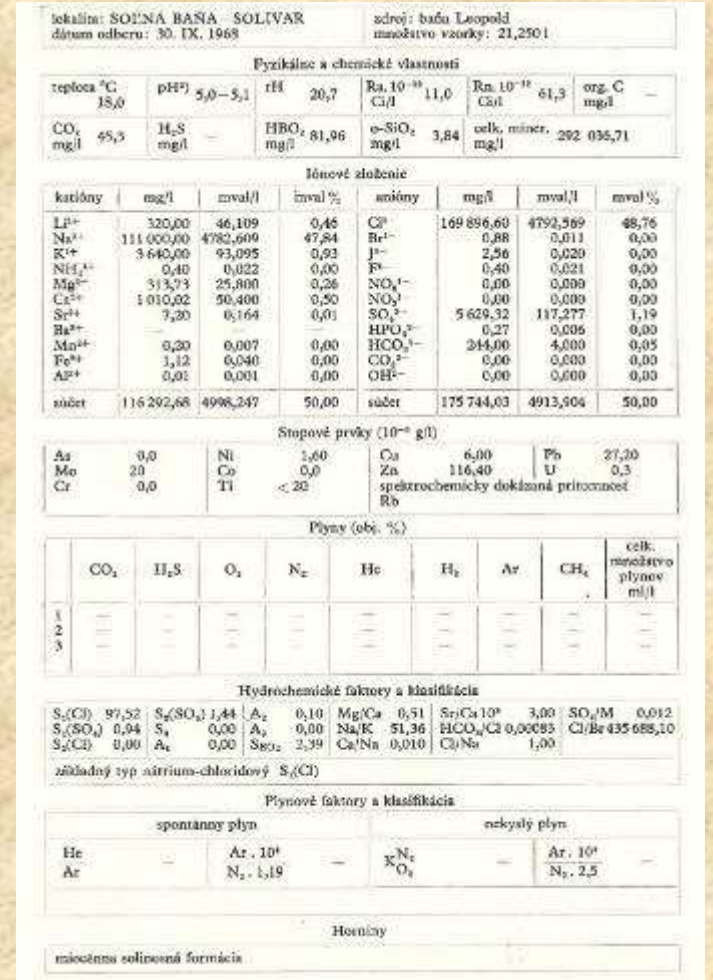
kvartér, v podloží pliocénne a miocénne sedimenty a triasové karbonáty

Detail:
Sobrance (N/Mz)
TDS: 10 g.l^{-1}
Twater: 18 – 35 °C
Na-Cl

Spring Hlavný prameň Sobrance
Twater = 18 °C, Li (mg.l^{-1}) = 10

Cross-section through Western Carpathians – digitized drawing by Professor D. ANDRUSOV, 1929

Groundwaters of the Western Carpathians potentially from the point of view extracting – secondary brine obtained during salt extraction.



lokalita: SOĽNÁ BAŇA SOLIVAR — zdroj: baňa Leopold
dátum odberu: 30. IX. 1968 — množstvo vzorky: 21,250 l

Fyzikálne a chemické vlastnosti

teplota °C	18,0	pH[a]	5,0–5,1	rH	20,7	Ra. 10^{-10} Ci/l	11,0	Rn. 10^{-10} Ci/l	61,3	org. C mg/l	–
CO_2 mg/l	65,3	H_2S mg/l	–	HBO_2 mg/l	81,96	o-SiO_2 mg/l	3,84	celk. miner. mg/l	292 036,71		

Iónové zloženie

katióny	mg/l	mval/l	mval %	anióny	mg/l	mval/l	mval %
Li^{1+}	320,00	46,109	0,46	Cl^{1-}	169 896,60	4792,569	48,76
Na^{1+}	111 000,00	4782,609	47,84	Br^{1-}	0,88	0,011	0,00
K^{1+}	3 640,00	93,095	0,93	J^{1-}	2,56	0,020	0,00
NH_4^{1+}	0,40	0,022	0,00	F^{1-}	0,40	0,021	0,00
Mg^{2+}	313,73	25,800	0,26	NO_3^{1-}	0,00	0,000	0,00
Ca^{2+}	1 010,02	50,400	0,50	NO_2^{1-}	0,00	0,000	0,00
Sr^{2+}	7,30	0,164	0,01	SO_4^{2-}	5 629,32	117,277	1,19
Ba^{2+}	–	–	–	HPO_4^{2-}	0,27	0,006	0,00
Mn^{2+}	0,30	0,007	0,00	HCO_3^{1-}	244,00	4,000	0,05
Fe^{2+}	1,12	0,040	0,00	CO_3^{2-}	0,00	0,000	0,00
Al^{3+}	0,01	0,001	0,00	OH^{1-}	0,00	0,000	0,00
súčet	116 292,68	4998,247	50,00	súčet	175 744,03	4913,906	50,00

Stopové prvky (10^{-6} g/l)

As	0,0	Ni	1,60	Cu	6,00	Pb	27,20
Mo	20	Co	0,0	Zn	116,40	U	0,3
Cr	0,0	Ti	< 20	spektrochemicky dokázaná prítomnosť Rb			

Plyny (obj. %)

	CO_2	H_2S	O_2	N_2	He	H_2	Ar	CH_4	celk. množstvo plynov ml/l
1	–	–	–	–	–	–	–	–	–
2	–	–	–	–	–	–	–	–	–
3	–	–	–	–	–	–	–	–	–

Hydrochemické faktory a klasifikácia

$S_1(Cl)$	97,52	$S_2(SO_4)$	1,44	A_1	0,10	Mg/Ca	0,51	$Sr/Ca\ 10^3$	3,00	SO_4/M	0,012
$S_1(SO_4)$	0,94	S_3	0,00	A_2	0,00	Na/K	51,36	HCO_3/Cl	0,00083	Cl/Br	435 688,10
$S_2(Cl)$	0,00	A_3	0,00	S_{SO_4}	2,39	Ca/Na	0,010	Cl/Na	1,00		

základný typ: natrium-chloridový $S_1(Cl)$

Plynové faktory a klasifikácia

spontánny plyn				nekyslý plyn			
He / Ar	–	$Ar \cdot 10^4 / N_2$	1,19	$K\frac{N_2}{O_2}$	–	$Ar \cdot 10^4 / N_2$	2,5

Horniny

miocénna solinosná formácia

Prešov- Solivar/ shaft Leopold

The highest value of lithium content was documented in the brine from Prešov Solivar, which represented **320** mg.l^{-1}.

It is a brine with a total mineralization value of 290 g.l^{-1}, significant Na-Cl type with a lithium content of 320 mg.l^{-1}. The Cl/Br ratio of this brine is 435 6881 indicating its origin by dissolution of salts by infiltrating meteoric waters.

This brine was used to produce salt by evaporation.

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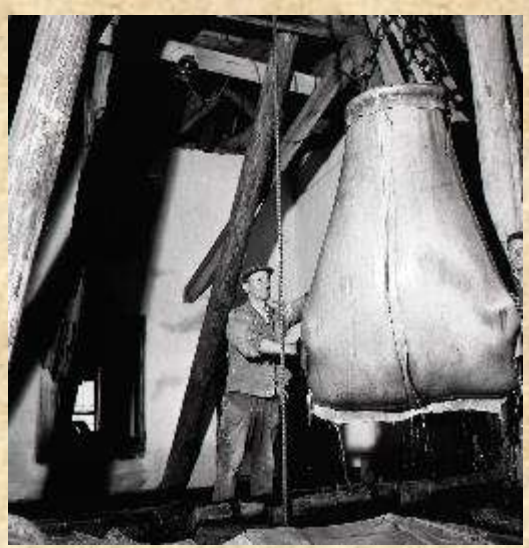
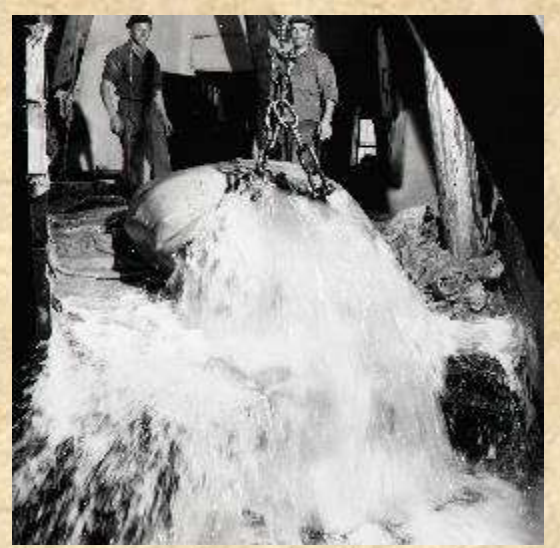
Groundwaters of the Western Carpathians potentially from the point of view extracting – secondary brine obtained during salt extraction.

Prešov- Solivar/ shaft Leopold

The process of brine collection to salt production.





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Groundwaters of the Western Carpathians potentially from the point of view extracting – secondary brine obtained during salt extraction.

Prešov- Solivar/ shaft Leopold
Evaporation of brine and its storage.

Evaporation basin

Storage of salt

Cross-section through Western Carpathians – digitized drawing by Professor D. ANDRUSOV, 1929

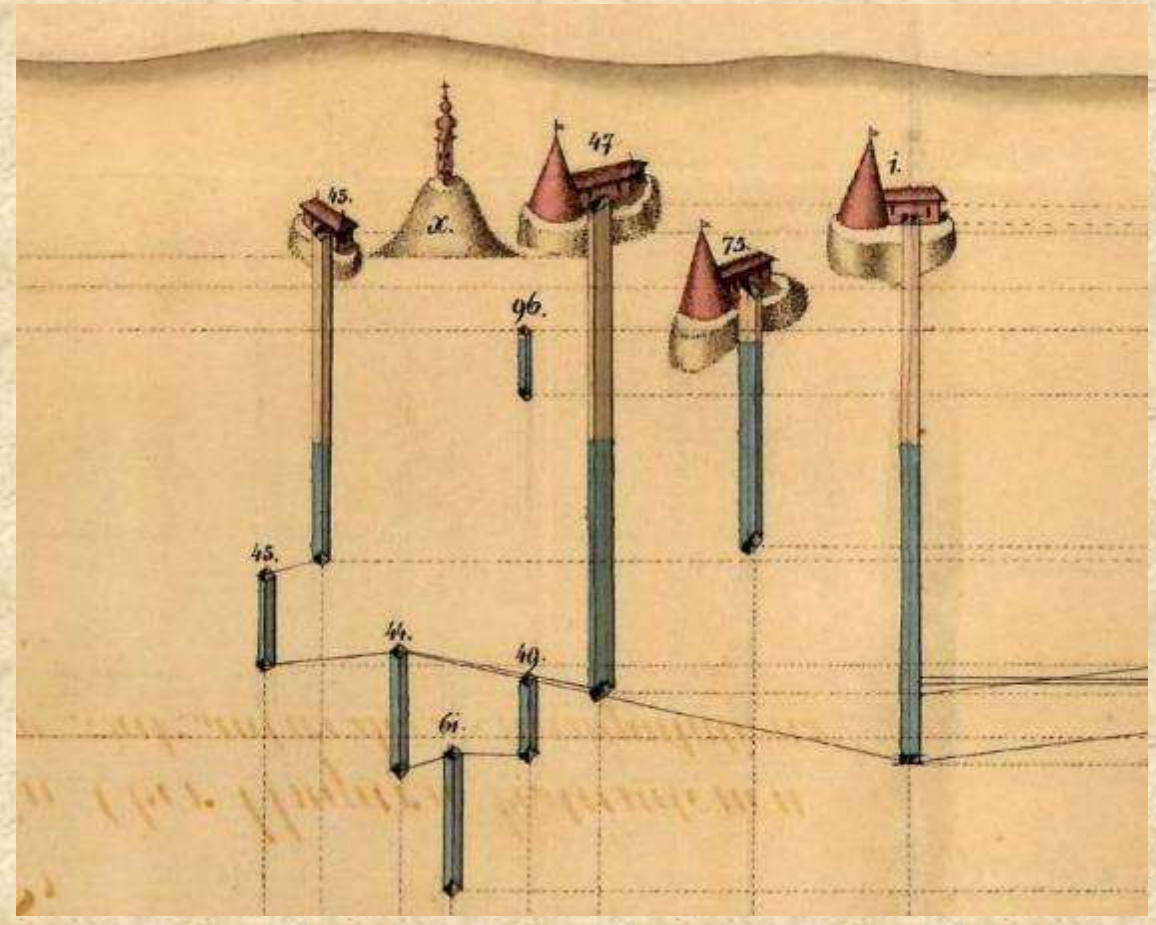
Conclusion

Groundwater suitable for the extraction of elements can be defined as water containing such an amount of elements that ensures their profitable production in specific hydrogeological conditions at a given technological level.

From the point of view of the exploitation of these elements, their maximum concentration, or concentration at all, just one of the factors. They only point to their potential for extraction from groundwater.

In the conditions of the Western Carpathians in Slovakia, based on existing knowledge, the following elements are potential for extraction from natural waters: **lithium, strontium, iodine, bromine, boron and copper**.

The mentioned selection of elements was made on the basis of geographical, geological and geochemical criteria and conditions. It follows that the potential contents have a rather **local meaning**, primarily because of their limited amount. We can partially eliminate the mentioned limitation by primarily using the heat of geothermal water and subsequently several elements.



Prešov - Solivar

Thank you for attention.