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THE UNUSUAL CHEMISM OF MINERAL WATERS AT DUDINCE

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Abstract: From the point of view of quality, the medicinal mineral waters of Dudince have an extraordinary position among the mineral waters of the Western Carpathians. The waters are of the Na-Ca-/Mg/-HCO_3-Cl-/SO_4/ type with M = 5 - 6 g.l^{-1}, temperature 28 °C, content of CO_2 up to 1.8 g.l^{-1} and H_2S up to 10 mg.l^{-1}. The waters are notable for the stability of their chemical composition, with the exception of gases. Apart from this, other mineral waters, belonging to neighbouring hydrothermal structures also occur at Dudince.

Key words: mineral waters, chemical composition, isotopes, stability of quality, Dudince, Western Carpathians.

Introduction

The mineral and thermal waters occur at Kalinčiakovo, Santovka, Dudince, Slatina and Túrovce, in the inner side of the Western Carpathians arc, the south western margin of the Central Slovak Neovolcanics, on the so-called Levice spring line. They are important sources of mineral waters for Slovakia, which are used for different purposes (bathing therapy, bottling, recreation). The mineral and thermal waters of Dudince have an extraordinary position among them. The mineral water with its physico-chemical composition and content of gases enables its wide use for bathing therapy and it occupies a special position among the mineral waters of the Carpathian arc.

Thanks to its beneficial effects, the mineral waters of Dudince were already known and used in the past. Twenty two small basins or baths cut into the travertine are often called Roman Baths, a remnant of the visit of Roman legions to the place. However material monuments to prove this view are lacking. In the work "Ungarnskurorte und Mineralquellen" (1859), D. Wachtel described 9 springs with temperatures of 13 - 19 °C at Dudince. He described the water as iodine, alkaline-saline, hydrogen sulphide acidulous water. According to Tognia (1843) the waters contain Na_2CO_3, $MgCO_3$, NaCl, Na_2SO_4, $CaSO_4$, Si, I, H_2S, and free CO_2. The first basin for the so called "Merovce Spring" was established in 1900, and according to some information from the Austro-Hungarian businessman Kálman Brazzay, Dudince mineral water was bottled in white, thick walled bottles.

The bottling of mineral water at Dudince later stopped. From the 1940s to 1960s, geologist as Ľ. Ivan, M. Maheľ and O. Hynie were especially devoted to the mineral waters and their infiltration area.

In 1953 research on the hydrogeological structure of Dudince was carried out. After completing the research, after a decade of observation, the total output of the Dudince spring was regulated at a consumption of 17 l.s^{-1}. This capacity was used as a basis for deciding the balance of uses of the water. The final capacity of the spa was set at 1,400 beds and bathing therapy at 1,200 procedures a day. On the basis of the quality of the mineral water, the baths of local importance, with only 16 beds up to 1968, was developed into a modern bathing therapy centre of international importance.

In 1959, O. Franko produced "A proposal for temporary protected zones of natural medicinal springs at the spas of Dudince, Slatina, Santovka and Malinovec". The basic principles of the internal and external protection and protective zones for the sources of natural medicinal water in Dudince, as well as the water tables at Santovka and Slatina were proposed by Melioris et al. (1986).

The spa of Dudince is situated in the basin of the river Štiavnica, laying on its left bank at a height of 139 m above sea level. The average annual total precipitation at Dudince is 616 mm, average annual total evapo-transpiration (E) is 464 mm, and the average annual air temperature over 10 °C.

Brief description of geological and tectonic relations

Pre-Tertiary Alpine folded rocks, Tertiary molasse sediments, Quarternary cover sediments and travertines form the region of the Levice spring line between Levice and Túrovce (Fig. 1).

Pre-Tertiary rocks outcrop on the surface in the area of the Túrovce-Levice horst. The Veporicum and higher nappes of the Western Carpathians form the pre-Tertiary underlying rocks. The Veporicum forms the pre-Tertiary underlying rocks in the eastern part of the spring district, between Horné Túrovce and Santovka. Crystalline shales (phylites and quartzites) - the Hron complex - represent the oldest formation known up to now in the region studied. A dynamo-metamorphic formation, which may be divided into a pelitic-psammitic (mostly Permian) horizon and a horizon of siliceous limestones represent the Permian (cover of the Veporicum).

Quartzites and siliceous shales of light colour form the Lower Triassic (cover of the Veporicum). At Dudince, Lower Triassic quartzites were found in boreholes at a depth of 70 - 80 m. The whole Permian formation is dynamo-metamorphosed.

Carbonates of the Middle and Upper Triassic or Jurassic, Mesozoic cover of the Veporicum were not directly found in the subject region. However, their presence in the underlying rocks is indicated not only by the chemical type of the waters, and the extensive deposits of travertine in Dudince, but also by the positive gravity anomaly found in this region (Vass et al. 1979).

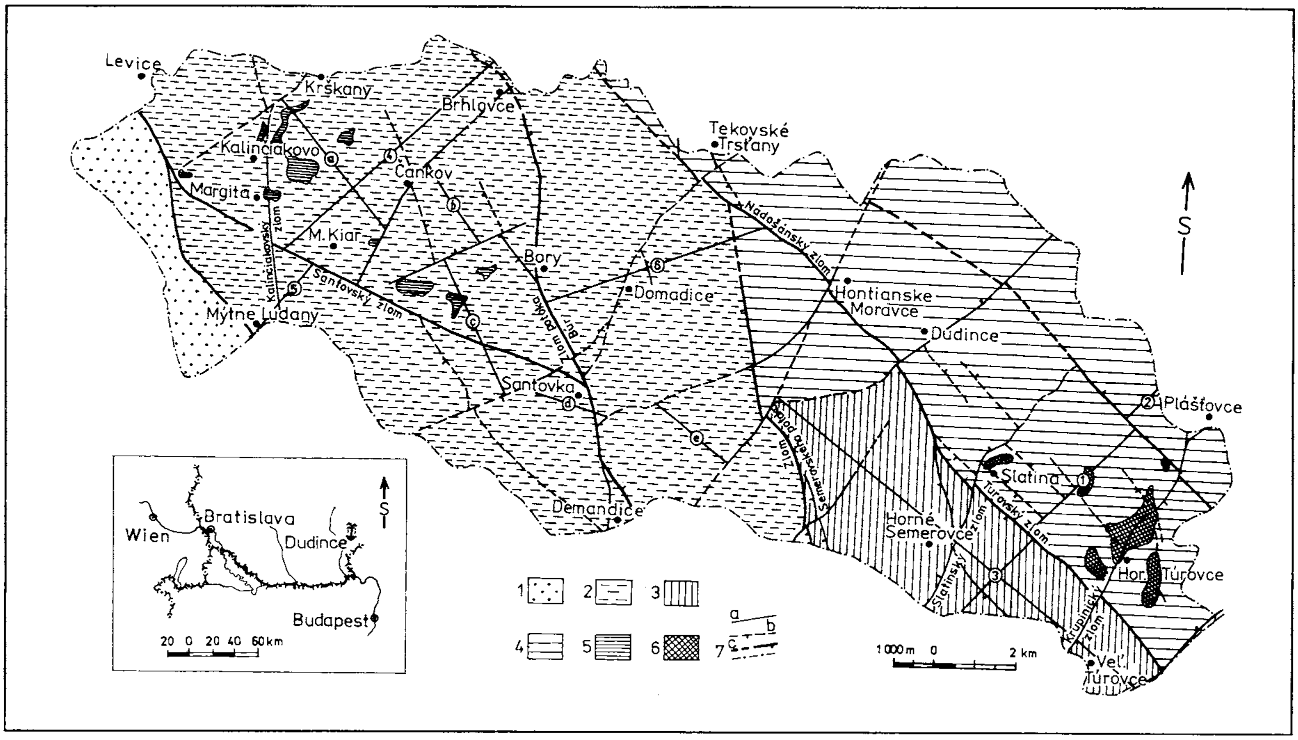

Fig. 1. Situation of the Levice spring line.
Legend: 1 - Pontian and Pliocene; 2 - Lower Sarmatian; 3 - Badenian pelitic and sandy facies; 4 - Badenian in volcano-detritic facies; 5 - Mesozoic of the higher nappes (or Choč -Gemerid); 6 - Veporide, Upper Paleozoic - Lower Triassic; 7 - a-known faults, b-supposed faults, c-faults limiting the NW to SE fault structures boundary of the protected region.
Fault structures of the NW-SE system: 1 - Túrovce partial horst; 2 - Plášťovce Depression; 3 - Semerovce Depression; 4 - Santovka-Levice partial horst; 5 - Ludany subsided block; 6 - Domadice subsided block.
Fault structures of the NE-SW system: a - Kalinčiakovo partial horst; b - Brhlovce subsided block; c - Bory raised block; d - Santovka subsided block; e - Demandice raised block.

Borehole GK-10 penetrated Triassic beds of Gemerid type near Ladzany, about 9 km north of Dudince, at a depth of about 470 m.

Miocene beds represented by Badenian and Sarmatian lie discordantly and transgressively on the pre-Tertiary underlying rocks.

Badenian beds occur on the surface east of the fault running along the valley of the Nadošanský and Semerovský brooks (Fig. 1). Quartzite gravels (in borehole HDV-1 at a depth of 45 - 81 m, in borehole HDV-2 at a depth of 50 - 71 m), quartzite and kaolinite sands, which probably represent the equivalent of Túrovce detritic beds (base of the Miocene) occur in the deposits overlying the quartzites of the Middle Triassic at Dudince. In the area north -east of the Túrovce horst, the Badenian marine beds are developed as volcano-detritic sediments, and south-east of the horst as pelitic to silty facies. (Fig. 1).

Fluvial sediments and travertines, of which the oldest may be of Pliocene age and others of Pleistocene and Holocene age and loess form the Quarternary.

The folding processes which formed the structure of the pre-Tertiary underlying rocks, occurred in the Upper Cretaceous, as everywhere in the Western Carpathians.

The faults interrupting the area of the Levice spring line, and the wider region of Dudince belong to two fault systems, north-west to south-east, and north-east to south-west (Fig. 1). There is also a fault system with a north to south direction. We think that all the faults have an old basis, but movements also occurred on them, in the Upper Miocene and Quarternary (Vass et al. 1979).

The fault system with the north-west to south east direction defines the most important elevated structure of the subject territory, the Túrovce-Levice horst (Vass in Melioris & Vass 1982). On it, the pre-Tertiary underlying rocks outcrop on the surface or are found at no great depth (in Dudince at a depth of 70 - 80 m). The horst is transversely divided into two segments - the Túrovce, and the Santovka-Levice. The horst is transversely divided by a fault with a north to south direction belonging to the Zázrivá-Budapest fault zone.

The north-east to south-west directed fault system transversely segments the fault system with a north-west to south-east direction. South of Dudince this fault system creates an extensive depression, the central part of which is covered by a hollow of the Semerovce fault system with a north-west orientation. The isometric division of the Semerovce depression is a significant effect of the crossing of faults. The modelling of the depression was effected by the faults of the north-east system, the fault of the Selecký brook and the Slatina fault (both oriented to the south-west) and faults with an opposite orientation running between Dolné Semerovce and Dudince (Vass in Melioris & Vass 1982).

Chemical characteristics of underground waters of the Quarternary sediments

The accumulation of ordinary underground waters in Dudince and its surroundings is connected with sands and gravels of the Quarternary sediments of the river Štiavnica, which reach a thickness of up to 15 m. The level of the underground waters is mostly confined and is found 4 - 6 m below the surface. The variation of the level is about two metres. During the year the river Štiavnica mostly drains the underground waters, the addition of sediments from the stream occurs only at high states in the surface stream.

The source of the underground waters is mostly water from precipitation, which infiltrates through the soil cover and the upper part of the Quarternary sediments (thickness up to 8 m) formed by clays, and sands as well as silty clays progressing to clayey sands and further to sandy gravels. Locally sandy layers are lacking, and loamy or clayey gravel. In some places clayey-sand and mud sediments or travertines were found. Mineralization of the waters of the Quarternary sediments, not influenced by mineral waters, is mostly up to 0.5 $g.l^{-1}$, the waters are of the Ca-Mg-HCO_3-SO_4 type (ions over 20 c_iz_i%). Part of the underground water is influenced by mineral waters, which confirms the wide dispersion of their mineralization (0.5 - 1.4 $g.l^{-1}$) as well as pH values (6.5 - 7.9) and varying water temperatures. Increased contents of carbon dioxide appear locally. The presence of mineral waters represented in different proportions especially indicates the type variation of the waters. Apart from the prevailing Ca-Mg-HCO_3-SO_4 type mentioned, other types of water also appear.

From the point of view of water works use, the fresh waters of the Quarternary sediments are problematic, especially for their increased content of iron and manganese. In the past, the influence of very intensive agricultural activity was also observed, with the content of nitrates in some sources reaching 0.8 - 1.0 $g.l^{-1}$. The concentration of other forms of nitrogen, potassium and phosphorus was also increased.

In the more distant past, in the area of the edge of the block to the north of the summit of Gestenec there were natural seepage flows of mineral waters, which after extensive borehole research in 1953 gradually disappeared. Travertine mounds are evidence of these seepage flows.

The surface extent of dispersal of the minerals and its intensity varies. According to research in 1965, the extent of the influence of mineral waters on the water of the Quarternary sediments was significant. Repeated research in 1985 found an essential difference.

In 1965 the presence of mineral water was indicated in 23 wells out of 48 observed, and from these, very strong influence (an average electric conductivity over 2,000 $\mu S.cm^{-1}$). In 1981, out of 60 wells studied, an average value of electric conductivity over 2,000 $\mu S.cm^{-1}$ was found in only one case, and over 1,000 $\mu S.cm^{-1}$ in 13 wells.

From the course of isolines of average electric conductivity it can be seen (Fig. 2) that in 1981 the isolines are moved towards the source of mineral water. The cause of change compared to 1965 is above all interference in the regime of the Quarternary waters by the influence of extensive construction in the spa area as well as long term exploitation of mineral water, as a result of which its pressure has reduced, and so its penetration into the Quarternary sediments has diminished. A decline similar to that in the average electric conductivity also appears in the content of free carbonate oxides.

The changes found call attention to the need to devote attention to the development of the quality of the shallow underground water, which is important from the point of view of the protection of the sources of mineral water.

The pressure of mineral water was a definite protection factor, which limits the occasional penetration of impure substances into the spring structure and in future could be maintained by regulation of the quantity of water consumed at an optimal level in the area of the exploitation boreholes.

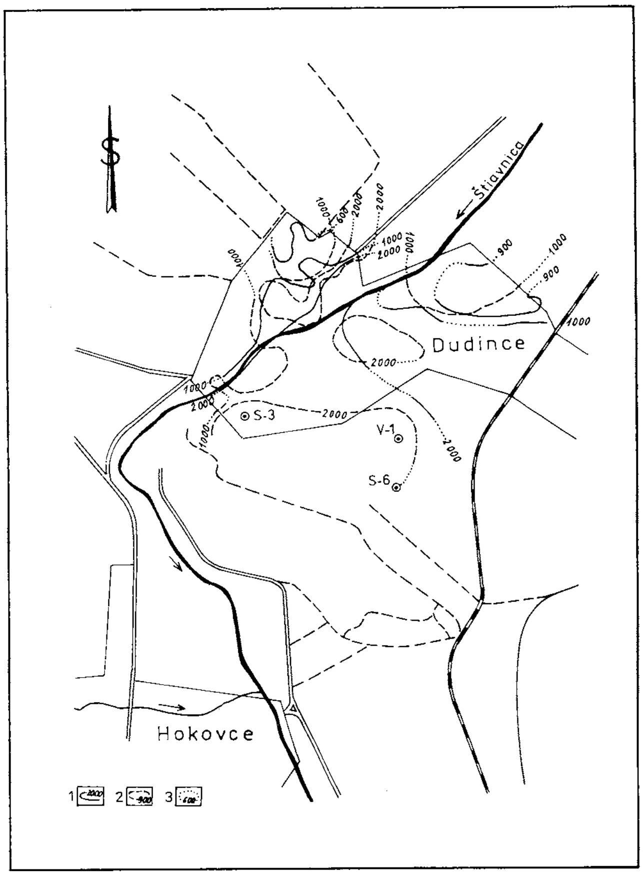

Fig. 2. Effects of mineral water on the quality of fresh water.
1 - isoline of average electric conductivity in 1981 (μScm^{-1}); 2 - isoline of average electric conductivity in 1985 (μScm^{-1}); 3 - unverified isolines of average electric conductivity.

Chemical composition of the mineral waters and their properties

Basic characteristics of the mineral waters

Water of the "Dudince type" is characteristic of the Dudince spring locality. Apart from this some sources occur here with water of a different chemical composition, similar to water of the "Slatina type" of the neighbouring spring structure.

The peculiarity of the Dudince mineral water rests in its mixed chemical type, combined with a high content of carbon dioxide and hydrogen sulphide and an increased content of various trace elements.

With mineralization of 5 - 6 $g.l^{-1}$, and a temperature of 27 - 28 °C, the water has a variable representation of ions. With consideration of all the ions represented above 10 c_iz_i%, the water is of the Na-Ca(Mg)-HCO_3-Cl-(SO_4) type (the ions in brackets are in the range 10 - 20 c_iz_i%). The content of free CO_2 varies around 1.4 $g.l^{-1}$, with the extreme content reaching 1.8 $g.l^{-1}$, and the content of H_2S around 6 $mg.l^{-1}$, with an extreme of 10 $mg.l^{-1}$. Among trace elements, there are increased concentrations of B, Br, Li, Rb, Cs, Sr, Ni, As.

Mineral water of practically identical chemical composition was also found in a borehole north-west of Dudince near Hontianske Moravce (settlement of Mačkáš), as well as at the more distant locality of Santovka.

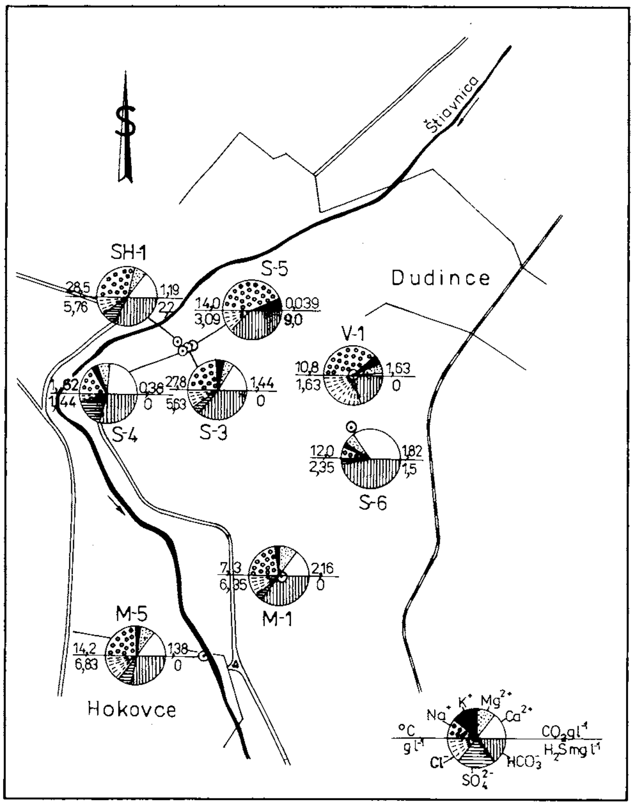

Fig. 3. Situation of boreholes at Dudince and the chemical composition of mineral waters.

Table 1: Chemical composition of "Dudince type" mineral water.

Source	Dudince bh.S-3 5.2.1986	Mačkáš bh. M-2 1.4.1985	Santovka bh.B-3 6.2.1986
mineralization [$g.l^{-1}$]	5.6	5.6	6.0
temperature [°C]	28	33	26.2
free CO_2 [$mg.l^{-1}$]	1.447	1.278	1.227
H_2S [$mg.l^{-1}$]	5.8	11.2	4.7
Na^+ [$mg.l^{-1}$]	819	802	888
K^+ [$mg.l^{-1}$]	121	113	124
Ca^{2+} [$mg.l^{-1}$]	491	478	503
Mg^{2+} [$mg.l^{-1}$]	131	139	159
Cl^- [$mg.l^{-1}$]	539	542	624
SO_4^{2-} [$mg.l^{-1}$]	522	496	565
HCO_3^- [$mg.l^{-1}$]	2.972	2.965	3.136
H_4SiO_4 [$mg.l^{-1}$]	11.2	15.6	18.3
HBO_2 [$mg.l^{-1}$]	18.0	30.0	14.5

The chemical analyses were carried out by IGHP Žilina.

On the other hand, other mineral waters of a different composition were also found directly at Dudince (Fig. 3).

The basic results about the physico-chemical properties and chemical composition of the waters of the "Dudince type" collected at Dudince, Hontianske Moravce and Santovka are given in Tab. 1.

In the past, there were many views on the genesis of these mineral waters. Today we consider the following hydrogeological model of their creation, to be the most probable.

As the infiltration area of the mineral waters, we consider that the territory in the foreland of the Central Slovak Neovolcanics, where a complex of volcanic and sedimentary rocks, especially gravels of the basal Badenian formation create favourable possibilities for the accumulation and transport of mineral waters.

Apart from this, a certain proportion of underground waters from Mesozoic carbonates is supposed. Although they were not directly proved in the rocks underlying the Neogene at Dudince, they occur in the wider district, and are directly connected by fault tectonics or hydraulic connections with the younger rocks. The more recent borehole M-2 near Hontianske Moravce, which found mineral water of the "Dudince type" directly in Mesozoic carbonates, is evidence.

The share of carbonates in forming the chemical composition of the mineral waters support the results of thermo-dynamic analyses indicating the saturation of the waters by calcite and dolomite. For a balanced state of reaction of the dissolution of calcite in water, the theoretical value of the ion product is 1.9, while the calculated value is 2.8. The value of the product of the dissolution of dolomite is $10^{-16.7}$, the calculated value $10^{-15.4}$. The waters are not saturated with gypsum, the product of dissolution is $10^{-4.6}$, while the calculated value reaches only $10^{-5.1}$. All the theoretical values are valid for 25 °C, so that they are close to the temperature of the mineral water.

The practically equal chemical composition of mineral waters at Dudince (borehole S-3), Hontianske Moravce (M-2) and Santovka (B-3) also confirmed by the results of isotopic analysis and the trace element content (see below), indicates the existence of a qualitatively united and relatively extensive reservoir of "Dudince type" mineral water.

The spring area of mineral waters directly at Dudince represents the marginal block north of Gestenec, where there were natural springs in the past. Mineral waters flowing from the north east are dammed by the horst of Permian rocks, which enables their significant concentration.

The idea mentioned on the origin of the mineral waters corresponds to their chemical composition, that is the varied representation of the main ions as a result of various mineralization processes.

The basic processes, of which the result is the presence of the Ca-Mg-HCO_3, Ca-SO_4 and Na-HCO_3 components, are the dissolution of carbonates, sulphates and the hydrolytic breakdown of silicates. As a result of the processes of ion exchange, the components Na-SO_4 (from original Ca-SO_4) and Na-HCO_3 appear. Oxidation-reduction processes also have an essential role in the creation of the chemical composition of the mineral waters, especially in relation to the presence of hydrogen sulphide. Apart from this, the important activities in the mineralization processes are thermodynamic conditions of the circulation of waters and their gasification by carbon dioxide.

Table 2: Basic information about borehole in the Dudince district.

Borehole No.	Year of drilling	Depth [m]	Depth interval [m]	Q [ls^{-1}]	T [°C]	Type of water	Notes
S-3	1954	60.65	53.5-60.5	70-80[1]	28.1	Na-Ca-Mg-HCO_3-Cl-(SO_4)	exploited
S-4	1955	71.23	53.7-60.9	206	28.0	Ca-Na-(Mg)-HCO_3-SO_4	unexpl.
S-5	1955	65.37	57.0	9.0	28.5	Na-HCO_3-Cl	unexpl.
HVD-1	1989	85.0	8-45 45-63 0-80	0.32 5.00 2.00	30.0 30.0 29-31	Na-Ca-(Mg)-HCO_3-Cl-(SO_4)	unexpl.
HVD-2	1989/90	80	8-47 45-63 0-75	010 2.00 3.3[2]	19.0 20.5 25.0	Na-Ca-(Mg)-HCO_3-Cl-(SO_4)	unexpl.
V-1	1953	103	57	15.0	17.5	Na-Ca-(Mg)-Cl-HCO_3	unexpl.
S-G	1956	12	10	0.3	11.0	Ca-Na-(Mg)-HCO_3-(SO_4)	exploited[3]
M-1	1979/80	321	50-100 150-186 300-321	0.07 1.0 1.0	10.3 11.3 16.2	Na-Ca-Mg-HCO_3-Cl	unexpl.
M-5	1982/83	220	50-150 150-202	2.2 2.5	12.4 13.0	Na-Ca-(Mg)-HCO_3-Cl-(SO_4)	unexpl.

1 - initiall Q; 2 - eruption; 3 - exploited for local purposes.

Sufficient uncertainty remains at present on the origin of the "salt component" of the mineral waters, which apart from Na-Cl and Na-HCO_3 also accompany some elements such as Br, B, or others. Their presence in the water indicates the influence of "marinogennic mineralization". According to some views, the "salt waters", which take part in the creation of mineral waters in this region have an origin in contrast to the preceding, to the south in Hungary.

O. Hynie supposed that waters of the Ca-Mg-HCO_3 type from Mesozoic carbonates with ascent through Badenian sediments are by processes of ion exchange metamorphosed and mixed with "salt waters" from the Badenian sediments.

Franko and Gazda in Vass et al. (1981), on the basis of results, which were obtained from borehole ŠV-8 near Dolné Semerovce, supported the opposite progression, that is water accumulated in Permian and Lower Triassic sediments, with a mixture of waters infiltrated to surface outcrops and epigenetic waters of the Badenian Sea. Since the Badenian formation was not hydrogeologically tested and laboratory leaching tests on sediments from the borehole mentioned did not prove the presence of the Na-Cl component, the question of the origin of the "salt waters" remains unsolved. We do not exclude the possibility of the origin of the Na-Cl components in relict mineralization from the Miocene transgression. Franko & Bodiš (1989) expressed similar conclusions on the origin of marinogennic mineralization in Triassic carbonates of the Inner Western Carpathians.

Up to 1953, when extensive borehole work began, mineral water was taken only from two natural springs (the Great and Little Spa Springs) and from one borehole HS-1.

In the following years new sources were constructed, boreholes S-3, S-4 and S-5 with water of "Dudince type", and boreholes V-1 and S-6 with water of a different type, from which only the water from borehole S-3 has a stable composition.

In 1989 - 90, were borred boreholes HVD-1 and HVD-2, with a chemical composition identical with the water of the "Dudince type".

Apart from these two boreholes already mentioned, borehole B-3 in Santovka (from 1957) and M-2, bored in 1984 near Hontianske Moravce (settlement of Mačkáš), both outside the area of Dudince, have too water of the "Dudince type" too.

On the other hand, sources with waters of a different composition also occur on the territory of Dudince: boreholes S-5 and V-1, and on the other side at Gestenec in the direction of the community of Hokovce boreholes M-1 and M-5. The basic information about all the boreholes is given in Tab. 2, and the present chemical composition of the waters in Tab. 3.

Water from borehole V-1 originally had a lower mineralization and a practical absence of carbon dioxide and hydrogen sulphide, a higher representation of "salt component", and a very low content of sulphates. The borehole was not used, but gave valuable information that sulphates are not part of the salt waters, which participate in forming the mineral waters of this district. Water from this borehole, as with that from boreholes S-4 and S-5, has a very changeable chemical composition, discussed in more detail in a further section of this paper.

A certain occasional transfer of "Dudince type" water to other sources in a wider area is hydro-chemically indicated in the more recent boreholes M-5 and especially in borehole M-1, which is situated on the other side of Gestenec. Under normal conditions of temperature, chemical composition and gas content, these sources clearly belong to the "Slatina tupe"mineral waters, but in relation to their marginal position between two structures, pumping them leads to mixing with waters of the "Dudince type". The occasional occurrence of hydrogen sulphide in the nearer borehole M-1, and on the other hand the more significant influence of deep salt waters in the more distant borehole M-5 is also clear evidence.

Water from the shallow borehole S-6 in Dudince is cold mineral water gasified by carbon dioxide. The chemical composition, especially the absence of the "salt component", is completely different from the mineral waters of both structures. Hydrogen sulphide occurs only sporadically.

Table 3: Basic information about the chemical composition of mineral water from the main sources.

Source (Borehole)	Data	T [°C]	M [g.l^{-1}]	CO_2	H_2S	Na^+	K^+	Ca^{2+}	Mg^{2+} [mg.l^{-1}]	Cl^-	SO_4^{2-}	HCO^{3-}	H_4SiO_4	HBO_2
S-3	5.2. 1986	28.0	5.6	1447	5.8	819	121	491	131	539	522	2972	11.2	18.0
S-4	17.11. 1982	16	1.4	381	0	142	34	194	26	81	307	1440	9.78	3.6
S-5	5.2. 1986	14	3.1	40	0	746	116	21	27	346	12	1776	23.39	16.0
HVD-1	11.9. 1989	31.0	5.9	1463	6.5	888	131	505	133	604	557	3051	29	30
HVD-2	18.2. 1990	23.5	6.4	1379	2.3	998	156	516	142	803	479	3252	26	32
V-1	17.11. 1982	11	1.6	24	0	422	72	12	32	513	5	549	3.61	23.8
S-6	5.2. 1986	12	2.4	1819	1.5	76	33	420	47	24	95	1599	45.6	2.6
M-1	6.2. 1986	7.3	6.4	2161	0	701	153	428	162	627	288	3624	12.6	0.5
M-5	6.2. 1986	14.2	6.8	1385	0	1003	179	537	187	899	649	3295	12.8	11.0

The differences in the chemical compositions of individual mineral waters in the Dudince district can be seen on the Piper's graph (Fig. 4). In relation to the absence of information about the quality of water from borehole V-1 in 1986, and its great variability over time, borehole V-1 is marked on the graph by two points with corresponding quality of the water in 1982 and 1988.

Secondary and trace elements in the mineral water

The increased representation of various secondary and trace elements also confirms the unusual chemical composition of the mineral water of the "Dudince type" (Tab. 4).

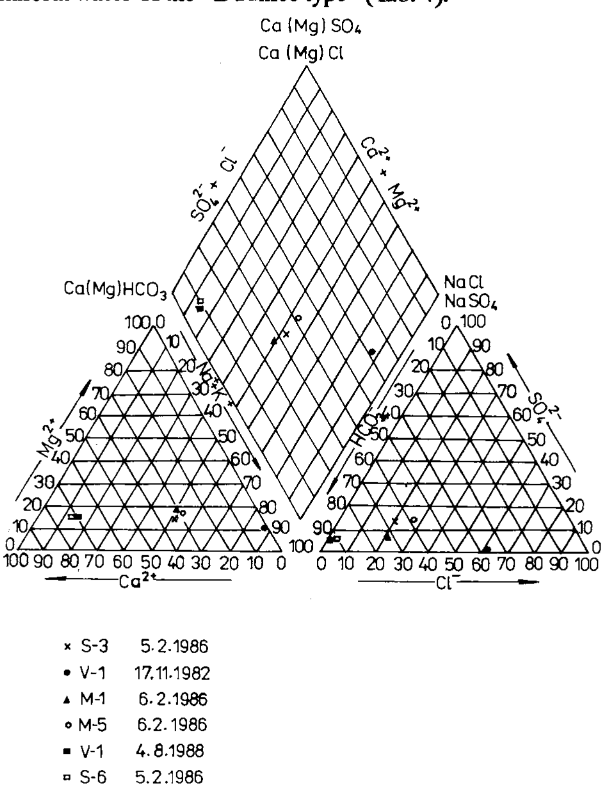

Fig. 4. Piper's graph - differences in chemical composition of water from boreholes S-3, S-6, M-1, M-5, V-1.

Among the mineral waters of Slovakia, the Dudince water has an increased concentration of alkaline metals, as well as strontium, nickel and arsenic. Among the halogenides, increased contents of bromides are typical. From the therapeutic point of view, the increased contents of fluorides, bromides, lithium, strontium, arsenic and some other elements, of which the beneficial effects on the human organism are still not clearly proved, are interesting.

The relative connection between the representation of the "salt component", the representation of chlorides and the content of boron in the Dudince water is not so clear as in the waters of the neighbouring structures. The values of the ratio of Cl/Br are also variable. In the Dudince water it varies around 1,200 - 1,400, while in the borehole M-5 belonging to the Slatina structure, with a significant influence of deep salt waters, the value varies around 450.

The contents of fluorides are also raised, indicating a great variability influenced by the varying ratios of the representation of the ions Na^+ and Ca^{2+}. The solubility of NaF is greater than that of CaF_2, and apart from this the influence of other salts is active in the water solution.

Table 4: The content of secondary and trace elements in "Dudince type" mineral water.

Element	Average content [mg.l^{-1}]	Element	Average content [mg.l^{-1}]	Element	Average content [mg.l^{-1}]	Element	Average content [mg.l^{-1}]
As	0.121	Cr	0.002	Pb	0.008	V	0.0001
Ba	0.036	Cs	0.120	Rb	0.170	F^- max.	4.00
Be	0.013	Cu	0.008	Sr	7.800	Br^- max.	7.64
Cd	0.005	Li	3.080	Tl	0.0009	I^- max.	0.93
Co	0.012	Ni	0.010	Zn	0.111	B max.	10.60

The analyses were carried out in the laboratory of the Geological Institute of Fac. of Natural Sci., Comen. Univ., Bratislava.

Gases in the mineral water

Characteristic for the "Dudince type" mineral water is the simultaneous, relatively strong gasification with carbon dioxide and hydrogen sulphide. This is a rare phenomenon, not only in the Western Carpathians, but also in other geological structures.

The absolute values of dissolved carbonate oxide show great variation with a maximum of 1.8 $g.l^{-1}$ noted in 1984. The contents of hydrogen sulphide are also very variable, with the highest values moving around 10 $mg.l^{-1}$, with one measurement of 13.6 $mg.l^{-1}$ in 1955 from borehole S-3.

From the point of view of acid gases, the water belongs to the type with a high carbon dioxide content (CO_2 over 1 $mg.l^{-1}$) and a weak to average hydrogen sulphide content (H_2S under 10 $mg.l^{-1}$). According to non-acidic gases, the Dudince water is nitrogenated (N_2 at 75%).

Values of K N_2/O_2 over 10 indicate a strongly reducing environment, with the appearance of hydrogen sulphide as well. A value of, K . He/Ar, equal to 0.02 according to Franko et al. (1975) indicates intensive water exchange, which corresponds to the results of hydrogeological relations. Tyčler (1975) mentions the presence of the gases mentioned in the relation equal to 0.2, that is already at the transition between intensive and limited water exchange.

Concrete information about the composition under layer conditions in sources with water of the "Dudince type" is given in Tab. 5.

Table 5: Gases in mineral waters (quantity %).

	Dudince S-3(1)	Dudince S-3(2)	Santovka B-3(3)	H. Moravce Mačkáš M-2(4)
CO_2	99.78	99.74	99.43	98.77 98.15 sg.
N_2	$2.1x10^{-1}$	$1.8x10^{-1}$	$3.4x10^{-1}$	1.07 1.56 sg.
O_2	$5.9x10^{-3}$	$4.0x10^{-3}$	$1.6x10^{-3}$	-
Ar	$3.9x10^{-2}$	$1.2x10^{-3}$	$5.3x10^{-3}$	-
He	$8.5x10^{-4}$	$3.0x10^{-4}$	$2.1x10^{-3}$	-
H_2	$8.8x10^{-5}$	$4.0x10^{-4}$	$2.9x10^{-3}$	$1.6x10^{-1}$
CH_4	$4.1x10^{-3}$	$5.9x10^{-1}$	-	-
C_2H_4	-	-	-	-
H_2S	-	$6.0x10^{-2}$	$2.2x10^{-1}$	-
Total gas content [Nml/l]	-	3231.75	4105.1	6671.6
Temperature [°C]	28	28	13.5	30.5
Phase ratio gas/water	-	2.5	-	3.801
Pressure [MPa]	-	-	$1.39x10^{-2}$	1.59

sg. - spontaneous gas

The results are taken from these works:

1 - Franko et al. (1975); 2 - Tyčler (1975); 3 - Krajča et al. (1975); 4 - Holuša (1985).

Representation of isotopes and radioactivity of mineral water

Isotopes of carbon, oxygen, sulphate and hydrogen sulphide sulphur, total beta-activity, tritium activity and radium activity were followed in the Dudince water. The results are given in Tab. 6.

Table 6: Isotopes and radioactivity of the Dudince water.

	Dudince borehole S-3	Dudince borehole S-6	
β activity [$pCi.l^{-1}$]	143.2	59.6	/1/
Tritium activity [TU]	4	114	/2/
$\delta^{14}C$ ‰	-77.8	-	/3/
$\delta^{13}C$ ‰	-2.5	-	/4/
$\delta^{18}C$ ‰	-15.9	-	/5/
$\delta^{34}S/SO_4/$ ‰	26.4	-	/6/
$^{34}S/H_2S/$ ‰	-16.2	-	/7/
Radium [$pCi.l^{-1}$]	36.3/32.0/	4.0	/8/

Sources of information:

1 - Laboratory of the Nuclear Power Station Jaslovské Bohunice (1972); 2 - 3 Department of Nuclear Physics PFUK (1973, 1974, 1975); 4 - 5 Kecskes (1978); 6 - 7 Šmejkal et al. (1981); 8 - Streška (1973).

The age of the water from borehole S-3, that is Dudince water was determined as 12,000 years, on the basic of $\delta^{14}C$. This result may be partly distorted by the influence of different processes, such as mixing of waters of different ages, isotopic exchange between water and the rocks, sufficient dissolution of carbonates without radionuclides etc., so that the calculated age of the water may be considered only as approximate.

In the framework of Slovakia, the low negative values for $\delta^{14}C$ in borehole S-3 are not typical of carbonatogennic waters from Mesozoic rocks, or of silicatogennic waters from the neovolcanics. Similar values were found in thermal water of mixed type in Komárno (borehole M-2), from Mesozoic carbonates of the Hungarian Central Mountains, which are a mixture of carbonato-sulphatogennic waters and waters of overlying Tertiary rocks with marinogennic mineralization.

A high negative value for $\delta^{18}O$ indicates an open structure, which is in harmony with the ratio of $rHCO_3/rCl$, which varies around the value 3. In spite of this, the value appears very low, for water which was in contact with rocks, that is, in comparison with contemporary water from precipitation, extremely light. Information about the representation of deuterium as a supplement to $\delta^{18}O$ are not available. More attention needs to be devoted to the problem of the representation of these isotopes in the Dudince water.

A high positive value for $\delta^{34}S(SO_4)$ is typical of sulphatogennic waters from carbonates of the Mesozoic of the Western Carpathians. The low degree of conversion of sulphates, reaching only 3.4‰, points to relatively unfavourable conditions for the change of sulphates to hydrogen sulphide. Measurement of $\delta^{34}S$ gave a value of +24.‰ (Šmejkal et al. 1981).

High values for total beta activity are influenced by the salt component, or concretely by the isotope of potassium ^{40}K. In the area of the "Levice spring line", the values for beta activity correlate very well with the content of chlorides, which is also seen in the difference of its value between borehole S-3 with Dudince water and water from borehole S-6 with shallow circulation, which is practically without chlorides.

Apart from beta activity, the different type of water from borehole S-6 also confirms low radium activity, and on the other hand raised values for tritium activity, which is evidence of the dominance of waters with shallow circulation.

Stability of the chemical composition of the mineral water

The mineral water at Dudince of the "Dudince type" is notable from the long term point of view for the stability of its chemical composition, with the exception of gases, the content of which is variable. The results of archive analyses from the years 1836 and 1893 and contemporary analyses document the constant representation of individual ions:

Year	Source	Na^+	K^+	Ca^{2+}	Mg^{2+}	Cl^-	SO_4^{2-}	HCO_3^-
1836	unknown	696	22	627	182	404	568	1614
1893	Main Spr.	851	129	498	133	564	559	2965
1957	bh. S-3	1097		459	137	597	567	3216
1986	bh. S-3	819	121	491	131	539	522	2972

Analyses carried out by: 1836 - B. Wehrle; 1893 - B. Lengyel; 1957 and 1986 - Engineering-geological and Hydrogeological Survey, Žilina.

In contrast to the character of the dissolved solids, the content of gases in the old and contemporary analyses are different. According to the oldest analysis, the content of carbon dioxide was 1.3 g.l^{-1}, for hydrogen sulphide only a trace amount was mentioned. After drilling borehole S-3 in 1954, the content of hydrogen sulphide was only 3 - 4 mg.l^{-1} H_2S. Later with a certain variation, it had a rising tendency. In 1964 - 65 it reached 10 mg.l^{-1}, in further years the concentration was lower, with a majority below 7 mg.l^{-1}. The carbon dioxide contents are always very variable, showing that the water had the highest gasification in the years 1983 and 1984. Water from borehole B-3 at Santovka, drilled in 1964, also had a similar series of gas contents.

We suppose, that the extensive borehole work, directly at Dudince, or in the neighbouring spring structures, have a large share in the varying degrees of gasification.

In contrast to borehole S-3 with a relatively stable representation of the individual ions, boreholes S-4 and S-5, originally also with water of the "Dudince type" did not show such a stability of quality. It can be seen from the Piper's graph (Fig. 5) and from Tab. 7, that in the years 1958 - 1982, a thining of the mineral water in borehole S-4 occurred, while in the borehole S-5, in the years 1958 - 1986, the character of the water changed, in the sense of shift to the Na-HCO_3-Cl type, with a simultaneous, significant lowering of the content of carbon dioxide and only occasional occurrence of hydrogen sulphide. It appears that these changes are not permanent, since, according to the latest information, water from borehole S-5 again approximates to the "Dudince type" of mineralization, with gasification for the type of water as well.

The quality of the water in borehole V-1 (Tab. 7, Fig. 5) showed the greatest change since it was bored and the beginning of observations. In 1988, the quality of the water was close to that from the shallow borehole S-6, on the margin of the spring

Table 7: Changes in the chemical composition of the mineral waters in the boreholes S-4, S-5, S-6, V-1, M-1, M-5 over time.

Source (Borehole)	Data	CO_2	H_2S	Na^+	K^+	Ca^{2+} [mg.l^{-1}]	Mg^{2+}	Cl^-	SO_4^{2-}	HCO^{3-}
S-4	18.11.1958	959	–	759	307	514	134	562	548	3081
S-4	1.4.1959	646	tr.	867	136	509	134	571	561	3057
S-4	17.11.1982	381	0	142	34	194	26	81	307	635
S-5	19.11.1958	1365	–	768	288	514	135	565	547	3083
S-5	9.2.1959	1534	tr.	868	148	506	136	578	566	3078
S-5	17.11.1982	542	1.3	733	113	22	29	369	4	1721
S-5	5.2.1986	40	0	746	116	21	27	346	12	1776
V-1	26.3.1964	46	0	630	102	40	73	555	24	1356
V-1	17.11.1982	24	0	422	72	12	32	513	5	549
V-1	4.8.1988	1656	1.2	79	40	391	46	17	83	1580
M-1	27.2.1980	–	–	26	14	55	16	29	95	146
M-1	6.2.1986	2161	0	701	153	428	162	627	288	3624
M-5	21.11.1982	986	0	567	92	297	93	462	375	1776
M-5	6.7.1984	1400	0	1107	179	524	166	893	704	3271
M-5	6.4.1959	1385	0	1003	179	537	187	788	649	3295
S-6	6.4.1959	2089	–	235	79	407	74	104	200	1925
S-6	5.2.1986	1819	1.5	76	33	420	47	24	95	1598

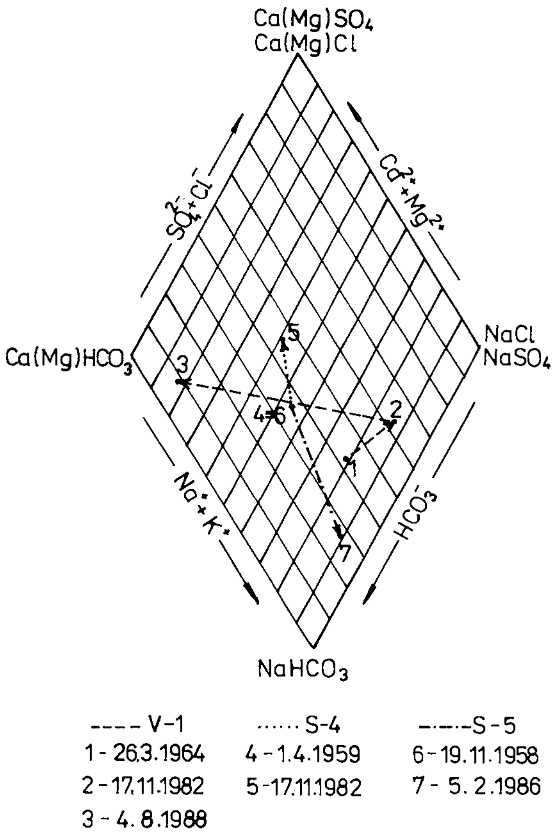

Fig. 5. Piper's graph - changes in the chemical compositions of water over time, from boreholes S-4, S-5, V-1.

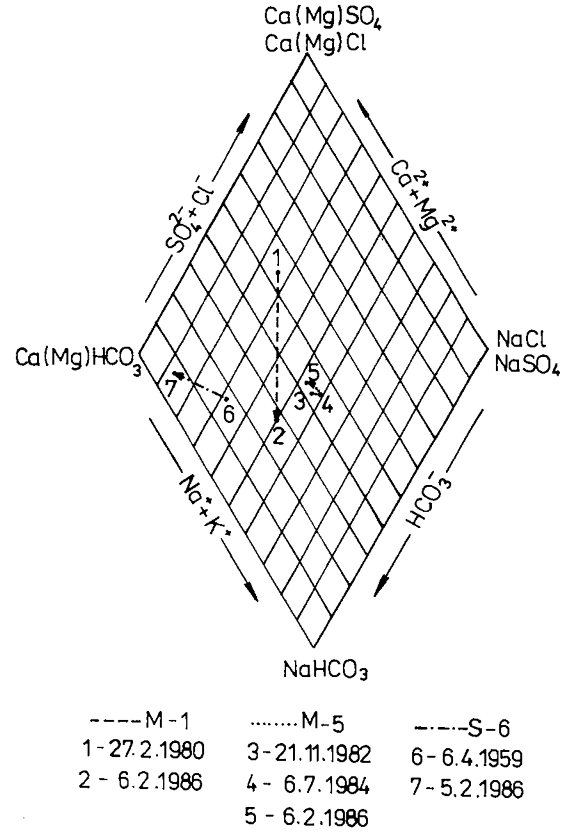

Fig. 6. Piper's graph - changes in the chemical compositions of water over time, from boreholes M-1, M-5, S-6.

structure. The similarity of type is evident from comparing Figs. 5 and 6. The changes are probably caused by increased consumption of water at the end of the 1980s and further interference with the spring structure (construction of new boreholes HVD-1 and HVD-2).

The unstable quality of the water from borehole S-6 (Tab. 7, Fig. 6) is a reflection of the shallow circulation of water. In the years 1959 and 1990, mineralization varied from 2.3 to 4.4 $g.l^{-1}$, carbon dioxide from 1.4 to 2.3 $g.l^{-1}$ CO_2, hydrogen sulphide was usually not present, but in individual cases it reached 1.5 $mg.l^{-1}$ H_2S.

Boreholes M-1 and M-5 belong to the neighbouring "Slatina type", which represents a mixture of two waters, distinguished by origin and quality. Low temperature and the absence of hydrogen sulphide is characteristic of this type. Boreholes M-1 and M-5 are also partly under the influence of Dudince water, especially borehole M-1, which is shown by occasional increased temperature, the presence of hydrogen sulphide (up to 1 $mg.l^{-1}$ H_2S), or other features of the type (Tab. 7, Fig. 6).

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