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Hydrogeochemical characteristics of mineral and thermal waters

title: **CO2-rich mineral waters from the area of Benedikt and Ščavnica Valley, North-Eastern Slovenia**

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INTRODUCTION

The Mura Basin, North-Eastern Slovenia, belongs to the south-westernmost extending of the system of Pannonian basins. It is filled with Neogene, Pliocene and Quaternary sediments developed mainly as clastic deposits in marine, brackish and continental – limnic and fluvial environment. Along the western basin margins, mineral waters are locally abundant, particularly in the Radenci, Benedikt and Ščavnica valley areas (Kralj and Kralj, 2000). Mineral waters occur in shallow aquifers or spring out along fault systems (Kralj, 2001, 2004). The main cause of their formation is penetration of carbon dioxide from pre-Tertiary basement towards the surface (Kralj et al., 2009).

MINERAL WATER COMPOSITION

At Benedikt and in the Ščavnica valley, mineral waters occur in shallow aquifers composed of Badenian and Sarmatian clastic sediments. Their composition is relatively variable; the waters belong to the Na-Ca-HCO_3, Ca-(Na)-HCO_3, or Ca-Mg-(Na)-HCO_3 hydrogeochemical facies (Tab. 1).

Table 1. Composition of mineral waters from Benedikt and Ščavnica valley.

Major ions (mg/L)	P 1	P 2	A 1	A 2	I	O	St	Sp
NH_3^+	0.41	1.74	4.83	2.05	3.07	0.90	0.86	0.44
Na^+	20	36	51	69	104	685	162	30
K^+	3.4	8.8	21	20	15	65	13	4.8
Ca^{2+}	246	420	800	660	487	417	375	570
Mg^{2+}	69	94	180	123	203	69	32	23
Fe^{2+}	4.56	8.40	7.20	2.90	6.63	1.22	2.67	0.84
Mn^{2+}	0.525	0.340	0.170	0.100	0.143	0.178	0.352	0.540
J^-	0.01	<0.05	<0.05	0.10	0.02	0.21	0.05	<0.01
F^-	0.10	0.13	0.04	0.10	<0.01	0.78	0.22	0.22
Cl^-	9.2	5.0	3.5	4.5	7	170	25	8
HCO_3^-	980	1800	3400	2900	2590	2970	1690	1620
SO_4^{2-}	15	14	23	22	2	118	19	37
Elements, gases, compounds, parameters								
CO_2	2000	1900	1830	1800	2500	3800	3300	2600
P	0.104	0.015	<0.015	0.024	0.016	0.058	0.023	0.180
SiO_2	17	27	43	80	18	15	17	30
TOC	1.5	1.7	1.3	1.0	0.9	0.8	0.6	0.8
TDI	1349	2391	4536	3885	3420	4499	2320	2295
pH	6.00	6.10	6.37	6.42	6.22	6.22	6.01	6.22
Trace elements (ppb)								
As	0.4	3.6	0.2	0.2	0.1	0.7	0.5	1.9
B	30	60	80	46	100	1400	200	34
Ba	98	230	520	350	640	63	210	170
Cd	0.04	<0.01	3.1	<0.01	0.21	0.13	0.01	1.3
Co	1.1	2.0	2.0	0.8	0.8	0.5	1.1	<0.1
Cr	7.3	1.0	0.4	0.5	6.7	5.5	0.7	0.3
Cs	<0.01	0.13	1.5	1.0	0.88	11.5	0.01	8.3
Cu	0.1	9.1	2.2	0.4	<0.1	10.0	1.4	5.4
Ni	16	14	24	16	32	20	25	1.9
Rb	13.9	24.8	106	82.4	53.4	346	61.2	213
Sc	7.8	7.7	13.4	8.9	25.9	23.2	9.3	1.9
Se	0.4	0.9	0.5	<0.1	0.7	9.4	1.8	2.1
Sr	577	1120	2330	1540	8180	1090	2170	876

P 1, P 2 — Pavla; A 1, A 2 — Ana; I — Ivanjševci, O — Očeslavci; St — Stavešinci; Sp — Špindler

The amount of total dissolved ions ranges from about 900 mg/L to over 4.5 g/L. In the Benedikt area, three shallow boreholes – Helena (H), Pavla (P) and Ana (A), reached a depth of 30 m, 60 m and 100 m, respectively. A natural spring of Špindler (Sp) occurs about 1 km southerly from the Helena, Pavla and Ana boreholes. In the Ščavnica valley, mineral waters are captured by boreholes at Očeslavci (O), Ivanjševci (I) and Stavešinci (St).

DISCUSSION

Three main processes are involved in the formation of mineral waters: 1, cooling and chemical change of deep thermal waters that rise from deeper parts of the Mura Basin, 2, their mixing with normal ground-waters from shallow aquifers, and 3, penetration of carbon dioxide from pre-Tertiary basement and water-rock interaction.

The waters originating from deeper thermal aquifers essentially belong to Na-HCO_3-(Cl) hydrogeochemical facies. The water captured in Očeslavci contains the highest recognised amount of sodium and chloride ions, potassium, sulphate, bromide, iodide and fluoride ions, boron, rubidium and cesium (Tab. 1; Fig. 1). A minimum proportion of modified thermal water in mineral water from Očeslavci is estimated to 25%. Mineral water from the Ščavnica valley captured at Stavešinci contains a lower proportion of modified and cooled thermal water – its content is estimated to 5–6%.

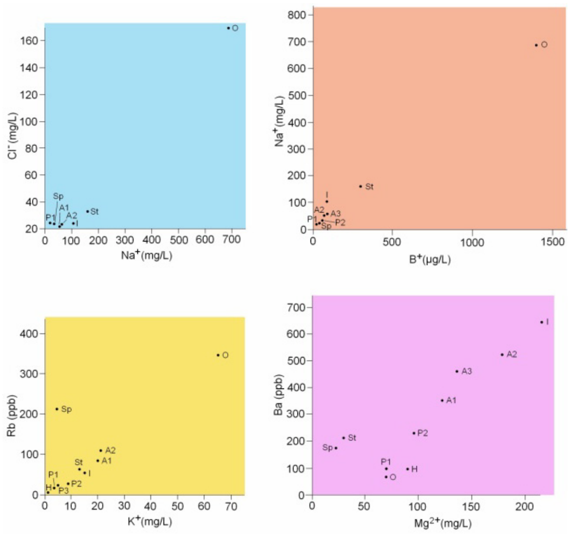

Figure 1. Elemental ratios in mineral waters from the Benedikt and Ščavnica valley areas: Na^+ vs. Cl^-; B^+ vs. Na^+; K^+ vs. Rb; Mg^{2+} vs. Ba. For sample explanation see Tab. 1.

Mineral waters captured in the wells Helena (H), Pavla (P) and Ana (A), and in the spring of Špindler (Sp) in the Benedikt area, are essentially ground waters having an increased amount of total dissolved solids owing to the penetration and mixing of carbon dioxide in the aquifers, and the consequent enhanced water-rock interaction. Calcite dissolves preferentially, while the dissolution of dolomite and illitic clays tends to become more intensive in deeper aquifers (Fig. 1, the diagrams K^+ vs. Rb and Mg^{2+} vs. Ba). The amount of magnesium seems to depend on local abundance in the aquifer sediment. The highest abundance of magnesium was recognised in the water from Ivanjševci. Barium mainly follows magnesium, the shift from the main trend (Fig. 1) can be related to preferential near-surface adsorption of magnesium on clay minerals leaving more barium in the solution. Chemical composition of carbonate precipitate from the Ana well in Benedikt (Tab. 2) has shown that the Mg/Ba ratio in the solid precipitate is relatively low and amounts to about 11, while the ratio in the water averages to 350. The Mg/Ba ratios in the precipitate and water do not indicate preferential incorporation of magnesium in the solid which would fractionate the elements towards the enrichment of barium in the water.

Potassium and rubidium originate from both, cooled thermal waters and from water-rock interaction (Fig. 1). They are higher in deeper aquifers in the Benedikt area and indicate that water-rock interaction probably affects to some extent illitic clays, too. Anomalously high rubidium with respect to potassium was analysed in the water from the spring of Špindler. It can be related either to preferential adsorption of the potassium ions on clay minerals or precipitation of solids that easily incorporate potassium and cause fractionation of potassium and rubidium. The content of both, potassium and rubidium was below their detection limit in the precipitate from the Ana spring, and no further conclusions can be done. Several other trace elements were analysed but their abundance was below their detection limits by the combined ICP-MS analytical method.

Table 2. Chemical composition of carbonate precipitate at the Ana spring, the Benedikt area.

Oxide (%)	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	P_2O_5
HB-1/05	0.31	<0.1	0.04	0.87	0.51	53.50	0.02	<0.04	0.02

Oxide (%)	MnO	FeO	LOI	TOT C	TOT S	CO_2	H_2O^+	Sum
HB-1/05	0.03	0.19	44.6	12.12	0.05	42.00	9.27	99.91

Element (ppm)	Ba	Sr	Ni	Co	Cu	Mo	Th	Y
HB-1/05	270.4	862.1	3.7	0.7	2.8	0.1	0.1	0.2

Element (ppm)	Zn	Pb	As	Sb	Se
HB-1/05	14	0.8	0.8	0.1	0.5

CONCLUSION

The formation of mineral waters in the Benedikt area and Ščavnica valley is rather complex. It is related to the mixing of deep waters and subsurface ground waters, and the reactions of carbon dioxide that penetrates from pre-Tertiary basement and dissolves in the waters. Higher proportions of cooled and chemically modified deep waters were recognised in mineral waters from the Ščavnica valley where the old thermal waters rise to the surface along deep faults. Carbon dioxide that mixes with, and dissolves in the waters enhances water/rock interaction which further modifies chemical composition of mineral waters towards the enrichment in calcium and magnesium ions.

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