Condition for formation and extension of mineral and thermal waters in the Western Carpathians

ONDREJ FRANKO[1] & LADISLAV MELIORIS[2]

[2]Department of Hydrogeology, Faculty of Science, Comenius University, Mlynská dolina, 842 15 Bratislava, Slovakia

Abstract: Based on the latest research the authors explain basic geologic conditions for mineral and thermal water formation in the Western Carpathians. They define extension of the waters in the structural-facial zones, hydrogeologic structures, chemistry, gas content and palaeohydrologic conditions. The last part of the paper is devoted to the regime, utilization and protection rules of mineral and thermal waters in Slovakia.
Key words: West Carpathians, mineral waters, thermal waters, genesis, extension, structures, hydrogeochemic provinces, palaeohydrogeology, regime, utilization, protection

1. Introduction

The Slovakia is relatively rich on mineral and thermal waters (MTW) considering its small areal extent (ca. 49 000 km 2). The richness does not only consist in a great number of springs (about 1150) but also in their relatively uniform distribution in the whole area (App. 1, about 1 spring of mineral or thermal water per 43 km^2). From the viewpoint of their utilization it is more important factor than an opposite case i.e. small number of springs with high discharge and uneven distribution. The discharge of natural outflows (localities) varies from an insignificant amount up to 100 l/s. Water temperature of natural springs varies from 15°C up to 70 °C.

In accordance with international and national standards mineral waters are defined as waters containing in 1 l of water from outflow more than 1 g dissolved solid substance or 1 g of dissolved carbon dioxide. Waters containing at least 1 mg of H_2S per liter in outflow are defined as hydrosulphide waters and waters having higher temperature than 20°C are defined as thermal waters.

Geologic condition of mineral and thermal water formations

The Slovakia extends in the area of the West Carpathians comprising a part of young, Alpine-Carpathian fold nappe system. Because the genesis of mineral and thermal waters reflects geological-tectonic environment in which they occur, we will obey the valid division of the West Carpathians into 5 structural-facial zones during their regional description (Andrusov 1958). The structural-facial zones are: 1. the Foredeep between the Bohemian Massive and the Carpathians, 2. the Flysch zone, 3. the Klippen belt, 4. the Central-Carpathian zone, 5. the zone of the inner Neogene depressions, lowlands and volcanics (App. 1).

The first two zones represent the outer zone, the two zones represent the inner zone of the West Carpathians. They are separated by the Klippen belt. Mineral waters are associated with all five zones, thermal waters are only associated with the inner zone of the West Carpathians.

Geological-tectonic development of the West Carpathians governed suitable conditions for mineral and thermal water formations (Mahel' 1952, Franko et al. 1975):

- a great number of the Mesozoic deposits, mainly Middle and Late Triassic carbonates (limestone and dolomites) as well as Permian, Early and Late Triassic evaporites occur here.
- The Tertiary (Paleogene and Neogene) marine and fresh-water deposits are widely extended here. They mainly consist of pelites containing aquifer psefites and psamites. Evaporites occur in the Miocene;
- The Alpine-type tectonics of the Mesozoic formations formed folds with large extent submerging from mountain slopes into deeper parts of the inner depressions and lowlands
- The Tertiary deposits have fold- and fault structural type of tectonics
- The axial and transverse direction of young faults
- The deep faults between individual blocks of the Earth crust
- The Late Tertiary volcanism
- The suitable geothermic conditions

The first condition: Large extension of the Mesozoic carbonates and evaporite occurrence (anhydrite - gypsum) governed relatively uniform distribution and formation of yielding thermal springs and small springs of carbon dioxide waters in the Inner West Carpathians. From the viewpoint of geochemistry the factor determines mainly formation of mineral waters with carbonatogenic and sulphatogenic mineralization. The maximum discharge of thermal water natural springs ranges up to 100 l/s. From the chemical viewpoint these waters are of Ca-Mg-bicarbonate character, Ca-Mg-bicarbonate-sulphate character and Ca-Mg-sulphate character with mineralization up to 5 g/l.

The second condition: a great extension of the Tertiary marine and fresh-water deposits with evaporite occurrence (mainly salt deposits) in the Miocene determines formation and uniform distribution of mineral and thermal waters in the Carpathian Foredeep, in the Flysch and partly Klippen zones, in the inner depressions and in the Neogene lowlands. Marine and fresh-water character of deposits and occurrence of the salt deposits caused the formation of mineral waters with marinogenic, halogenic and hydrosilicatogenic mineralization. Discharge of natural springs is in most cases very small and it reaches values up to 1 l/s. The maximum discharge of boreholes attains 20 l/s. According to chemical content these waters are of Na-Ca-Mg-bicarbonate, Na-bicarbonate, Na-bicarbonate-chloride and Na-chloride characters with mineralization mainly reaching up to 50 g/l, less frequently up to 300 g/l and occasionally up to 500 g/l.

The third condition: the alpinotype (fold) tectonics of the Mesozoic formations enabled conditions for entering waters into deeper parts of the rock environment governing formation of thermal waters of relatively high temperatures. The natural springs attain maximum temperature of 70°C. The boreholes in the Mesozoic basement of the inner depressions and lowlands revealed waters with temperature up to 100° C and more.

The fourth condition: the alpinotype (fold) and germanotype (fault) structure of the Tertiary deposits enabled position of the Miocene aquifers in great depths governing warming up of waters. In case of closed hydrogeological structures the waters of these aquifers preserved synsedimentary salinity which was only metamorphosed in a closed rock – water system. The resupply of waters in the Paleogene deposits of the Outer West Carpathians is restricted by flysch character of deposits. The mineral water springs having very low discharge (up to 0.1 l/s) occur in the shallow and on the surface cropping Paleogene aquifers. Due to Germanotype structure of the Miocene deposits the basal Eggenburgian, Ottnangian and Badenian clastics were locally displaced into greater depths determining warming of waters and at the same time resupply by infiltration through the mountain margins. The basin-like structure of the Pliocene deposits results in the increasingly higher temperature of waters toward the centre of depressions and constant resupply by infiltration. The temperature of waters exploited from boreholes located in the Tertiary deposits varied up to 25° not long ago. At the moment waters having temperature up to 100° are known.

The fifth condition: Young axial and transverse faults result in moving up of waters on the surface in the form of natural springs. Together with the first and second factors it determines the uniform distribution. The waters move up along axial faults of regional character from depths to surface. Close to surface the function of axial faults is is taken over by transverse faults which determine the location of outflows. The regional faults are more open in the greater depths while near the surface younger, transverse faults are more open.

The sixth condition: Deep faults on boundaries between individual blocks of the West Carpathians effect topographic distribution of carbon dioxide waters which go along these faults and are also concentrated at their crossings (Franko & Kolářová 1985). Seismically active faults as well as others, less important faults are included to the deep faults.

The seventh condition: The Late Tertiary volcanism with associated major amount of carbon dioxide together with tectonics governed formation of a large amount of carbon dioxide waters. The Late Tertiary volcanism played also role on the formation of suitable geothermic conditions.

The eights condition: The suitable geothermic conditions actually represent increasing values of geothermic gradient and Earth heat flow. The mean geothermic gradient attains 39°C/km and the mean density of heat flow 82 mW/m^2 (Franko et al. 1995).

Extension of mineral and thermal waters in structural-facial belts

Varied geological structure of the West Carpathians is reflected not only in the richness of mineral and thermal waters but mainly in the quantity of their types (Tab. 1). In this part we characterized mineral waters according to the salt content what conveniently expresses conditions of their formation (balneologic classification of J. Hensel 1951). We state discharge for localities.

The Carpathian foredeep is essentially filled by the Neogene marine pelites containing psefite and psamite beds representing mineral water aquifers. The most known among them (Tab. 1) are cold strongly mineralized (10-35 g/l) J-Br salt waters in Darkov (Nr. 6) with discharge up to 1 l/s. In this zone also cold Ca-Mg-carbon dioxide (Horné Moštenice, Nr. 11) and thermal Ca-Mg (Teplice nad Bečvou, Nr. 3), slightly mineralized (1-5 g/l) waters with discharge up to 9 l/s occur. However, they are associated with the Devonian limestones occurring on slopes of the Bohemian Massif submerging beneath the West Carpathians.

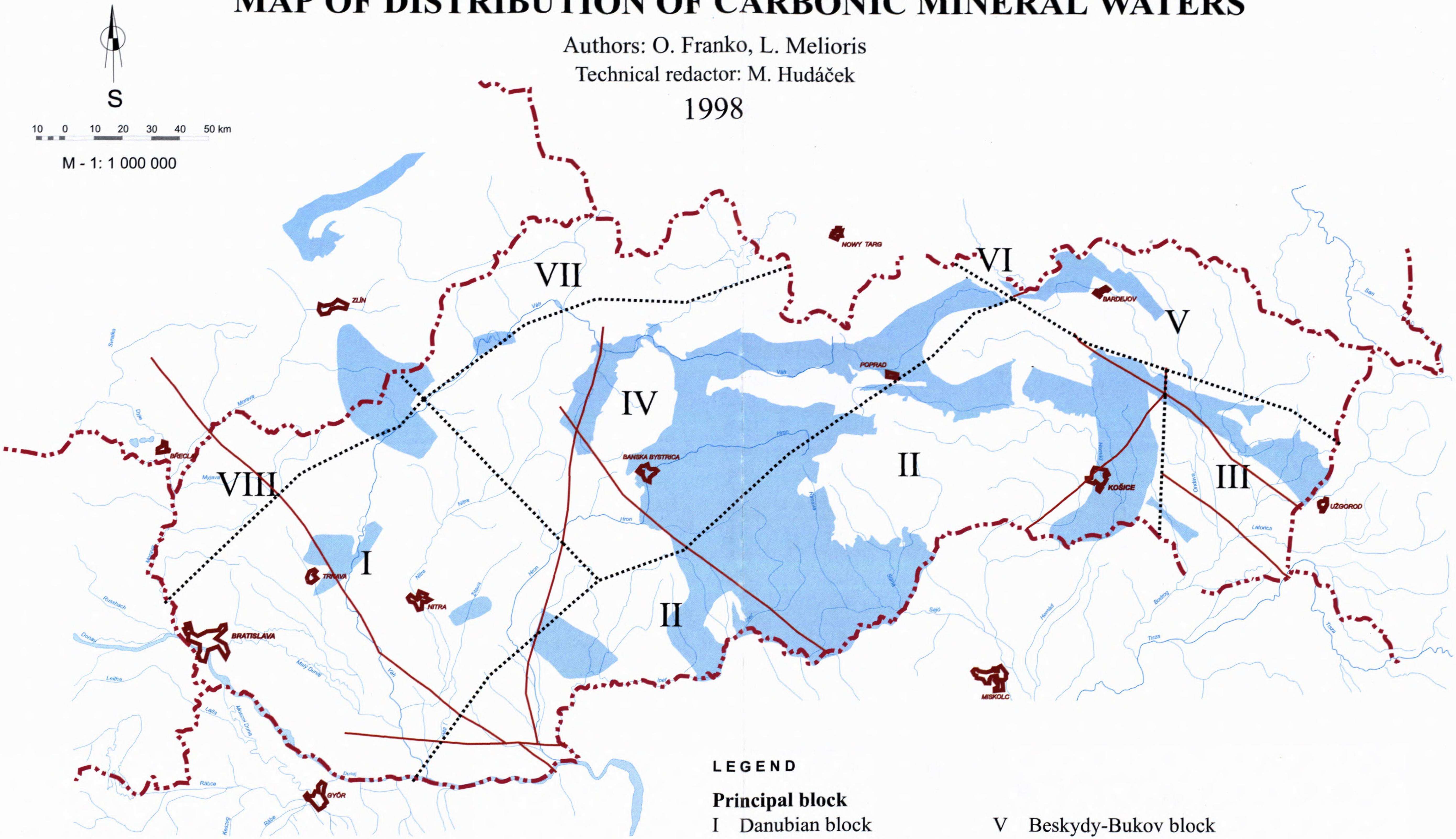
The Flysch zone mainly consists of Cretaceous and Paleogene marine alternating claystones and sandstones. Four kinds of water are represented here (Fig. 1). The most known are strongly mineralized carbon dioxide Ca-HCO_3 salt waters with discharge up to 4 l/s in Luhačovice (Nr. 15), Cígeľka (Nr. 27) and Bardejov (Nr. 28). Equally known are cold (springs) and thermal (borehole) very strongly mineralized (35-50 g/l) salt J-Br waters with discharge up to 1 l/s in Oravská Polhora (Nr. 25). The third important kind is represented by cold and strongly mineralized Na-Mg-SO_4 waters with discharge up to 0.1 l/s in Šaratica (Nr. 9). However, the most extended outflows are abundant small springs of cold H_2S and carbon dioxide ranging to very slightly (up to 1 g/l) and slightly mineralized Ca-Mg and Na-HCO_3 waters with discharge up to 0.1 l/s. Carbon dioxide Na-HCO_3 and Na-HCO_3 Ca-Mg medium mineralized (5-10 g/l) waters in Šarišský Štiavnik (Nr. 31) and Malý Sulín (Nr. 26) are more known.

The Klippen belt is composed of numerous Triassic, Jurrasic and Early Cretaceous limestone cliffs. The cliffs are enveloped by marl beds and assigned to the Late Cretaceous and Paleogene. The most known waters are

MAP OF DISTRIBUTION OF CARBONIC MINERAL WATERS

Authors: O. Franko, L. Melioris
Technical redactor: M. Hudáček

1998



LEGEND

Deep faults extending to the upper part of mantle

Faults extending to the lower part of crust

Province of carbonic minerals waters

Principal block

I Danubian block
II Rudohorie - Pilíš block
III Tisa block
IV Fatra - Tatry block
V Beskydy-Bukov block
VI Krakow block
VII Slovak - Silesian block
VIII Slovak - Moravian block

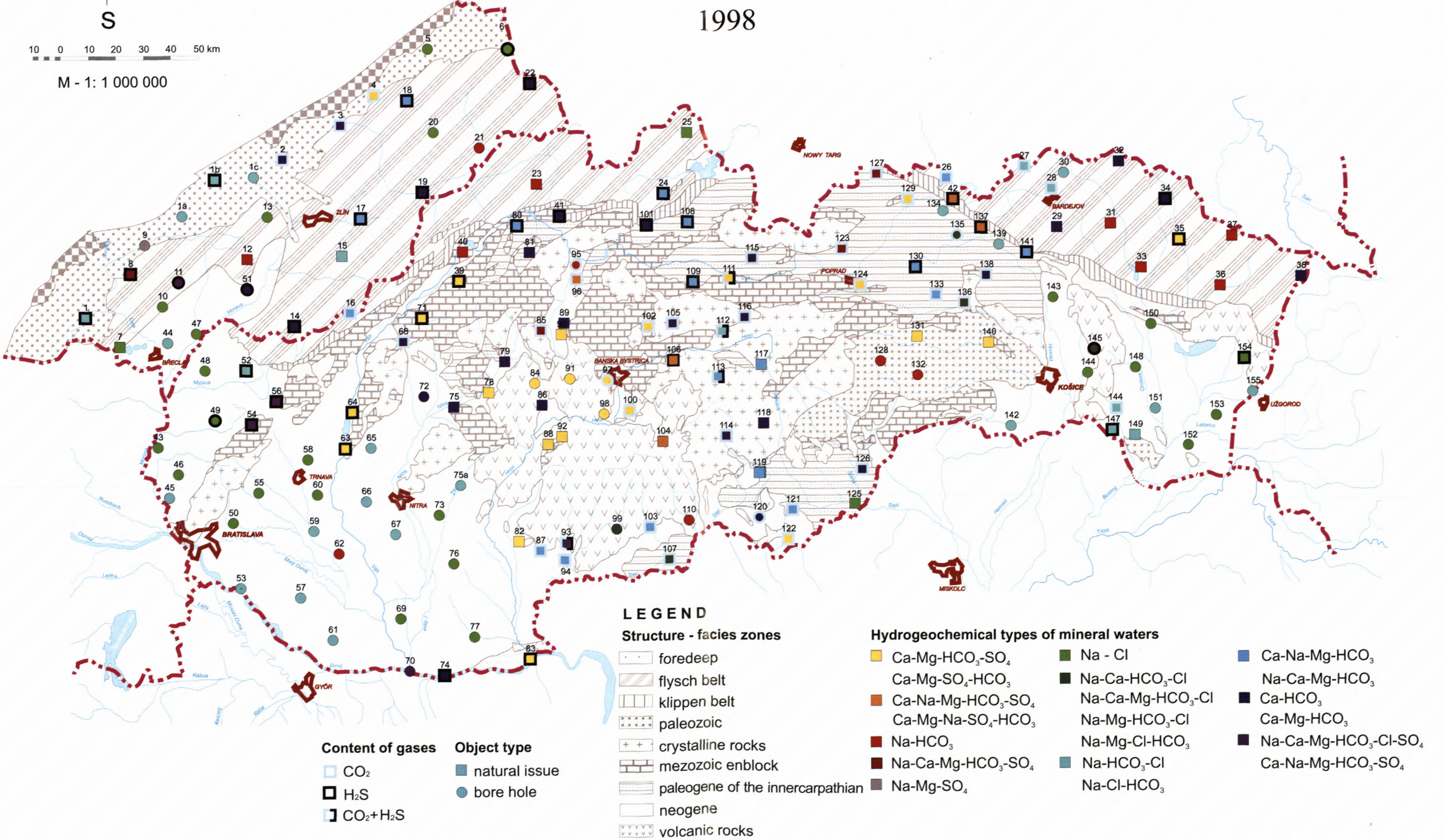
Tectonic basement: J. Ibrmajer - J. Plančár - O. Fusán

design & printing by Marek Hudáček 1998

MAP OF MINERAL AND THERMAL WATERS OF SLOVAKIA

Authors: O. Franko, L. Melioris
Technical redactor: M. Hudáček

1998



design & printing by Marek Hudáček 1998

Tab. 1 Hydrogeochemic characteristic and distribution of mineral and thermal waters in the Western Carpathians according to structural-facial zones

	Dominant 〉20 $c_i z_i$ %	CMV $(g.l^{-1})$		CO_2 $(g.l^{-1})$		H_2S $(g.l^{-1})$		Q $(g.l^{-1})$		T °C
		min.	max.	min.	max.	min.	max.	min.	max	max
1. The Foredeep										14,0
A) Min.W.with carbonatogenic min.	Ca-HCO_3	0,3	53,1	0,2	1,7	2,6	24,5	0,2	3,5	
B) Min.W. with mixed mineraliz.	Na-Cl	2,5	20,6	-	-	-	-	0,1	0,7	
2. The Flysch zone	Cu-Mg-HCO_3									14,0
A) Min.waters with carbonatogenic min.	Ca-HCO_3	0,5	2,6	0,2	1,2	0,0	16,0	0,02	9,5	
B) Min.w.with hydrosilicatogenic min.	Na-Ca-HCO_3	0,4	25,0	0,02	2,5	0,0	30,4	0,01	0,3	
	Ca-Mg-HCO_3									
C) Min.waters with marinogenic min.	Na-Cl	14,0	42,0	0,00	0,00	0,0	0,0	min.	min	
3. The Klippen Belt										
A) min.waters with carbonatogenic min.	Ca-Mg-HCO_3-SO_4	0,5	3,2	0,0	1,7	0,0	4,4	0,07	2,7	11,5
	Na-HCO_3									
4. The zone of the Central West Carpathians										
a) The Crystalline basement										10,4
A) Min.waters with silicatogenic min.	Ca-Mg-HCO_3	0,1	9,6	0,0	1,6	0,0	8,5	0,01	2,4	
	Na-HCO_3									
b) The Choč Nappe										48,0
A) Min.waters with carbonatogenic min.	Ca-Mg-HCO_3	0,7	3,5	0,07	2,2	0,0	1,7	0,5	71,2	
	Ca-Mg-HCO_3-SO_4									
c) The Krížna Nappe										47,5
A) Min.waters with carbonatogenic min.	Ca-Mg-HCO_3-SO_4	1,5	3,9	0,01	1,7	0,0	4,0	0,9	47,5	
B) Min.waters with sulphatogenic min.	Ca-Mg-SO_4-HCO_3	0,5	3,9	0,1	1,4	〈0,6	〈0,6	7,1	37,0	
d) The envelop units										69,5
A) Min.waters with carbonatogenic min.	Ca-Na-Mg-HCO_3-SO_4	3,1	8,4	2,0	2,2	st.	st.	0,4	1,5	
	Ca-Na-Mg-HCO_3									
B) Min.waters with sulphatogenic min.	Ca-Na-Mg-SO_4-HCO_3	2,7	3,6	0,2	2,9	0,0	12,0	1,0	56,6	
e) The Inner-Carpathian Paleogene										10,5
A) Min.waters with carbonatogenic min.	Ca-Mg-HCO_3	0,5	2,6	0,04	1,2	0,0	11,0	0,01	10,0	
B) Min.waters with hydrosilicatogenic m	Ca-Na-Mg-HCO_3	0,6	0,7	0,02	0,03	3,2	16,6	0,04	0,2	
C) Min.waters with marinogenic min.	Na-HCO_3									
	Na-Ca-Mg-HCO_3	0,4	0,5	0,0	0,03	0,0	0,0	0,2	0,6	
5. The Neogene										
A) Min. waters with carbonatogenic min.	Ca-Mg-HCO_3	0,2	2,7	0,7	2,5	0,0	0,0	min.	min	94,0
	Ca-Na-Mg-HCO_3-SO_4									
B) Min.waters with hydrosilicatogenic m	Ca-Mg-Na-HCO_3-SO_4	1,2	3,6	0,04	0,6	0,0	0,6	min.	min	
C) Min.waters with marinogenic min.	Na-Cl	1,2	41,6	0,0	0,5	0,0	0,0	0,08	14,5	
D) Min. waters with halogenic min.	Na-Cl-HCO_3									
	Na-Cl	9,5	292,0	0,04	0,8	0,0	0,0	0,2	0,6	
6. The West Carpathians										
A) Min.waters with mixed mineralization	Na-Ca-Mg-HCO_3-Cl-SO_4	0,8	28,8	0,04	2,5	0,0	10,8	0,25	5,0	54,0
B) Min.waters with polygenic mineralization	Na-HCO_3-Cl									
	Na-Ca-Cl-SO_4	1,6	25,0	0,0	0,4	0,2	500-700	0,2	2,2	
	Ca-Mg-Na-HCO_3-Cl-SO_4									
	Na-Mg-SO_4									

cold carbon dioxide and slightly mineralized Na-HCO_3 waters in Nimnica (Nr. 40) having discharge about 2 l/s. Another known waters are cold and thermal slightly mineralized Ca-Mg-Ca-SO_4 waters in Belušské Slatiny (Nr. 39) with discharge up to 10 l/s. Except these waters small springs of cold carbon dioxide and H_2S Ca-Mg, Ca-Mg-Na-HCO_3 and Ca-Mg-Na-HCO_3-SO_4 very slightly and slightly mineralized waters occasionally occur. The discharge of springs is up to 0.1 l/s.

The zone of the Central West Carpathians with inner depressions, Late Tertiary volcanic mountains and lowlands is most rich in mineral and thermal waters. It consists of pre-Neogene crystalline basement croping out in the core mountains and normal and detached envelop.

Mostly cold carbon dioxide, very slightly mineralized Ca-Mg waters with discharge up to 0.1 l/s are associated with crystalline rocks. The more known water occurrences are in Starý Smokovec (Nr. 123), Mýto pod Ďumbierom (Nr. 112) and Jasenie (Nr. 105). Thermal, nitrogenous, very slightly mineralized Na-HCO_3 waters ((from boreholes) are associated with Cretaceous granites in the Paleozoic of the Slovenské Rudohorie Mts. The waters have discharge 2-3 l/s and they occur in Vlachovo (Nr. 128) and Čučma (Nr. 132).

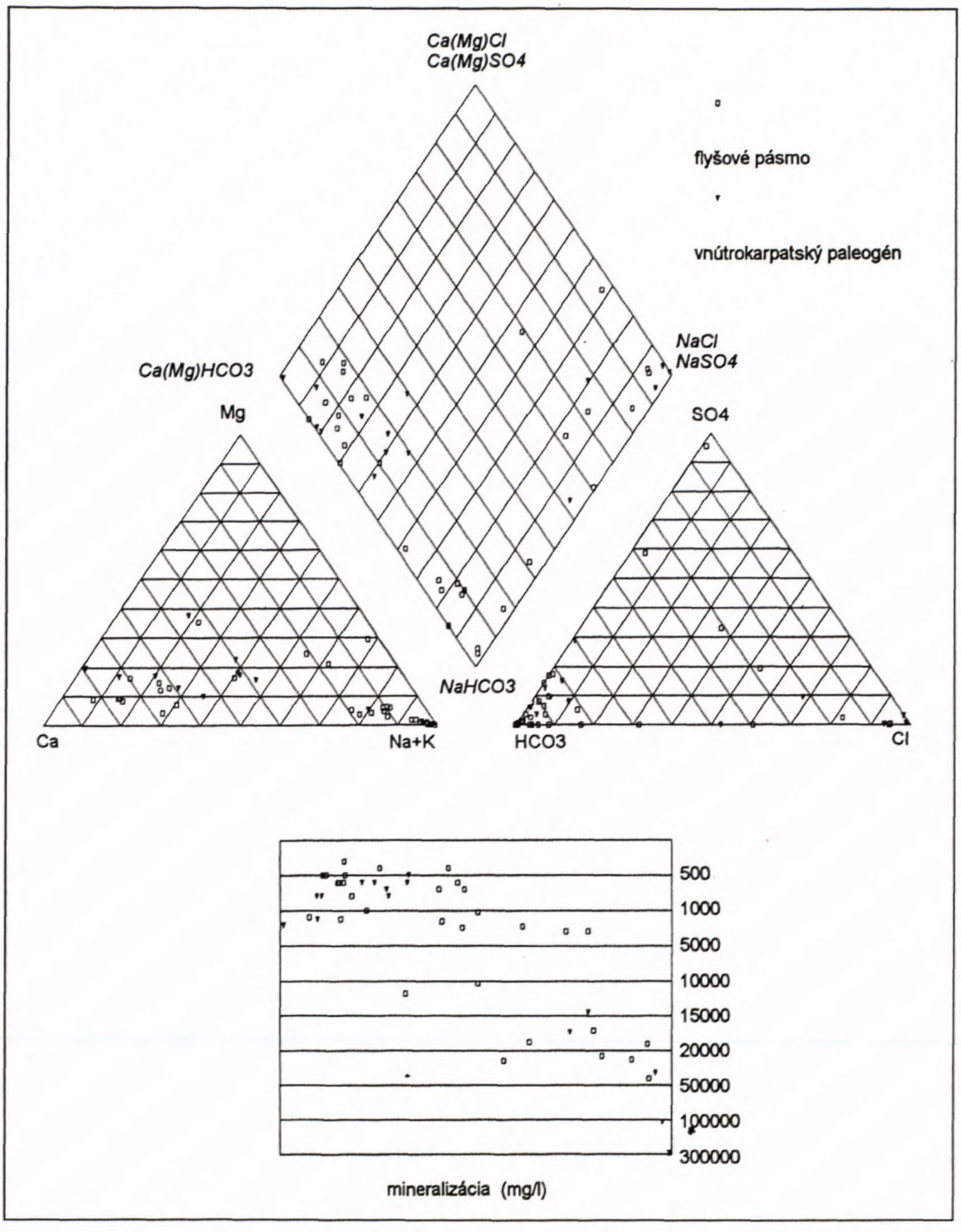


Fig. 1: Pipper graph - mineral and thermal waters of the Flysch zone and the Inner-Carpathian Paleogene

Cold and thermal waters are associated with Triassic carbonates (limestones and dolomites) of various tectonic units. Mainly Ca-Mg acratotherms (waters with very slight mineralization and temperature above 20° C) are associated with middle (Choč) nappe. The most known are waters in Rajecké Teplice (Nr. 81), Bojnice (Nr. 79), Malé Bielice (Nr. 75) and Vyhne (Nr. 88). Waters occurring in Kalinčiakovo (Nr. 75) are associated with Choč and upper nappes. The waters in Patince (Nr. 74) and Štúrovo (Nr. 83) are associated with carbonates of Hungarian Middle Mts. The discharge of above mentioned localities ranges from 15 – 70 l/s and the water temperature ranges from 20 – 48°C. Besides these waters also carbon dioxide, Ca-Mg, slightly mineralized waters are associated with carbonates of the above mentioned units, e.g. waters in Trenčianske Mitice (Nr. 68), Gánovce (Nr. 124), Lipovce (Choč nappe Nr. 138), Santovka (Choč and upper nappes, Nr. 87) and Šafárikovo (Silica nappe, Nr. 126). The discharge of the above mentioned localities ranges from 1 – 15 l/s and the temperature of the waters ranges from 10 – 27°C.

Mainly thermal, slightly mineralized, Ca-SO_4 waters are associated with the lower (Križná) nappe. The waters extends on the northern margin and in the centrum of the

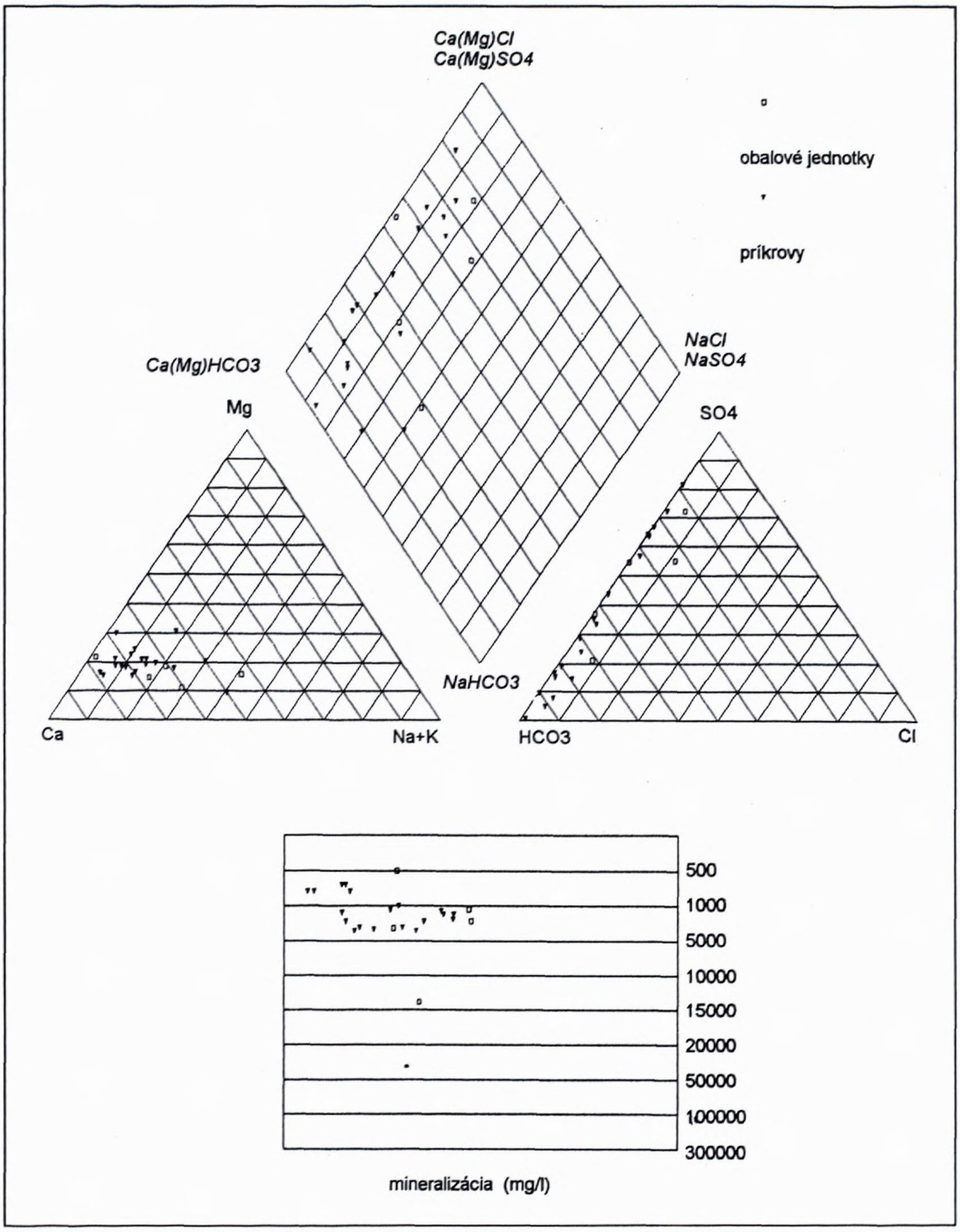


Fig. 2: Pipper graph - mineral and thermal waters of the Central West Carpathians.

Middle Slovakian Neovolcanics. The most known are waters in Sliač (Nr. 100), Kováčová (Nr. 98), Sklenné Teplice (Nr. 92), Kremnica (Nr. 91) and Chalmová (Nr. 78). The discharge of the localities ranges from 4 – 40 l/s and temperature of waters ranges from 33 – 53°C . Also thermal carbon dioxide, slightly mineralized waters in Liptovský Ján (Nr 111), Vyšné Ružbachy (Nr. 129), Banská Bystrica (Nr. 97) and Turčianské Teplice (Nr. 90, they are not carbon dioxide) are associated with carbonates of this nappe. The discharge of these localities ranges from 20 – 50 l/s and temperature of waters ranges from 20- 45°C (Fig. 2).

Thermal and slightly mineralized Ca-SO_4 waters in Piešťany (Nr. 64) and Trenčianské Teplice (Nr. 71) are associated with normal envelop. The discharge of waters at these localities ranges from 20 – 40 l/s and temperature of waters ranges from 40 – 68°C . Also cold carbon dioxide slightly mineralized Ca-Mg (Baldovce, Nr. 133, Slatina Nr. 94) and Ca-SO_4 (Korytnica, Nr. 102) waters are associated with the Triassic dolomites of the normal envelop. Their discharge ranges from 1 – 4 l/s and temperature of water ranges from 4.5 – 16.5 °C (Fig. 2).

In the Inner Carpathian Paleogene consisting of flyschoid development of deposits the mineral waters are

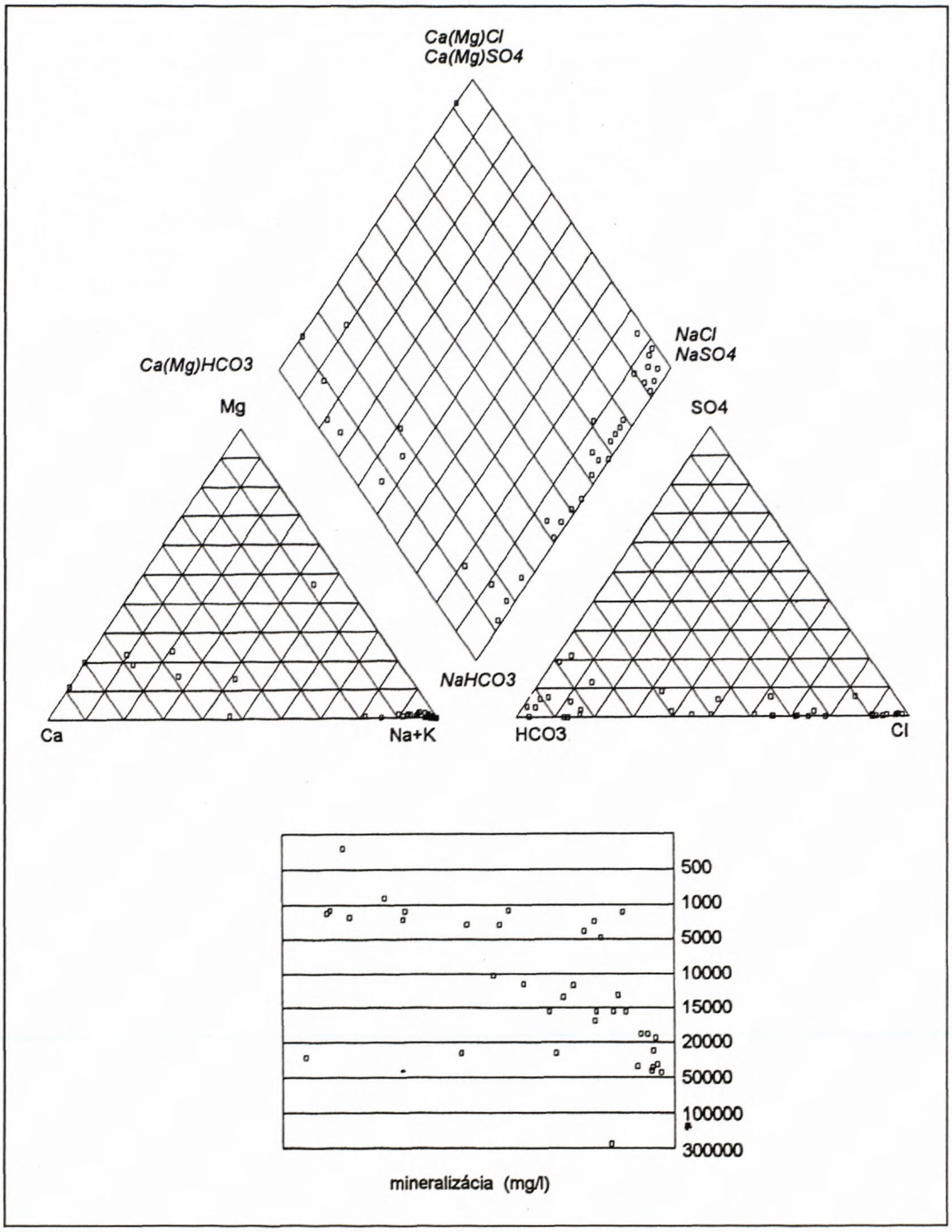


Fig. 3: Pipper graph - mineral and thermal waters of the Neogene

associated with conglomerates and sandstones. Mineral waters resemble similar waters in the Flysch zone. Cold H_2S, very slightly mineralized Ca-Mg and Na-HCO_3 waters having discharge up to 0.1 l/s prevail. The more known are waters from springs in Levoča on the foothill of Marianska hora hill (Nr. 130). Smaller amount of waters is represented by cold, carbon dioxide, slightly mineralized Ca-Mg waters with similar discharge. The more known waters occur in Nová Ľubovňa (Nr. 134) with occasional discharge about 10 l/s. Thermal, carbon dioxide, medium to strongly mineralized Na-Cl-HCO_3 waters were found by oil boreholes in the pre-Paleogene basement (the Triassic carbonates, crystalline rocks) in the Levoča Mts. The boreholes Plavnica–2 (Nr. 134), Šariš-1 (Nr. 135) and Lipany–2 (Nr. 139) comprise a part of these oil boreholes.

The Neogene mainly consists of claystones. The mineral and thermal waters here are associated with beds of basal clastics, sands and sandstones alternating with pelites. The waters are extended in the inner depressions and in the Vienna, Danube, South Slovakian and East-Slovakian Basins (Fig. 3). Considering the vertical and also the horizontal hydrogeochemical zonality cold and thermal, very slightly and slightly mineralized springs occur in the basins. The waters have from the surface and margin Ca-Mg character (e.g. Martin, Nr. 96, Trubín Nr.

Tab. 2 Distribution of hydrogeologic structures and outflow areas (Franko 1975)

Structure types	Area			Outflow area type	It is open	Water outflow
	infiltration	transition-accumulation	outflow			originates from:
open	+	+	+	open	by own aquifers, by the Quaternary pelites	aquifers and faults
semi-open	+	+	- + (artificial)	semi-open	by permeable covering deposits	secondary accumulations (from wells)
semi-closed	-	+	+	semi-closed	by impermeable overlying deposits of small thickness (up to 100-300 m) and by covering deposits	faults in overlying deposits and from covering deposits
closed	-	+	- + (artificial)	closed	by covering deposits of larger thickness (above 100 -300 m)	wells

86, Horné Plachtince Nr. 103 and Hodejov Nr. 121) and Na-HCO_3 character (e.g. Martin-Fatra Nr. 95, Šišov Nr. 72, Diakovce Nr. 62, Vieska Nr. 101). In deeper and more distal areas from the basin margins the thermal, medium and strongly mineralized, Na-Cl waters (e.g. Gajary Nr. 43, Gbely Nr. 48, Báhoň Nr. 55, Sereď Nr. 60, Dunajská Streda Nr. 57, Veľké Zalužice Nr. 66, Mojmírovce Nr. 67, Nesvady Nr. 69, Nová Vieska Nr. 77, Číž Nr. 125, Buzica Nr. 142, Hencovce Nr. 150, Trebišov Nr. 151). The highest discharge (10-20 l/s) and temperature (40-90°C) have waters occurring in the sands of Dakian, Pontian and Late Pannonian in so called central depression of the Danube Basin (Franko et al. 1989). The Na-Cl waters having very strong mineralization (35-50 mg/l) and brines with mineralization above 50 g/l mainly occur in the East-Slovakian Basin where halite occurs in the Karpatian and Badenian deposits. The most known is the water in Solivar (Nr. 143) with mineralization 292.0 g/l.

Hydrogeologic structures

Characteristics and division of mineral and thermal water hydrogeologic structures stem from its definition and heterogeneousness in the Western Carpathians. According to Franko et al. (1975) they are defined as follows: Hydrogeologic structure is a geologic-tectonically, hydrogeologically and geothermally restricted unit associated with groundwater with its own conditions (natural, natural-artificial) of movement and formation.

Based on this definition and according to existence of the infiltration, transitional-accumulation (or accumulation) and outflow area the hydrogeologic structures are divided into four types (Tab. 2). According to direct outflow of mineral water from its aquifer or to outflow through different overlying and covering rocks the spring areas are divided into four types (Tab. 2). Examples of individual structures are Trenčianske Teplice (Nr. 137, open structure), Diakovce (Nr. 62, half-open structure), Oravská Polhora (Nr. 25, half-closed) and Podhájska (Nr. 76, closed structure). Kalinčiakovo (Nr. 82) is an open spring area, Malé Bielice (Nr. 75) is a half-open spring area, Gánovce (Nr. 124) is a half-closed area and Kováčová (Nr. 98) is a closed spring area.

Origin of mineral content and chemistry of mineral water

Mineral and thermal water occurring in the geologic conditions of the Western Carpathians have atmospherogenic and marinogenic origin. According to the origin of their mineral content they represent waters with petrogenic, marinogenic and mixed mineralization (Franko et al. 1975).

Waters with carbonatogenic mineralization originate by solution of carbonates (dolomites, limestones). Solution of evaporites (gypsum and anhydrite) gives rise to waters with sulphatogenic mineralization. According to the prevailing process we can distinguish Ca-Mg-HCO_3 or Ca-Mg-SO_4 type of waters.

Ca-Mg-HCO_3 type of waters are mainly associated with the Triassic dolomites and limestones of the Choč Nappe (Tab. 1) because they overlie Cretaceous marls of the Križná Nappe without anhydrites. Minor amount of this water type is associated with the Devonian limestones of the Bohemian Massif in the foredeep, carbonates of the Silicikum and the Hungarian Middle Mts. Occasionally, they are associated with the Križná Nappe.

The waters with this mineralization are extended in the Flysch zone and in the Klippen Belt. They represent shallow circulation in degraded zone of infiltration. As an example may serve waters in Třinec (Nr. 22), Halenkovo (Nr. 19), Javorník (Nr. 14), Vyšná Písaná (Nr. 32), Malá Poľana (Nr. 34), Vyšná Radvaň (Nr. 35), Zboj (Nr. 38) and Kotrčiná Lúčka (Nr. 41). A small amount also accurs in the Neogene rocks of the Inner Carpathians e.g. in Martin (Nr. 96), Trubín (Nr. 86) and in the South-Slovakian Basin e.g. in Horné Plachtince (Nr. 103), Hájnačka (Nr. 122) and Hodejov (Nr. 121). They represent Ca-Mg-HCO_3 waters with TDS up to 2 g/l.

Ca-Mg-SO_4 waters are mainly associated with the Križná Nappe and the covering units because the Middle and Late Triassic carbonates overlie the Early Triassic schists, sands and quartzites with intercalations and inclusions of evaporites. Evaporites also occur in the Late Triassic dolomites (Keuper). In the covering units (partly in the Choč Nappe) the sulphates may origin from the Permian evaporites. The Permian rocks comprise the Early Triassic basement (Fig. 2).

If the both above mentioned processes approximately form the same part in the mineralization process, waters of transitional intertypes originate. A typical example represents waters from Turčianske Teplice (Nr. 90) and Banská Bystrica (Nr. 97) where no one of the type characteristics exceeds 50%.

Waters with silicatogenic dissolved solids originate by hydrolytic disintegration of silicates. According to the mineralogic-petrographic composition of rocks they occur in several units and areas of the Central-Carpathian Zone. They are described from the crystalline rocks of the High Tatra (Starý Smokovec, Nr. 123), Low Tatra (Vyšná Boca, Nr. 116), Neogene sands of the Turiec Depression (the Fatra in Martin, Nr. 95), Ipeľ and Lučenec Depressions (Vieska Nr. 110, Maštinec Nr. 119), Danube Lowland (Diakovce, Nr. 62). They were also referred from the area of the Neovolcanics (Stožok, Nr. 104). They mostly represent waters with TDS up to 1 g/l of the Ca-Mg-HCO_3 and Na-HCO_3 type.

The waters with hydrosilicatogenic mineralization originate by ion-exchange processes. They are mainly associated with the Flysch zone and Klippen Belt and with the Central-Carpathian Paleogene. Their chemism is formed nearby surface in the strongly degraded infiltration rock environment (Fig. 1). Na-Cl component is small or insignificant. Depending on the degree of the substitution of Ca^{+2} for Na^{+} mainly waters of Ca-Mg-Na-HCO_3, Na-Ca-Mg- HCO_3 up to Na - HCO_3 types occur. The waters mostly have TDS up to 1 g/l. The waters in Vizovice (Nr. 17), Rybi(Nr. 18), Hruštín (Nr. 24), Staré Hámry (Nr. 21) and Nesluší (Nr. 23) may serve as examples in the western part of the Flysch zone. In the eastern part of the Flysch zone waters in Kelča (Nr. 33) and Osadné (Nr. 37) may serve as an example. An example in the Klippen Belt is Hajtovka (Nr. 42) and in the Central-Carpathian Paleogene rocks the examples are waters from springs in Levoča at the foothill of the Marianska Hora hill (Nr. 130) and Jakubovany (Nr. 141). Between the most characteristic waters with hydrosilicatogenic mineralization belongs carbon dioxide waters with mineralization up to 7 g/l in Nová Bošáca (Nr. 16), Nosice (Nr. 40), Malý Sulín (Nr. 26) and Šarišský Štiavnik (Nr. 31).

Waters with halitogenic mineralization originate by dissolution of halite. The waters mostly occur in the East-Slovakian lowland where salt-bearing formations occurs in the Karpatian and Badenian. As examples may serve waters in Soľná Baňa (Nr. 143), Veľaty (Nr. 149), Hencovce (Nr. 371) and Sobrance (Nr. 154). The water in Soľná Baňa has TDS 292 g/l, the TDS at other localities varies from 9.5 to 12.3 g/l- The infiltration brines with TDS 90 – 130 g/l and temperature as high as 125°C were found out in the boreholes in the Mesozoic basement of the Vienna Basin e.g. at the locality Láb (Nr. 46).

Waters with sulphidogenic dissolved solids form by oxidation of sulphides (pyrite). They occur in the areas of sulphide deposits. As examples may serve waters in Hnilčík (Nr. 131) and Perlová Valley (Nr. 140) in the Slovenské Rudohorie Mts.

When chemism of mineral waters is formed by several mineralization processes having approximately this same intensity, waters with polygenous mineralization originate. As example may serve the mineral water Šaratica (Nr. 9) of Na-Mg-SO_4 type with TDS 25 g/l. Its chemism is formed in the western part of the flysch zone by gypsum and dolomite dissolution and by ion-exchange metamorphosis of the generated Mg or Ca-Mg-sulphate component. In the Klippen Belt as an example may serve the water in Červený Kláštor (Nr. 127), in the Central West Carpathians it is the water in Brusno (Nr. 106) and in the Neogene rocks the examples are waters in Smrdáky (Nr. 52) and Herľany (Nr. 145). They belongs to the Na(Ca)-HCO_3-Cl, Ca-Mg-Na-SO_4-HCO_3 and Na-Ca-Mg-SO_4-HCO_3-Cl types of water with TDS 1.6 – 2.9 g/l. All of them besides Šaratica are at the same time H_2S waters containing 1.4 – 4. 76 mg/l of H_2S. The water in Smrdáky contains 500 – 700 mg/l H_2S.

Relic marine waters are waters with thalasogenic mineralization. The waters can not be preserved in an unchanged form. According to the degree and lenght of the hydrogeologic opening of structures during the geologic evolution the waters were infiltration degraded with various intensity. This is manifested by a decrease of TDS and by a shift of chemism from the Na-Cl type to the Na-HCO_3 type. The degradation intensity is the lowest in the centre of the Tertiary basins and it increases toward the basin margins. Natural springs of these waters are known in the Carpathian Foredeep iin Darkov (Nr. 6) with TDS 20.6 g/l, in Skalka (Nr. 16) and Brod n/Dyjí (Nr. 1) with TDS 1.1 – 1.2 g/l. They are known in the Oravská Polhora (Nr. 25) in the Flysch zone with TDS 42.0 g/l. In the South-Slovakian Basin they occur in Číž (Nr. 125) with TDS 13.8 g/l and in the East-Slovakian Basin they occur in Slivník (Nr. 146) with TDS 5.3 g/l and with prevailing ions HCO_3^- and in Kuzmice with TDS 14.93 g/l. The waters containing this type of mineralization were found in oil boreholes in all Slovakian Tertiary basins. In the Carpathian Foredeep they occur for example in Polanka (Nr. 5) with TDS 11.0 g/l, in the Flysch Zone they occur for example in Kobylí (Nr. 10), Lubná (Nr. 13), Trojanovice (Nr. 20) and in Smilno (Nr. 30) and they have TDS 12.1 – 26.6 g/l. In the Inner-Carpathian Paleogene Basin they are for example known in the boreholes Plavnica – 2 (Nr. 134, Šariš (Nr. 135) and Lipany-2 (Nr. 139). They have TDS 8.7-12.4 g/l. In the Vienna basin they are for example known in the boreholes Gajar (Nr. 43), Lozorno (Nr. 45), Harušky (Nr. 44), Hodonín (Nr. 47) and Gbely (Nr. 48). Their TDS is 10.5 – 19.3 g/l. In the Danube Basin they were found in the boreholes Chorvátsky Grob (Nr. 50), Báhoni (Nr. 55), Špačince (Nr. 58), Sereď (Nr. 60), Ripňany (Nr. 65) Čilistovo (Nr. 53), Galanta (Nr. 59), Dunajská Streda (Nr. 57), Čalovo (Nr. 61), Veľké Zálužie (Nr. 66), Mojmírovce (Nr. 67), Nesvady (Nr. 69), Zlaté Moravce (Nr. 75a), Podhájska (Nr. 76) and Nová Vieska (Nr. 77). The TDS is 1.9 – 32.6 g/l. In the East-Slovakian Basin they were revealed from the boreholes Buzica (Nr. 142), Ďurkov (Nr. 144), Hencovce (Nr. 150), Trebišov (Nr. 151), Zatín (Nr. 152), Inačov and Stretava (Nr. 153). The TDS is 3.3 – 26.8 g/l.

If two or more waters having different mineralizations accumulate in an aquifer, waters with mixed mineraliza-

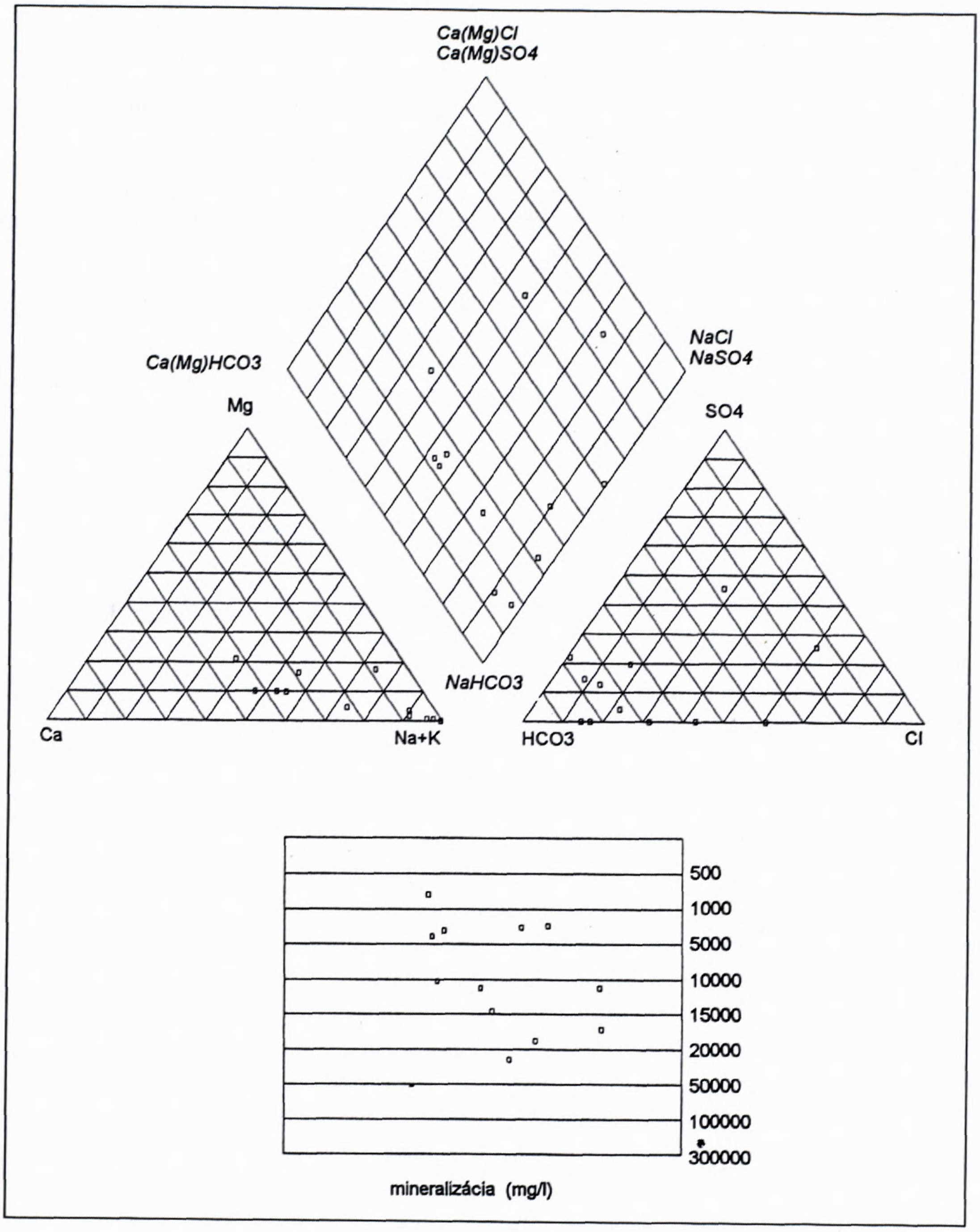


Fig. 4: Pipper graph - mixed mineral and thermal waters

tion are formed (Fig. 4). They occur in the Flysch Zone in Luhačovice (Nr. 15), Cígeľka (Nr. 27), Bardejov (Nr. 28) and Smilno (Nr. 30). The waters are assigned to the Na-HCO_3 type with TDS 9.6 – 28.8 g/l containing mixed waters with hydrosilicatogenic and marinogenic mineralization. The proportion of waters with marinogenic mineralization is shown in Fig. 4. Similar waters occur in the Polish part of the Flysch Zone. In the Inner-Carpathian Paleogene the water in Slatvina (Nr. 136) is assigned to this type. It consists of waters with carbonatogenic and marinogenic mineralization. In Neogene this type of waters occur in Budiš (Nr. 85), Želovce (Nr. 107) and Byšta (Nr. 147). The waters consist of Na-Ca-Mg-HCO_3-SO_4 type with TDS 4.2 g/l (Budiš) and Na-Mg-HCO_3-Cl-SO_4 type with TDS 6.3 g/l (Želovce) and Na-Cl-HCO_3 type with TDS 2.1 g-l (Byšta). In Budiš the waters consist of mixed silicatogenic (the Neogene sands) and carbonate-sulphatogenic (the Mesozoic carbonates) mineralization. In Želovce the mixed waters consist of waters with marinogenic (the Neogene sands) and carbonato-sulphatogenic (shallow calcareous sands) mineralization. The water in Byšta consists of halogenic (the Badenian salt-bearing formation) and carbonatogenic (the Quaternary deposits) mineralizations. In Komárno (Nr. 70) and

Dudince (Nr. 93) occur mixed waters having carbonate-sulphatogenic (the Mesozoic carbonates) and marinogenic mineralizations (the Neogene clastics, Melioris & Vass 1982).

Hydrochemical provinces

Three provinces occur in the Slovakia or in the West Carpathians:

- the carbon dioxide province
- the nitrogenous thermal water province
- the province of nitrogen, nitrogen-methane and methane waters

The province of carbon dioxide waters is planetary associated with areas where young magmatic and thermometamorphic processes occur. The carbon dioxide waters of the West Carpathians are a part of the most extended European-Asian or Alpine-Himalayan zone of the carbon dioxide waters. The topographic distribution of the carbon dioxide waters in the Slovakia is determined by deep-reaching faults at boundaries of individual deep blocks (Franko & Kolářová 1985). The carbon dioxide waters have largest extent in the area of a deep fault separating Moravia-Slovakian and Danube blocks in the SW from the Slovakia-Silezian and Fatra-Tatric blocks in the NE as it is depicted in the attachment Nr. 2. A similar extent have the waters in the area of the fault separating Danube, Fatra-Tatric and Krakowian blocks in the NW from the Rudohorie-Piliš and Beskydy-Bukovina blocks in the SE. In the Eastern and Western Slovakia the carbon dioxide waters are extended in the area of the Klippen Belt or in the area of the seismically most active Záhor-Humenné fault. The fault separates the Slovakia-Moravian and Slovakia-Silezian blocks in the NW from the Danube and Fatro-Tatric blocks in the SE. In the Eastern Slovakia it separates the Krakowian and Beskydy-Bukovina blocks in the NE from the of Fatra-Tatric, Rudohorie-Piliš and Potisia blocks in the SE. In the Middle Slovakia they occur in the area of an important NE Zázrivá-Budapest fault. Similarly in the Košice Depression they occur in the SE in the area where a deep fault separates the Rudohorie-Piliš Block in the west from the Potisia Block in the east. The largest occurence of carbon dioxide waters is associated with crossing of these deep faults.

The origin of CO_2 by ^{13}C isotope was investigated in the Slovakia in 1971 – 1982 (Cornides & Kecskés 1982). Totally 89 sources were analysed (Tab. 3).

Tab. 3 Carbon isotopes from carbon dioxide waters (I. Cornides - A. Kecskés, 1982).

Area	δ^{13} C%		$\Delta\, \delta^{13}$ C	δ^{13}C	n
	min.	max.			
Neovolcanics	-6,5	-2,5	4,0	-4,6	28
Trenčín	-7,0	-3,0	4,0	-4,9	17
Northern part of the Middle Slovakia	-6,4	-2,4	4,0	-4,8	16
North-Eastern Slovakia	-6,0	-0,7	5,3	-2,8	28

According to mean ó^{13}C value the difference between the first three and the fourth area is seen. In spite of this the values of ó^{13}C ranging from –7 to –3‰ almost occur in the first three areas in 90% and in the fourth area in more than 80%, thus this range occurs in 72 sources out of 89 sources. The CO_2 is of deep origin because the values of ó^{13}C in this range are commonly considered as an indicator of juvenile, magmatic or envelop origins. I. Cornies and A. Kecskés accepted a range –7.5 - -4.5 ‰. A shift into higher values of ó^{13}C as –3 ‰ may occur by isotope fractionation in the water-carbonate systems especially when a significant amount of carbonate rocks is dissolved by waters rich in CO_2.

The nitrogenous thermal water province is planetary extended in crystalline massives with young tectonic movements (of Mesozoic-Cenozoic age). In the West Carpathians it is associated with greisens of Gemeric granites in the eastern part of the Slovenské Rudohorie Mts. They were found by the boreholes in Čučma (Nr. 132) and Vlachovo (Nr. 128). The N_2 content ranges from 84 – 96 vol.% and F^- in a range 4.8 – 10 mg/l.

The province of nitrogen, nitrogen-methane and methane waters of sedimentary basins consists of the Carpathian Foredeep waters and waters of the Flysch and Klippen Belt zones. Also areas of the inner Neogene depressions, lowlands and volcanics are a part of this province. The waters of atmospherogenic origin with petrogenic mineralization contain predominantly nitrogen. The waters with marinogenic and mixed mineralization contain nitrogen-methane, methan-nitrogen and methane gases.

Besides the mentioned provinces it is yet possible zonaly distinguish „province" of H_2S waters. H_2S mostly occurs in the waters of the Flysch and Klippen zones and in the zone of the Central West Carpathians (Tab. 4). Based on the study of sulphur isotopes in dissolved disulphates and H_2S the H_2S waters were divided into (Šmejkal et al. 1981):

- sulphatogenic waters
- sulphidogenic waters

Sulphatogenic waters occur in the zone of the Central West Carpathians. As we stated, they are associated with carbonates of the Krížna Nappe and „normal" envelope from which rise springs with discharge from 5 to 40 l/s and with temperatures up to 60°C. The sulphate to hydrogen sulphide conversion reaches about 3% resulting in prevailing sulphate sulphur. Sulphate content are relatively high and they commonly reach above 500 mg/l. The sulphate and total sulphur are isotopically strikingly positive and maximum for the total sulphur is identical to ó^{13}S values found for the Triassic gypsum and anhydrite of the Middle Europe, i.e. from +16‰ to +27‰ (Tab. 4). The most known and most important localities are Piešťany (Nr. 64) with H_2S content 11 mg/l, Dudince (Nr. 93) with H_2S content 7 mg/l, Smrdáky (Nr. 52) with H_2S content 450-600 mg/l and Sobrance (Nr. 154) with H_2S content 220 mg/l.

Sulphidogenic waters occur in the Flysch and Klippen zones and in the Inner-Carpathian Paleogene. The waters in the Flysch zone only have small discharge (below 0.1 l/s). It

Tab. 4 Mean values of sulphur isotopes from hydrogen sulphide mineral waters (V. Šmejkal, J. Hladíková, M. Michalíček & V. Procházková (1981).

Structural-facial zone	SO_4^{2-} (mg/l)	H_2S (mg/l)	$\delta^{34}S$ (SO_4^{2-})	$\delta^{34}S$ (H_2S)	$\delta^{34}S$ (ΣS)	Conversion (%)	I.F.	n
Mesozoics of the Central West Carpathians	570	5,8	+25,6	-15,0	+24,5	2,8	1,025	18
Paleogene of the Flysch zone (Magura)	69	18,0	+4,7	-28,6	-9,3	42,0	1,026	14

Tab. 5 Ratio of intervened marinogenic mineralization into thermal waters of the pre-Tertiarybasement

Number	Locality	T.D.S. ($g.l^{-1}$)	S_1(Cl)	A_1	A_2	HCO_3/Cl	Cl/Br
133	Baldovce	4,24	14,76	0,00	69,26	4,47	1034,4
neighbour	Sivá Brada	7,19	8,36	0,00	66,24	8,04	570,4
415	Lipovce	3,61	6,46	9,71	77,85	13,55	-
neighbour	Šindliar	2,61	4,32	1,36	84,52	20,45	142,80
124	Gánovce	3,65	1,94	0,00	57,82	36,65	195,70
neighbour	Vrbov well VR-1	3,99	4,6	0,00	69,15	15,01	0,0
64	Piešťany	1,26	17,26	0,00	23,28	1,40	1536,0
93	Dudince	5,34	12,96	17,46	52,96	5,55	202,3

is in average almost in an order lower than the amount outflowed by sulphatogenic waters (Tab. 4). The dissoluble sulphure compounds originate from the pyrite oxidation. The isotopic composition of the sulphidic and sulphate sulphure sum is conspicuously lighter ($\delta^{13}S_{?S}$ = -26.2 up to +1.6‰). Relatively large isotopic variability is determined by both higher variability of pyrites and relatively high and uneven degree of bacterial conversion of sulphates to H_2S. The Oravská Polhora (Nr. 25) and Šaratica (Nr. 9) are the most known localities

Palaeohydrology

Investigation of the origin and genesis of the mineral water chemical compositions in many aspects depends on understanding of palaeohydrogeology, i.e. on mineral water evolution in time and space. The development of the problem is based on the palaeogeographic evolution of the West Carpathians from which individual phases of the hydrogeological development are derived. Four phases are recognized in the West Carpathians: the Senonian-Paleocene, the Eocene-Oligocene (Eggerian), the Eggenburgian-Karpatian and the Badenian-Recent phases (Franko & Bodiš 1989). In each phase some part of the area was a land with occurring denudation, precipitation, water infiltration, circulation and sediment washing. Other part of the area was flooded by sea with prevailing sedimentation processes and soaking of marinogenic mineralization into rocks comprising sea bottom. The soaking resulted in many mineral, mainly thermal waters as a part of the NaCl component in their chemical composition. In closed or semi-closed structures Na-Cl waters are recovered in the boreholes penetrating the pre-Tertiary basement (Tab. 5). The isotope ratio H_d /[18] proves an atmospherogenic origin of the naturally outflowing waters (Fig. 5).

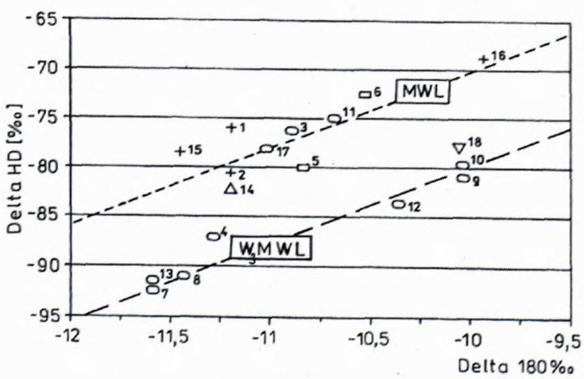


Fig. 5: Relation of ó H_d /[18]O in mineral waters
4 - Gánovce, 7 - VR-2 Vrbov, 9 - Lipovce, 10 - Šindliar, 12 - Baldovce, 18 - Trenčianske Teplice
+ cristalline rocks, ▭ križna nappe, ∇ envelop units, ⬭ choč nappe, Δ gemerikum unit

At the first 6 localities (Tab. 5) marinogenic mineralization intervened in the second phase (the Triassic carbonates underlie the Paleogene rocks), at the locality Piešťany the mineralization intervened in the 3rd phase, (the Triassic carbonates underlie the Karpatian rocks), and at the locality Dudince it intervened in the 4th phase (the Triassic carbonates and quartzites underlie the Badenian rocks).

The graphic expression of the $H_d/^{18}O$ ratio shows that the thermal waters are of atmospherogenic origin. They follow the todays MWL, however, they originate from the interstade W3 commencing some 26 000 Y.B.P. The age of these waters ranges according the ^{14}C isotope from 25 200 to 27 800 years. As a matter of fact, it is not the age of the waters but the retardation time from infiltration (in the W3) up to todays outflow from springs and boreholes.

According to the geologic age of travertines, the waters in Piešťany and Dudince began to spring at the end of the Late Pliocene, the waters in Baldovce started to spring in the Gunz-Mindelian interglacial and the waters in Gánovce began to spring in the interglacial Mindelian-Rissian.

Regime of the mineral and thermal waters

The regime of the atmospherogenic waters depends on climatic conditions. The discharge and temperature of the mineral waters with a shallow circulation (cold) immediately react on climatic changes. The thermal waters associated with deep hydrogeologic structures are assigned to the waters with confined surface of a deep circulation.

The water regime is basically influenced by precipitation in the infiltration area or by fluctuation of the groundwater level occurring in the aquifers (i.e. dolomites, limestones) of the associated hydrogeologic structure. It is also influenced by shallow groundwaters or surface waters in the outflow area. In the first case it is a pressure transformation from the infiltration area to the outflow area resulting in level fluctuation or discharge fluctuation in the catchworks (wells, boreholes, Fig. 6). The deeper and deeper is the water circulation, the later pressure changes are expressed. The circulation depth is reflected in the water temperature thus between the depth and retardation almost a direct relationship exists (Fig. 7, Franko 1970).

In the second case the original regime of a deep circulation is entirely suppressed by a regime of surface or shallow groundwaters (Fig. 8, Franko 1998). For example, a change in the thermal water level in the Trajan well in Piešťany (it catches the water in the gravelly deposits of the Váh river) directly depends on the change of the surface water level in the tail race (the reaction is immediate).

Regime of the waters having marinogenic origin follows laws of the closed hydrogeologic structures where a change of the piezometric surface occurs only at the expense of elastic reserves.

Regime of qualitative parameters - chemical composition of the mineral and thermal waters depends on pressure, temperature, gas content, characteristics of the physical-chemical processes occurring at the phase boundaries water-rock-gas and also on the hydrogeologic and hydraulic ratio in the hydrogeologic structure, mainly in the outflow area. Mainly in the semi-open and semi-closed outflow areas mixing processes of waters having various origin occur. These processes influence the stability of chemical composition of mineral waters

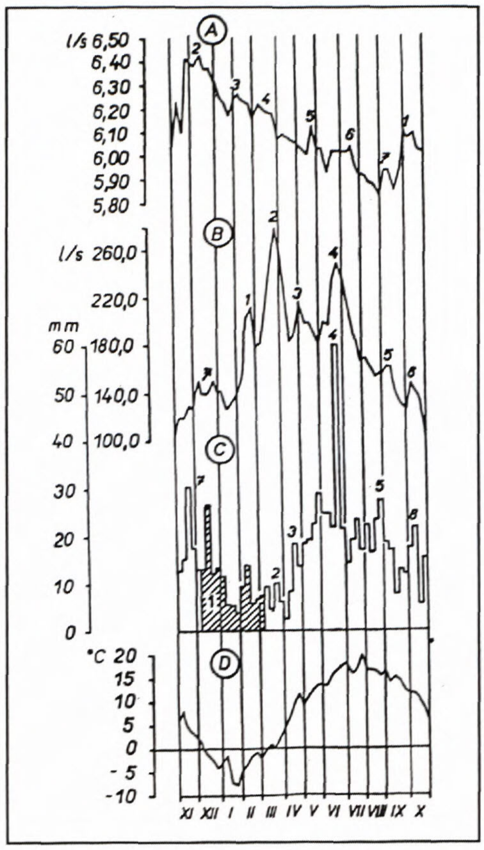


Fig. 6: Regime of mineral waters in Trenčianske Teplice (1963-1966)
A - spring P-1 (40°C), B - Žihlavník, C - precipitation (T.Teplice), D - air temperature (T. Teplice)

Fig. 7: Thermal water retardation discharge vs. their temperature relationship
1 - Vajar (15°C – 3- 4 weeks), 2 - Bojnice (28°C - 7 weeks), 3 - Trenčianske Teplice (40°C 8 3/4 month), 4 - Bojnice (45°C - 9 month), 5 - Baden (48°C - 12 months), 6 - Sklenné Teplice (53°C - 13 months), 7 - Karlové Vary (73°C - 2 years)

(Baldovce, Budiš, Lipovce, Santovka, Dudince, Komárno etc.). The origin of the final chemical composition is often more complicated by mixing partly occurring in the natural conditions and partly occurring in the catchworks

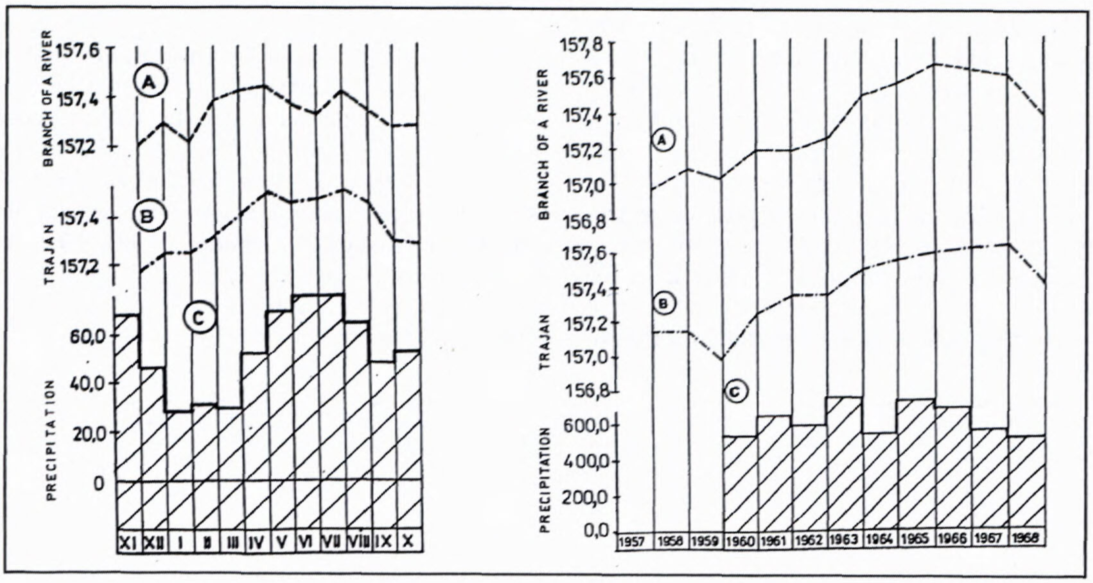


Fig. 8: Mineral and thermal water regimes in Piešťany
A – Tail race, B-spring Trajan, C-precipitation (Piešťany)

Tab. 6 Main data on mineral and thermal waters of the natural healing spas

Nr	Locality	Nr. of used new sources	Q $l.s^{-1}$	Water type ()10-20 c_iz_i%	CMV $mg.l^{-1}$		CO_2		H_2S		T °C	
					min.	max.	min.	max.	min.	max.	min.	max.
1	Bardejov spa	8	2,6	Na-(Ca)-HCO_3-Cl	1541	9336	2094,8	2994,0	-		6,5	18,0
2	Bojnice	8	27,6	Ca-Mg-HCO_3-SO_4	676,6	768,1	17,6	55,0			28,6	48,1
3	Brusno	6	2,25	Ca-Na-Mg-HCO_3-SO_4	1268,8	3348,2	768,7	1210,4	-		16,4	20,5
4	Číž	1	0,3-0,5	Na-Cl	13162,2		57,2		-		10,8	
5	Dudince	3	8,2	Na-Ca-(Mg)-HCO_3-Cl-(SO_4)	4654,2	6433,3	1227,1	1447,0	4,7	11,2	27,0	28,3
6	Korytnica	8	1,1	Ca-Mg-SO_4-HCO_3	1945,5	3587,4	1506,6	3318,8	-		6,5	9,0
7	Kováčová	1	15,0	Ca-Mg-SO_4-HCO_3	2816,1		696,7		poz.		40,5	
8	Lúčky	5	16,5	Ca-Mg-SO_4-HCO_3	1000	2900	250,0	990,0	-		22,2	31,5
9	Nimnica	3	2,1	Na-HCO_3	4161,4	7579,5	1392,0	2180,0			11,2	13,2
10	Piešťany	8	33,0-40,0	Ca-Na-(Mg)-SO_4-HCO_3-(Cl)	1254,8	1426,1	0	35,2	2,5	10,9	31,0	69,5
11	Rajecké Teplice	7	6,4	Ca-Mg-HCO_3-(SO_4)	713,9	861,6	95,0	101,2	0	0,24	33,4	38,2
12	Sklenné Teplice	10	15,0	Ca-Mg-SO_4-(HCO_3)	2071	2536	-	-	-		33,0	54,2
13	Sliač	4	5,4	Ca-Mg-SO_4-HCO_3	633,4	3940,0	1250	1840	0	0,3	12,0	33,2
14	Smrdáky	3	1,4	Na-Cl-HCO_3	3159,8	7438,5	0	589,0	0	673,0	11,4	16,5
15	Trenčianske Teplice	7	14,3	Ca-Mg-(Na)-SO_4-HCO_3	2690,1	2970,0	0	372,2	2,8	4,2	37,7	40,0
16	Turčianske Teplice	8	20,6	Ca-Mg-SO_4-HCO_3	1221,4	1580,7	44,2	450,0	0	3,0	22,0	45,7
17	Ružbachy	13	47,5	Ca-Mg-HCO_3-SO_4	296,0	3130,5	283,7	2900,2	0,14	0,55	16,0	23,0

(Melioris 1996). Chemical composition of the mineral and thermal waters may show short-time and mainly season and long-time changes.

In spite of complicated geologic-tectonic conditions of mineral and thermal water formation in the West Carpathians, the most of sources (mainly with higher discharge) show a stability of chemical composition depending on time.

As an example we show the mineral water from the spring Salvátor in Lipovce, which origin was a result of mixing of waters originated in limestones and dolomites of the Choč Nappe and in the Quaternary fluvial accumulations. After realization of the boreholes in 1953 became a change in chemical composition of the mineral water.

The mineral and thermal water with mixed mineralization at Dudunce (well S-3) is too 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 (Hyánková, Melioris, 1993). The results of archive analyses from the years 1836 and 1893 and contempory analyses document the constatnt representation of individual ions.

Year analyst	Na^+	K^+	Ca^{2+}	Mg^{2+}	Cl^-	SO_4^{2-}	HCO_3^-
1882 Prof.M.Balló	22,7	1,9	46,6	28,1	6,6	6,6	83,5
1901 Prof.M.Balló	20,7	2,3	48,2	28,0	6,10	5,9	85,2
18907 Prof.M.Balló	20,22	1,96	47,73	29,33	5,92	5,81	86,04
1914 Dr.K.Emszt	21,46	2,03	47,98	27,81	6,37	7,17	84,13
1926 Hochstadter.	22,06	2,53	45,28	28,03	6,13	5,95	84,77
1926 Dr.V.Veselý	19,59	2,03	48,61	28,60	6,05	6,26	87,63

	Source	Na^+	K^+	Ca^{2+}	Mg^{2+}	Cl^-	SO_4^{2-}	HCO_3^-
1836	not marked	696	22	627	182	404	568	1614
1893	Main spring	851	129	498	133	564	559	2965
1957	Well S-3		1097	459	137	597	567	3216
1986	Well S-3	819	121	491	131	539	522	2972
18.1.1995	Well S-3	810	121	498	135	567	510	2953

Analyses performed by: B. Wehrle (1836), B. Lengyel (1893), IGHP, n.p. Žilina (1957 and 1986) and INGEO as.s. Žilina (1995)

Use and protection of mineral and thermal waters

Health resorts based on the use of mineral and thermal waters have long-term traditions in the Slovakia. The healing effects of mineral waters on human organism are known from immemorial although the commencement of the Slovak health resorts was given by historians at the end of the 15th century. The available data suggest that the potential of mineral waters for healing aims was used in the spas of various importance and positions, for example in the Eastern Slovakia, for 80 % up to the 2nd world war . After 1920 and 1945 it came to a decrease of importance and even to the end of some local spas. On the other hand, a big development of the health resorts became on the basis of the most important mineral and thermal water sources.

A big richness of mineral waters occurring in the Slovakia (Tab. 1), their qualitative variability as well as historical development and spa positions in the past give a real assumption to the more extensive use of the mineral and thermal water potentials for:

- improving the health of the population
- to do more effective tourism
- to improve the environment

Seventeen natural spas with use of mineral and thermal waters for balneotherapeutic purposes (Tab. 6) occur in the Slovakia at the moment. By the Slovak Ministry of Health and its competent precursors 102 sources of mineral waters are recognized. 83 of them were recognized as natural healing sources and 19 of them were recognized as sources of mineral table waters.

The natural mineral table waters are suitable as healing and refreshing beverages. The table mineral waters are filled in 10 filling plants at the moment (Tab. 7) which supply business network. The total consumption of natural mineral waters for drinking purposes including use of the local sources probably exceeds 50 l/year/man (Melioris 1996).

Protection of mineral waters of all kinds (natural healing sources, natural mineral table waters, thermal waters) is an inseparable part of their use and their preservation for future. Based on other knowledge the protec-

Tab. 7 Basic data on chemical composition of potable mineral waters

	Locality	Source	Q [l.s-1]	M [g.l-1]	T [°C]	CO_2[g.l-1]	Na^+	K^{2+}	Ca^{2+}	Mg^{2+}	Cl-	SO_4^{2-}	HCO_3^-	Water type ()-10-20 c;z;%
							[mg.l-1]							
1	Baldovce	BV-1	2,0	2,378	11,4	2,384	91,8	21,4	392,7	85,9	75,2	197,1	1474,1	Ca-Mg-(Na)-HCO_3-(SO_4)
2	Budiš	B-3	0,4	4,259	14,0	3,238	655,9	69,5	310,2	85,6	28,4	615,2	2398,0	Na-Ca-(Mg)-HCO_3-SO_4
3	Cígeľka	CH-1	0,5	29,16	11,3	1,883	7984,5	200,9	181,3	73,6	3616,3	28,1	16397,3	Na-HCO_3-Cl
4	Čerín Aqua Prima	ČAM-1	2,0	2,232	15,7	2,059	25,6	7,8	405,8	76,5	8,8	3,5	1678,6	Ca-Mg-HCO_3
5	Korytnica	Klement S-7	0,31	3,274	8,0	2,850	6,5	6,0	594,8	164,9	2,8	1376,5	1037,3	Ca-Mg-SO_4-HCO_3
6	Lipovce Salvaror	S-II	3,5	3,569	15,5	2,20 SH - 1,40 H_2S	209,4	-	458,5	166,4	107,8	139,5	2495,6	Ca-Mg-(Na)-HCO_3
7	Santovka	B-6	0,35	3,5	14,5	2,4	339,0	64,3	457,47	88,44	259,7	386,0	1856,3	Ca-Na-(Mg)-HCO_3-(SO_4)-(Cl)
8	Slatina	BB-1	2,5 dop.odb1,5	4,9	14,7	2,12	676,8	116,8	316,7	116,6	570,1	483,7	2629,5	Na-Ca-(Mg)-HCO_3-Cl-(SO_4)
9	Tornaľa Magneral	HVŠ-1	7,0	2,715	18,0	1,865	69,8	15,1	429,3	130,2	51,6	320,0	1675,0	Ca-Mg-HCO_3-(SO_4)
10	Záturčie Fatra	BJ-2	0,45	3,570	12,0	0,859	800,0	18,5	38,48	50,6	30,1	137,0	2240,7	Na-HCO_3

Lipovce SH - 1,40 H_2S; Analysis performed: Nr. 1,3,7,8 – Geologický ústav PRIF UK Bratislava; Nr. 2,5,6,10 - IGHP, š.p. Žilina, and. INGEO a.s. Žilina, Ref. Centrum Piešťany, Nr. 4,9

tion of the waters is performed as internal and external protections, protection of attributes and products of the mineral water source as a balneotherapeutic factor and the protection of the spa environments. The internal protection includes the protection of hydrogeologic existence of the source and its crenotechnical facilities.

The resolution of the Slovak government No. 56/1974 specified protection zones and protection actions of three degrees. The specification was based on an extensive hydrogeologic research and investigation. The protection zone of the 1st degree includes the spring area, the protection zone of the 2nd degree includes the transition-accumulation area and the protection zone of the 3rd degree includes the infiltration area of the natural healing sources and natural mineral table waters.

References

Cornides, I. a Kecskés, A., 1982: Deep - seated carbon dioxide in Slovakia; the problem of its Origin. Geol. Zbor. - Geologica Carpathica. Bratislava, 33, 2, 183-190.

Franko, O., 1970: Bojnické termálne vody a ich vzťah k ťažbe uhlia na nováckom ložisku (Bojnice thermal waters and their relations to Nováky coal deposit). Geologické práce, Správy 52, GÚDŠ Bratislava, 59-155.

Franko, O., Gazda, S. a Michalíček, M., 1975: Tvorba a klasifikácia minerálnych vôd Západných Karpát (Genesis and classification of mineral water in West Carpathins). Geol. ústav D. Štúra, Bratislava, 230 s.

Franko, O. a Kolářová, M., 1983: Mapa minerálnych vôd ČSSR 1:500 000 (Map of mineral waters in Czechoslovakia 1:500.000). Geol. ústav D. Štúra. Bratislava, Ústř. úst. geol. Praha.

Franko, O. a Kolářová, M., 1985: Vysvetlivky k mape minerálnych vôd ČSSR 1:500 000 (Explanations to the map of mineral waters in Czchoslovakia 1:500.000). Geol. ústav D. Štúra, Bratislava, s. 4-24.

Franko, O., Kolářová, M. a Mateovič, L., 1985: Katalóg dokumentačných bodov k mape minerálnych vôd ČSSR 1:500 000 (Katalogue of dokumental points to the map of mineral waters in Czechoslovakia 1:500.000). Geol. úst. D. Štúra, Bratislava, s. 2-103.

Franko, O., Bodiš, D., Fendek, M., Remšík, A., Jančí, J. a Král, M., 1989: Methods of research and evaluation of geothermal resources in pore environment of Pannonian Basin. Západ. Karpaty, Sér. Hydrogeol. a inž. geol. 8, Geol. ústav D. Štúra, Bratislava, s. 165-192.

Franko, O. a Bodiš, D., 1989: Paleohydrogeology of Mineral Waters of the Inner West Carpathians. Západ. Karpaty. Sér. Hydrogeol.a inž.geol. 8. Geol. ústav D.Štúra. Bratislava, s.145-163.

Franko, O., Remšík, A. a Fendek, M., eds. 1995: Atlas of geothermal energy of Slovakia. Geol. ústav D. Štúra Bratislava, 268 s.

Hensel, J. a i., 1951: Balneografia Slovenska. SAV Bratislava. 455 s.

Hyánková, K. a Melioris, L., 1993: The Unusual Chemism of Mineral Waters at Dudince. Geol. Carpatica, 44, 2. Bratislava, s. 123-131.

Maheľ, M., 1952: Minerálne pramene Slovenska so zreteľom na geologickú stavbu (Études des rapports entre les sources minérales et la structure géologique en Slovaquie). Práce ŠGÚ Bratislava. 62 s.

Melioris, L. a Vass, D., 1982: Hydrogeologické a geologické pomery levickej žriedelnej línie (Hydrogeological and geological conditions in Levice hydrogeological structure). Západné Karpaty. Ser. Hydrogeol. a inž. geol. 4. GÚDŠ Bratislava. s. 7-57.

Melioris, L., 1996: Kvalitatívne parametre prírodných minerálnych vôd - alternatívnych pitných vôd (Qualitative parameters of natural mineral waters - alternative potable waters). Podzemná voda. Roč. 2, č. 2, Bratislava, s. 74-78.

Šmejkal, V., Hladíková, J., Michalíček, M. a Procházková, V., 1981: Schwelisotopenuntersuchungen an Sulfaten der Mineralwässer im Westkarpaten - System der ČSSR und in Westböhmen. Freib. Forsch. - H. C 360. Freiburg, 57-74.