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Mineral Waters of the Cigeľka Spa

Natália Bačová[1], Jozef Komoň[2], Juraj Michalko[3]

[1] State Geological Institute of Dionýz Štúr, Dept. of Hydrogeology and Geothermal Energy, Regional Centre, Jesenského 8, 040 01 Košice, Slovakia, natalia.bacova[a]geology.sk
[2] Koral, s.r.o., Nad Medzou 2, 052 01 Spišská Nová Ves, Slovakia, info[a]koral.sk
[3] State Geological Institute of Dionýz Štúr, Dept. of Hydrogeology and Geothermal Energy, Mlynská dolina 1, 817 04 Bratislava, Slovakia, juraj.michalko[a]geology.sk

Abstract: Cigeľka Village is located in the NE Slovakia, about 20 km NW of Bardejov. Thanks to the mineral waters occurrence with beneficial effects for humans troubled with the digestive system, it has been known since the thirties of the 19th Century. Cigeľka natural mineral water (exploited borehole at CH-1) is a strongly mineralized, carbonic Na-HCO_3-Cl type. The resulting chemical composition is formed by mixing two chemical types of water – Na-HCO_3-(Cl) and Na-Cl – well insulated from the "live" circulation. It gets to the surface along a deep reaching system of faults of NE-SW direction (likely NW continuation of the Muráň tectonic system). The paper is devoted to past achievements (especially the latest) of hydrogeological, hydrogeochemical and geophysical works carried out in the discharge area of the natural mineral water Cigeľka, macrochemical description of the composition of mineral water in Cigeľka, patterns of formation and relationship between this mineral water the and the mineral waters of the Flysch Zone of the Western Carpathians.

Key words: geological and hydrogeological conditions, Flysch Zone, Cigeľka natural mineral water, macrochemical composition, vertical electrical sounding, stable isotopes O and H

7.1 Introduction

On Slovakia-Polish border about 20 km NW of the town of Bardejov is the village Cigeľka. It is known mainly thanks to mineral waters. Their unique properties were reported to Hungary and throughout Europe already in the thirties of the 19th Century by Ludvig Tognio (Rebro, 1996). Already in the fifties of the 19th Century the mineral water was bottled and since 1918 the mineral water from three wells – Slovan, Štefan and Ľudovít – has been used for balneotherapeutic purposes. The natural mineral water Cigeľka (from source CH-1), available on the market today, has beneficial effects on the digestive system, it helps at excessive consumption of food and also in the lack of appetite to eat, at the problems with excess stomach acid.

Geological and hydrogeological conditions of the discharge area of the Cigeľka natural mineral water and its surroundings have been studied since the 50's of the last Century by many prominent hydrogeology and geochemistry experts (Hynie – the first hydro-geological survey drillings in Cigeľka in the years 1953-1957, Jarchovský, Kellner, Haluška, Struňák, Malatinský, Klago, Michalíček and others). For bottling of the mineral water the greatest importance had the results of hydrogeological research of the discharge area in the years 1972 – 1984 (Malatinský et al., 1984), when natural mineral source – borehole CH-1 was developed. In the period 1990 – 1997 in the broader area of Cigeľka a search hydrogeological survey was executed to obtain a basis for drafting the buffer zones of the Cigeľka natural mineral water (Pacindová et al., 1997). Later, the interpreting of original data and the description of these waters and hydrogeological structure were dealt by Marcin (1996, 1999), Bačová & Bačo (1998), Bačová (2006), and Bačová & Michalko (2007).

The paper is focused in selected geological and hydrogeological facts about the discharge area of the Cigeľka natural mineral water. It is dedicated to patterns of forming macrochemical composition of mineral water in the Flysch Zone and Foredeep of the Western Carpathians and in particular to relation between the Cigeľka mineral waters and other mineral waters of the Flysch Zone.

7.2 Methodology

In a summary processing and interpreting the results of hydrogeological research carried out in Cigeľka it is important to consider a number of very relevant knowledge about mineral waters of the Flysch Zone of the Western Carpathians. This results from the fact that, in the case of the Cigeľka natural mineral water the water has high content of dissolved solids, with the likely deep circulation. Therefore it is not possible to describe the formation of the resulting chemical composition without examining the broader context – rules of forming and occurrence of mineral waters within the Flysch Zone. Hydrogeochemical evaluation of the original data always requires selecting the appropriate classifications – those that most contribute to the systematization of knowledge to the clear and vivid interpretations.

For the classification of chemical water types under prevailing ion-chemical type we include in the name the ions with more than 25 meq . l^{-1} % share (classification of Kurlov in Klimentov, 1980); in opposite to commonly used more than 20 meq . l^{-1} %. We point out that in the case of the Cigeľka natural mineral water the chemical symbol is the same in both cases.

To assess the total dissolved solids in mineral waters of the Flysch Zone with wide interval of values (from

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230 mg . l^{-1} to 130 g . l^{-1}) the most appropriate is classification by Ivanov (in Franko et al., 1975) with supplementary resolution of weak brines with TDS from 50 to 100 g . l^{-1} and strong brines with TDS greater than 100 g . l^{-1} (in accordance with the classification of groundwater by Švarcev, 1996).

When describing the mineralization processes share in the resulting chemical composition of mineral water we are using genetic classification of the chemical composition of the groundwater of the Western Carpathians (Gazda, 1974), adapted for the purposes of Geological dictionary, part Hydrogeology (Hanzel et al., 1998) by Fľaková et al. (2010).

In terms of origin investigations we term mineral waters in accordance with the genetic classification of groundwater prepared by Kirjuchin et al. (in Švarcev, 1996).

7.3 Geological and hydrogeological conditions of the discharge area

The Cigeľka natural mineral water (CH-1 borehole) is located in the western part of the Nízke Beskydy Mts. (whole Busov) in Rača Partial Nappe of the Magura Nappe (Flysch Zone). Geological and tectonic site conditions and its wider surroundings are described in detail in the work by Bačová and Bačo (1998).

Flysch sediments of the Rača Partial Nappe are represented by Zlín Fm. – Makovica Sandstone (Tvarožec by Nemčok et al., 1990) and Bialowieza Fm. (Figs. 7.1, 7.2). The Makovica Sandstone complex consists of massive sandstone layers over- and under-lain by approximately 1000 m thick fine-rhythmic flysch (Nemčok l. c., 1990). It is a light, coarse-grained sandstone with abundant feldspar, often hued by limonite. Foraminiferal community notes Early Eocene age, but Nummulites facies on the Palaeocene age (Nemčok et al., l. c.). Above the sandstone bodies the Bialowieza Fm. is present. It develops from the sub-base of thick-bedded sandstone. Sandstone and claystone ratio is 1 : 1; thin-bedded fine-grained sandstone is rich in hieroglyphics of organic origin. The claystone at the bottom of the formation is variegated (red, green, grey); in the top of grey and greenish hue. The stratigraphic range is from the Palaeocene to the bottom of the Middle Eocene. It is overlain by the Bystrica Fm. (Luthetian – Latest Eocene). It is a thick- layered alternation of thick-bedded to thin-bedded greywacke sandstone with thick layers of dark grey claystone with shell-like jointing.

Hydrogeological structure of the Cigeľka natural mineral water is considered (in accordance with the classi-

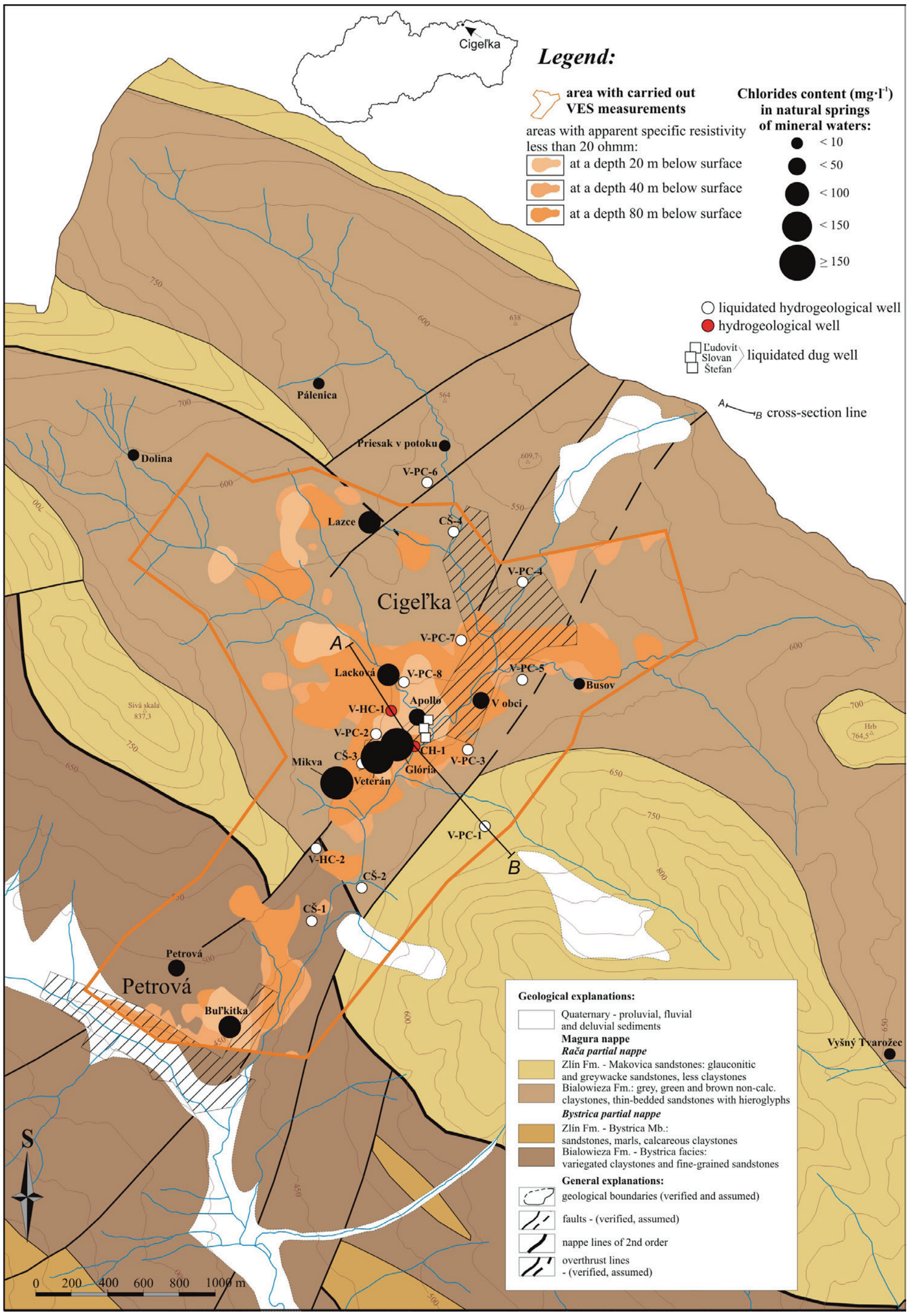

Fig. 7.1 Map of the results interpretation of hydrogeochemical and geophysical work carried out in the years 1990 – 1997 in the field of the Cigeľka natural healing water (based on documents by Straník, 1965; Bačo in Pacindová et al., 1997, modified)

fication of Franko et al., 1975) for semiclosed structure (without catchment) with partially covered discharge area. In more detail it is characterized in work by Bačová and Bačo (1998). In the area studied and its surroundings, there are many natural springs of mineral water. They are depicted in Fig. 7.1. In the same figure there are located former trial wells and hydrogeological boreholes that provided significant knowledge on mineral waters, but later they were destroyed.

Schematic geological section across the Oľchovec Valley (Fig. 7.2) through hydrogeological drillings V-HC-1, CH-1 and V-PC-1.

The Cigeľka natural mineral water is exploited of the hydrogeological borehole CH-1 (202.5 m) excavated in the years 1972 – 1973 (Malatinský et al., 1984). The borehole lithology consists of Bialowieza Fm. (top depth interval – mainly claystone facies, bottom depth interval – mostly sandstone facies, Fig. 7.2). Heavily mineralized carbonated water with a chemical type of $Na\text{-}HCO_3\text{-}Cl$ is tapped at a depth of 178 – 200 meters. The yield is about 0.15 – 0.40 l . s^{-1}.

In the scope of the search hydrogeological survey in the years 1990 – 1997 (Pacindová et al., 1997) hydrogeological well V-HC-1 was excavated (between 1/1992 – 2/1992). It reached a depth of 212.6 meters (from 75.9 m to the final depth – mostly sandstone Bialowieza Fm. or bottom of the Bialowieza Fm. Late Palaeocene to Early Eocene in age – Samuel, in Pacindová et al., 1997). The progress of technical work in the hole development was quite complicated.

CO_2 present in rocks and mineral water was causing the problem. Since the drilling was performed in the protection zone of mineral water, it was not possible to use a sufficiently heavy drilling mud, which would prevent eruptions emerging. The first eruption of the drilling fluid with mineral water occurred at a drilling laydown to a depth of 79 m. It lasted about 15 minutes, the height of jet of water reached up to 3 m. When casing a borehole interval from 50 to 130 meters there was another eruption of up to 15 m, lasting about an hour. After washing the well it occurred incoherent impulsive overflow of mineral water from the well. The average yield of the overflow calculated from measuring the volume of water spilled from the well over two hours, was 0.021 l . s^{-1}. Heavily mineralized water (20.5 g . l^{-1}) had a chemical type of $Na\text{-}HCO_3\text{-}Cl$. In the course of further borehole development the eruption happened through the drill rod (height of about 16 m, the duration of about 30 minutes, the well produced the fragments of the rock with a diameter of 0.5 cm). With increasing depth of the borehole, the duration of the eruption increased. After the final hole casing it was found that eruptions of mixture of gas and water occurred about once a day after water level in the well reached to a about 1 m below the surface. After the eruption the water table dropped to a depth of about 75 – 80 meters.

Due to the high gas-saturation of rocks and mineral water and more or less regular eruptions, overflow tests were carried out by so-called siphoning. The tests preceded the execution of reconstruction works in bottling borehole CH-1 in order to monitor the pressure on its collar and overflow yield. It was necessary to replace the incrusted

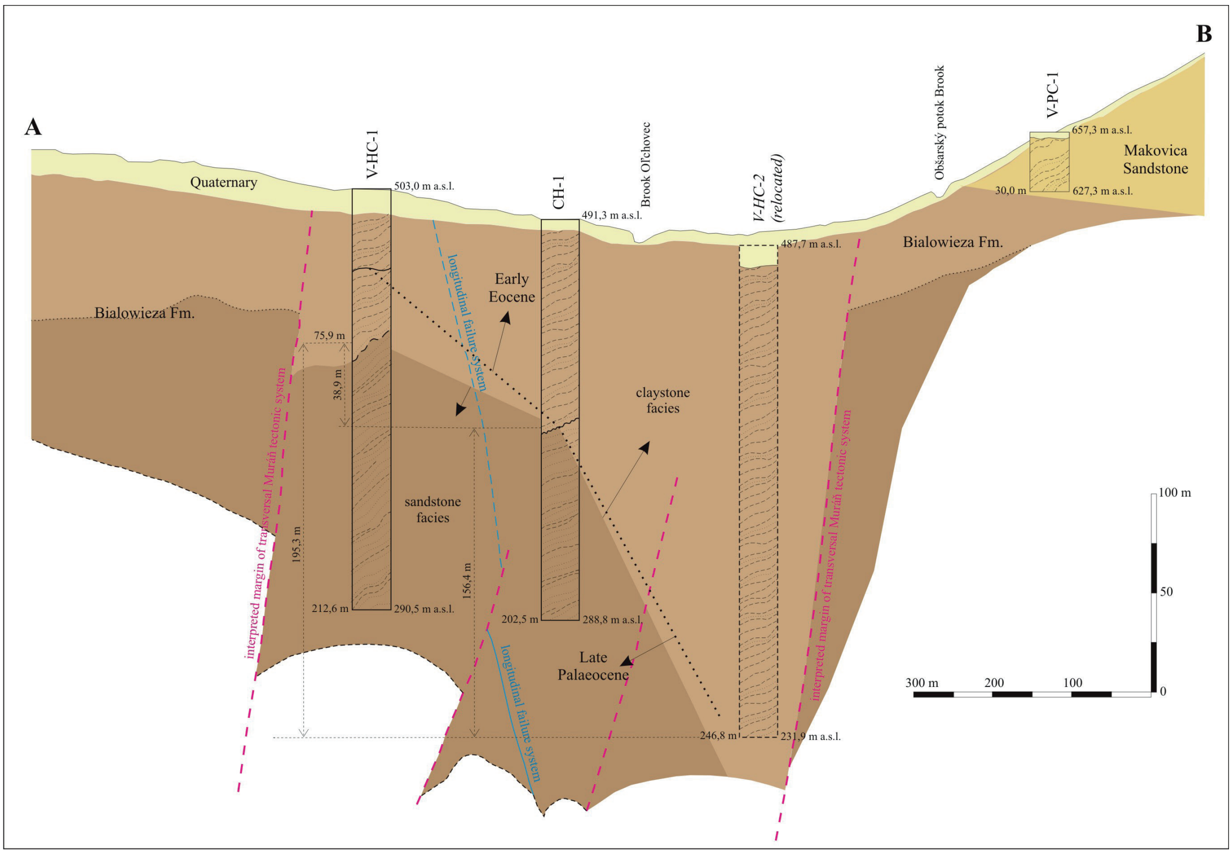

Fig. 7.2 Schematic litho-geological section through discharge area of the natural healing water Cigeľka (compiled by Bačo, 1997; modified)

discharge pipe and install functional gauges. The incrust is formed in the pressure pipe from the depth of about 50 m below the surface (Fig. 7. 3). During operation of the Filling Plant in Cigeľka it is necessary to replace the discharge line after about seven to ten years.

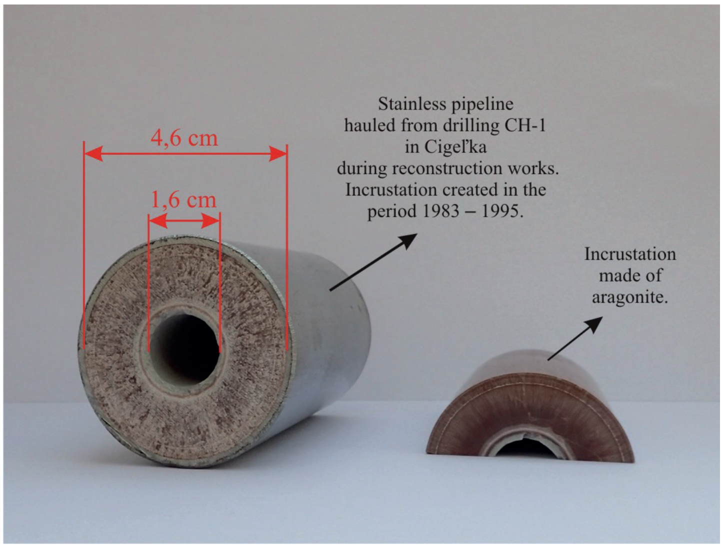

Fig. 7.3 Incrust in the discharge line of the well CH-1 in Cigeľka (photo: Bačová)

The overflow tests in borehole V-HC-1 consisted of three stages – three embedment depths of the discharge pipe (201, 150 and 102 m). During the hydrodynamic tests two-phase fluid – a mixture of gas and water – existed in the borehole V-HC-1. In place of inflow into the borehole the pressure was below the saturation pressure of water with carbon dioxide at the beginning of hydrodynamic tests even when borehole was capped, indicating the existence of the two-phase flow in the collectors immediately surrounding the well. For exploitation of mineral water from the well W-HC-1 based on the results of carried out hydrodynamic tests it was recommended to embed the column to the technically real depth (Jetel, in Pacindová et al., 1997). In the last phase of the first stage of the hydrodynamic test the overflow yield reached 0.076 l . s^{-1}.

Hydrogeological borehole V-HC-2 began to be drilled in August, 1992. The projected depth of 650 m was breached because of considerable technical problems during drilling and casing. The difficulties were caused by different borehole lithology than anticipated, and by the drilling fluid used, which was not sufficiently dense due to the pressure conditions in the borehole (bentonite, lovosa, micro-crushed limestone). Under these circumstances it was not possible to keep the design well structures, therefore the excavation completed at 246.8 meters.

In the scope of the search hydrogeological survey in the years 1990 – 1997 (Pacindová et al., 1997) in the discharge area of the spring the Cigeľka natural mineral water VES field measurements were made (Komoň et al., in Pacindová et al., l. c.). The intention was to distinguish lithological interface between claystone – sandstone. Special conditions in this area – claystone rock environment and underneath environments with a predominance of sandstone with heavily mineralized water (TDS with 30 g . l^{-1}) – did not achieve this goal, but brought another important lesson. Minimum resistance anomalies (below 20 ohmm) substantially correspond to the chemical composition of mineral water from the natural springs known and hydrogeological boreholes. In the most extensive central anomaly (Fig. 7.1) there is documented the presence of mineral water with the highest total dissolved solids content. It can therefore be assumed that space with minimal resistance of the ground follows the presence of strongly mineralized water in a predominantly sandstone Bialowieza Fm.

The following figures (Figs. 7.4, 7.5, 7.6) document CO_2 effervescences in natural mineral springs in the area of deep fault zone of NE-SW direction (likely NW con-

Fig. 7.4 CO_2 effervescence observed in the spring Veterán (photo: Bačová, 24. 8. 2009)

Fig. 7.5 Intense CO_2 effervescence in the spring Mikva (photo: Bačová, 11. 6. 2014)

Fig. 7.6 CO_2 effervescence in the spring Buľkitka (photo: Bačová, 29. 10. 2014)

tinuation of the Muráň tectonic system – Pospíšil et al., 1989). Springs, Pramene Veterán, Mikva and Buľkitka are depicted in Fig. 7.1. Currently they are abandoned, except the first one. Even at the end of the last Century at the margin of the discharge area of the Cigeľka mineral water there were observed effervescences of CO_2 in the artificial pond, used for recreational purposes (Fig. 7.7).

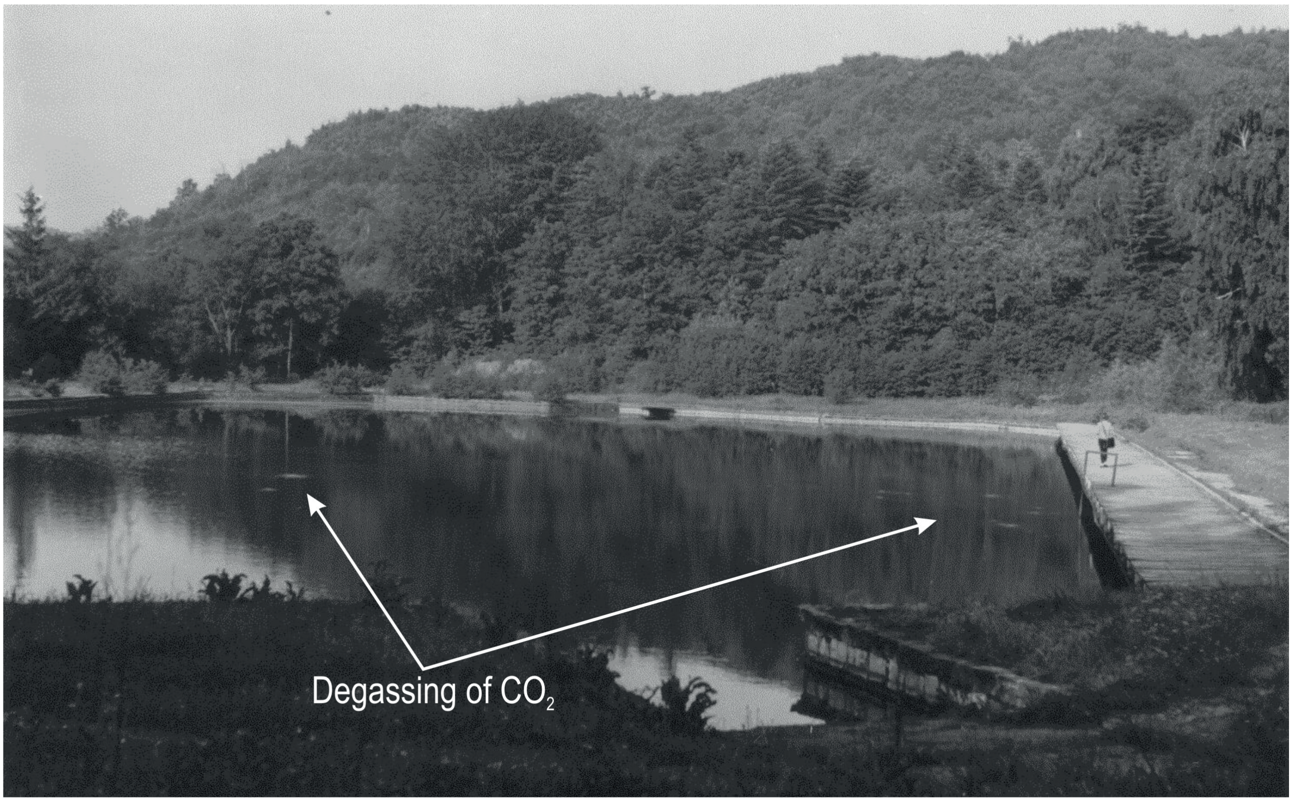

Fig. 7.7 CO_2 effervescence in the pond in Cigeľka (photograph of 1995)

Tab. 7.1 Chemical composition of the Cigeľka natural mineral water from the well CH-1 and V-HC-1

Analysis Date	TDS	Li^+	Na^+	K^+	Ca^{2+}	Mg^{2+}	SO_4^{2-}	HCO_3^-	CO_2	I^-	B	Br^-	Analysis by
	[g . l^{-1}]	[mg . l^{-1}]											
well CH-1													
1973	28.98		8,295		208.42	78.79	16.46	16,657.9	2,710	2.60	98.77	28.0	IGHP
25.3.1981	30.30	12.70	8,286	285	207.60	91.40	17.20	16,845.7	2,250		139.41		Slovakoterma Piešťany
10.2.1982	29.15		8,217	340	201.10	56.10	19.70	16,138.5	2,253				Slovakoterma Piešťany
16.8.1983	29.48		8,203	850	209.10	80.50	18.30	16,791.5	2,250				Slovakoterma Piešťany
22.8.1984	29.52	12.70	8,001	345	208.45	79.80	17.50	16,461.0	2,803	6.72	143.30	24.1	Slovakoterma Piešťany
24.6.1986	29.76	10.20	8,379	154	163.53	74.42	376.32	16,474.9	1,950				Slovakoterma Piešťany
29.9.1987	29.64		8,145	205	204.70	75.00	18.50	16,783.1	2,670		135.22		Slovakoterma Piešťany
27.8.1992	29.37		8,336	135	184.20	92.00	15.00	16,690.3	1,925				GSSR Bratislava
14.9.1993	29.57		8,401	141	170.80	88.85	22.00	16,894.3	2,177				GSSR Bratislava
21.7.1994	28.91	9.80	7,680	145	200.96	85.31	17.29	16,962.5					GSSR Bratislava
5.10.1994	30.46	7.20	8,453	150	169.00	90.70	15.00	17,125.7	2,012				GSSR Bratislava
27.3.1995	28.07	7.46	7,500	140	267.65	46.37	7.82	16,626.9					GSSR Bratislava
11.4.1995	29.23	10.42	8,410	156	172.06	92.75	18.93	16,657.4		12.69	110.90		GSSR Bratislava
2.5.1995	29.26	10.71	9,067	286	168.24	68.40	9.88	15,868.3		13.55	173.40		GSSR Bratislava
9.12.2005	30.31	10.80	8,385	235	173.00	78.30	17.05	16,653.0	2,187	1.53		19.8	BEL/NOVAMANN International. s.r.o.
well V-HC-1													
2.6.1992	15.99	5.20	4,150	1	250.50	18.23	71.61	9,304.9	2,150				GSSR Bratislava
30.6.1992	20.50	6.85	5,950	208	80.16	72.92	174.09	10,744.9	2,360				GSSR Bratislava
30.9.1992	28.65	8.85	8,050	156	241.15	170.61	15.64	14,918.4	2,620				GSSR Bratislava
10.2.1993	29.21	9.50	8,125	190	26.95	4.84	45.29	16,840.4	2,680				GSSR Bratislava
24.3.1993	29.15	18.10	8,050	16	259.48	66.57	4.12	16,809.9	2,230				GSSR Bratislava
1.6.1993	26.87	9.10	7,500	145	54.17	58.40	16.87	13,210.0	2,750				GSSR Bratislava
24.8.1993	27.59	6.48	6,514	145	230.74	66.92	4.52	14,826.9	1,950				GSSR Bratislava
24.11.1993	30.48	7.20	7,717	148	29.94	296.55	9.88	17,938.7	2,040				GSSR Bratislava
8.4.1995	29.61	9.94	8,620	165	210.30	75.36	23.46	16,748.9	2,640	12.69	102.60		GSSR Bratislava
1.5.1995	29.20	10.75	8,978	173	195.01	2.90	9.88	14,662.1		14.00	160.50		GSSR Bratislava
1.5.1995	29.64	42.60	8,200	200	216.43	77.82	26.13	16,470.0	1,210	13.75	128.00	19.05	Unigeo. a.s. Ostrava

7.4 Chemical composition of mineral water in Cigeľka and its vicinity

The Cigeľka natural mineral water (previously supplied to the commercial network as a "natural healing water Cigeľka", later "natural healing water Cigeľka") is exploited at the well CH-1; the chemical type is Na-HCO_3-Cl. In accordance with the Health Ministry Decree no. 100/2006 Coll. as amended (with effect from 1. 7. 2013) is a bicarbonate-chloride sodium carbonic brine, with increased content of *sodium, chlorides*, *iodine, hydrogen-carbonates* with increased content of nutrient-physiological elements – *lithium, magnesium, calcium and boron*, neutral, cold. It is likely formed by mixing two types of water – Na-HCO_3-(Cl) and Na-Cl – at the conduits to the surface (Bačová & Bačo, 1998), where it penetrates thanks to deep-reaching fault system of NE-SW direction. Its presence (dispersion) in the rock environment of the discharge area is manifested in increased chloride content of weakly mineralized waters of natural springs (Fig. 7.1). Selected characteristics of the chemical composition of mineral water from boreholes CH-1 and V-HC-1 are shown in Tab. 1. Analyses of deep gas samples and samples taken from the separator in the course of hydrodynamic tests in borehole V-HC-1 (in 1995) are presented in the Tab. 7.2.

Tab. 7.2 Gas analyses – well V-HC-1 (Prokop, 1995 in Pacindová et al., 1997)

Gas composition	CO_2	CH_4	N_2	H_2
Gas sample	[meq . l^{-1} %]			
From separator	98.646	0.716	0.637	0.001
Deep sampling - 98 m	99.012	0.93	0.006	0.053
Deep sampling - 100 m	99.16	0.833	0.007	0

Macrochemical composition of mineral water in Cigeľka and its wider area is described in Tab. 3. In the case of water from the hydrogeological boreholes and dug wells (including perished or destroyed) situated nearby bottling plant in Cigeľka (Fig. 7.8 right – green circles), the water is of the type Na-HCO_3-Cl with a TDS of greater than 10 g . l^{-1}, except for the well TD-3 (4.8 g . l^{-1}). The content of chloride and bicarbonate indicate a positive linear correlation with high level of significance.

Dark blue triangles in the diagram (Fig. 7.8) represent the mineral water springs:

- In the discharge area of the Cigeľka natural mineral water,
- Buľkitka in Petrová (springing south of Cigeľka, also in the area of deep reaching fault zone of NE-SW direction – likely NW continuation of the Muráň tectonic system),
- in Frička,
- in Nižný and Vyšný Tvarožec.

They are waters of the type Na-HCO_3 with high chloride content (range 9 – 12 meq . l^{-1} %; in the case of mineral water from the spring Buľkitka in Petrová 7 meq . l^{-1} %). Here, too, we observe significant positive linear relationship between the content of bicarbonate and chloride.

Other mineral water springs remote off the discharge area of the Cigeľka natural mineral water and from the surrounding area (Hrabské, Petrová, Gaboltov; Fig.7.8 – blue circles) have indeed increased the TDS with varying proportions hydro-silicatogenic mineralization, but they are not impacted by heavily mineralized water with high chloride content (deeper circulation).

The relationship between sodium and chlorides in the mineral waters of Cigeľka and its surroundings (Fig. 7.8

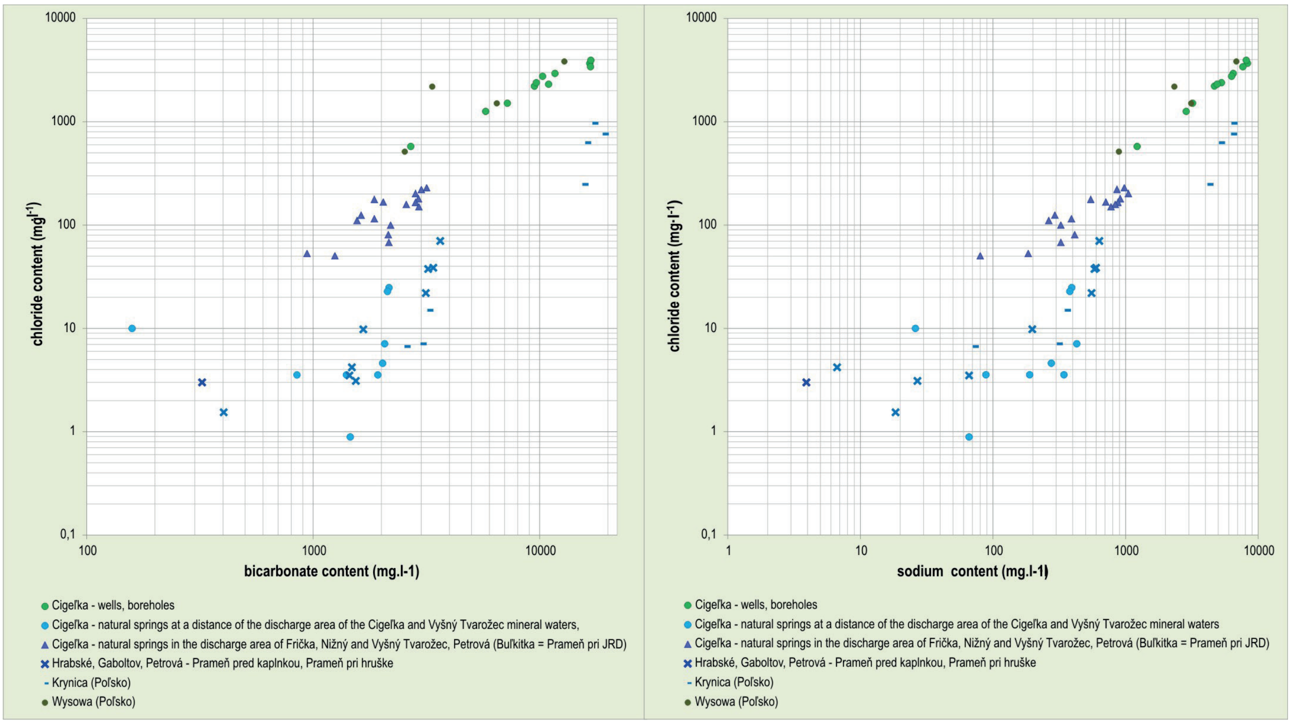

Fig. 7.8 Bicarbonate, chloride and sodium content in the Cigeľka mineral waters source and its surroundings

Tab. 7.3 Selected data on the macrochemical composition of mineral waters in wider surroundings of the discharge area of the Cigeľka natural mineral water

Source of mineral water (depth)	TDS	Na^+	Cl^-	HCO_3^-	Chemical water type [≥ 25 meq . l^{-1} %]	Data source
	[mg . l^{-1}]					
Cigeľka, Štefan (BV-26G), 29 m	19,145	4,670	2,212	9,484	Na-HCO_3-Cl	Krahulec et al., 1978
Cigeľka, VIII (CH-1; BV-99), 200 m	28,976	8,295	3,680	16,658	Na-HCO_3-Cl	Krahulec et al., 1978
Cigeľka, (V-HC-1) 212 m	29,214	8,125	3,936	16,840	Na-HCO_3-Cl	Pacindová et al., 1997
Cigeľka, well P-1 (BV-92)	28,800	7,655	3,408	16,775	Na-HCO_3-Cl	Franko & Kolářová, 1983
Cigeľka, well CŠ-3 (90 m)	4,802	1,220	576	2,697	Na-HCO_3-Cl	Haluška, 1967
Cigeľka, Ľudovít	21,868	6,475	2,936	11,690	Na-HCO_3-Cl	Hensel et al., 1955
Cigeľka, Ľudovít	12,290	3,200	1,511	7,200	Na-HCO_3-Cl	Michalíček & Květ, 1960
Cigeľka, Štefan (BV-26G), 29 m	17,978	5,287	2,389	9,675	Na-HCO_3-Cl	Hensel et al., 1955
Cigeľka, Štefan (BV-26G), 29 m	18,581	4,900	2,312	10,959	Na-HCO_3-Cl	Michalíček & Květ, 1960
Cigeľka, Slovan	10,072	2,860	1,259	5,773	Na-HCO_3-Cl	Michalíček & Květ, 1960
Cigeľka, well V-PC-8	21,946	6,300	2,757	10,312	Na-HCO_3-Cl	Pacindová et al., 1997
Cigeľka, Mikva	4,380	1,050	202	2,831	Na-HCO_3	Pacindová et al., 1997
Cigeľka, Mikva (BV-24)	4,372	911	180	2,917	Na-HCO_3	Krahulec et al., 1978
Cigeľka, Prameň v obci	2,902	393	25	2,163	Na-Ca-HCO_3	Pacindová et al., 1997
Cigeľka, Prameň v obci (BV-25)	2,922	380	23	2,130	Na-Ca-HCO_3	Pacindová et al., 1997
Cigeľka, Veterán (BV-26)	4,211	874	166	2,831	Na-HCO_3	Krahulec et al., 1978
Cigeľka, Veterán* (BV-26)	3,825	835	159	2,578	Na-HCO_3	Pacindová et al., 1997
Cigeľka, Dolina	1,879	189	4	1,403	Na-Ca-Mg-HCO_3	Pacindová et al., 1997
Cigeľka, Busov	1,150	89	4	848	Ca-Na-HCO_3	Pacindová et al., 1997
Cigeľka, Pálenica	1,949	66	1	1,458	Ca-HCO_3	Pacindová et al., 1997
Cigeľka, Lazce I (BV-21)	2,727	275	5	2,026	Ca-Na-HCO_3	Krahulec et al., 1977
Cigeľka, Lazce II (BV-22)	3,050	414	81	2,148	Na-Ca-HCO_3	Krahulec et al., 1977
Cigeľka, Lazce*	2,824	546	177	1,861	Na-Ca-HCO_3	Pacindová et al., 1997
Cigeľka, Glória*	3,117	710	168	2,041	Na-HCO_3	Pacindová et al., 1997
Cigeľka, Lacková*	1,778	80	51	1,248	Na-Ca-HCO_3	Pacindová et al., 1997
Cigeľka, Matka (BV-26D)	324	26	10	159	Ca-Na-HCO_3-SO_4	Krahulec et al., 1977
Nižný Tvarožec	1,410	184	53	940	Na-Ca-HCO_3	Pacindová et al., 1997
Nižný Tvarožec, Kvašna voda (BV-53)	2,264	263	111	1,562	Na-Ca-HCO_3	Krahulec et al., 1977
Vyšný Tvarožec 1	2,687	343	4	1,931	Ca-Na-HCO_3	Pacindová et al., 1997
Vyšný Tvarožec 2	2,753	428	7	2,068	Na-Mg-HCO_3	Pacindová et al., 1997
Vyšný Tvarožec (BV-76)	2,374	292	125	1,629	Na-Ca-HCO_3	Krahulec et al., 1977
Frička, Frička 1	4,389	860	222	3,002	Na-HCO_3	Pacindová et al., 1997
Frička, Frička 2	4,145	775	151	2,929	Na-Mg-Ca-HCO_3	Pacindová et al., 1997
Frička, Frička 3 - Plazínska	2,669	390	115	1,861	Na-Ca-HCO_3	Pacindová et al., 1997
Frička, Kyselka (BV-29)	4,688	979	231	3,170	Na-HCO_3	Krahulec et al., 1977
Hrabské, Prameň na hraniciach (BV-40)	516	4	3	323	Ca-HCO_3	Krahulec et al., 1977
Hrabské, Prameň nad potokom (BV-35)	4,355	582	38	3,220	Na-HCO_3	Krahulec et al., 1977
Hrabské, Prameň na hornom konci (BV-36)	4,355	554	22	3,145	Na-Ca-HCO_3	Krahulec et al., 1977
Hrabské, Prameň pri poľnej ceste (BV-38)	2,149	7	4	1,482	Ca-HCO_3	Krahulec et al., 1977
Hrabské, Prameň pri gerlachovskom chotári (BV-39)	4,569	598	39	3,390	Na-Ca-HCO_3	Krahulec et al., 1977
Hrabské, Tri pramene v potoku (BV-41)	4,998	633	70	3,640	Na-Ca-HCO_3	Krahulec et al., 1977
Petrová, Prameň pred kaplnkou (BV-54)	1,949	66	4	1,445	Ca-HCO_3	Krahulec et al., 1977
Petrová, Prameň pri hruške (BV-55)	2,074	27	3	1,544	Ca-HCO_3	Krahulec et al., 1977
Petrová, Prameň pri JRD (BV-56)	3,026	325	68	2,160	Ca-Na-HCO_3	Krahulec et al., 1977
Petrová, Buľkitka	3,085	325	100	2,197	Ca-Na-HCO_3	Pacindová et al., 1997
Gaboltov, Prameň pri kríži (BV-30)	2,217	198	10	1,666	Ca-Na-HCO_3	Krahulec et al., 1977
Gaboltov, Prameň pri ceste (BV-87)	610	18	2	403	Ca-HCO_3	Krahulec et al., 1977
Krynica - Zuber I	22,619	5,074	628	15,921	Na-HCO_3	Rajchel, 2012
Krynica - Zuber II	21,045	4,151	248	15,494	Na-HCO_3	Rajchel, 2012
Krynica - Zuber III	25,372	6,311	968	17,141	Na-HCO_3	Rajchel, 2012
Krynica - Zuber IV	27,218	6,270	762	19,038	Na-HCO_3	Rajchel, 2012
Krynica - Mieczyslaw	4,278	350	15	3,202	Ca-Na-HCO_3	Rajchel, 2012
Krynica - Glówny	3,434	71	7	2,537	Ca-HCO_3	Rajchel, 2012
Krynica - Slotwinka	3,927	304	7	2,988	Mg-Na-HCO_3	Rajchel, 2012
Wysowa - Alexandra	24,714	6,834	3,829	12,850	Na-HCO_3-Cl	Rajchel, 2012
Wysowa - Franciszek	8,936	2,333	2,187	3,356	Na-Cl-HCO_3	Rajchel, 2012
Wysowa - Anna	11,738	3,122	1,507	6,468	Na-HCO_3-Cl	Rajchel, 2012
Wysowa - Władysław	4,376	890	514	2,538	Na-HCO_3-Cl	Rajchel, 2012

right) is also characterized by significant dependence in the above-described two Na-HCO_3-Cl and Na-HCO_3 types.

Both graphs (Fig. 7.8) are supplemented by information on the content macro-components in the mineral waters from the nearby border area in Poland (Tab. 7.3). Weakly to strongly mineralized waters from the sources in the Wysowa Spa (aboutan 4 km of Cigeľka and located on NE continuation of the same deep-reaching fault zone) have nearly identical macrochemical composition (dark green circles in Fig. 7.8). Mineral waters known in Krynica (14 km west of Cigeľka) differ from these waters by significantly lower chloride content.

Carbon dioxide in the rock environment of the Cigeľka discharge area and its wider surroundings is an important phenomenon affecting the transport of mineral water. It is manifested by a large number of natural springs of carbonic mineral waters and the dry spontaneous emissions of CO_2. In Poland they are termed mofettes (e.g. mofettes near Zlockie described in detail by Rajchel & Rajchel (2006), mofettes in the wider area of the spa of Krynica). The origin of this gas (significantly affecting the chemical composition of mineral water) is mainly associated with deep-reaching faults (Muráň tectonic system; Pospišil et al., 1989) with signs of Neogene magmatism in closer but especially in the wider area. The presence of oxalates (whewellite) found in borehole V-HC-1 in the cracks of sandstone around Cigeľka (Bačo & Pacindová, 1993) may also point to a probable, but not a substantial proportion of carbon (and thus CO_2) of organic origin (Bačo & Pacindová, l.c; Hofmann & Bernasconi, 1998). This is the first description of whewellite (Fig. 7.9a, b) in the Slovak part of the Western Carpathians. On steeply dipping fractures, with a width of up to 1 cm it forms translucent to white--grey crystalline aggregates. In the cavernous parts there are developed crystal planes with a strong glassy luster.

The high presence of CO_2 and the mineral water of Na-HCO_3 type is generally characterized by the formation of dawsonite (Uher & Michalík, 1991). This mineral has been described in the cracks of sandstone from the hydrogeological boreholes V-HC-1 and V-HC-2 (Bačo & Pacindová, 1993) as a relatively abundant filler (Fig. 7.9c, d). In the cracks with a width of a few millimetres to 1.3 centimetres it forms snow-white radiate aggregates with pearl luster.

Results of the determination of stable isotopes of hydrogen and oxygen in the mineral waters of natural springs in the discharge area in Cigeľka and Frička (Michalko, in Pacindová et al., 1997) significantly complement the findings described above. The Cigeľka natural mineral water is not participating in the "live" water cycle, which is confirmed by its isotopic composition [$\delta^{18}O_{H_2O}$ 4,22 ‰ and δD_{H_2O} -37,2 ‰]. These mineral water springs in the discharge area in Cigeľka and the Frička have an increased chloride content, and at the same time increased content of the isotopes ^{18}O and D in comparison with the ordinary groundwater of the territory of interest. This is likely manifestation of strongly mineralized water originating in greater depth.

7.5 The Cigeľka natural mineral water in relation to mineral waters of the Flysch Zone in the Carpathians

Study of the processes of formation and genesis of the Cigeľka mineral water requires to perform the analysis of voluminous information gathered so far – geological, geochemical, hydrogeological and hydrogeochemical. The basis for the subsequent image processing and interpreting the relationship between selected qualitative characteristics of mineral water is a set of data on the chemical composition of mineral waters of the Flysch Zone and the Foredeep of the Western Carpathians (in Moravia, Slovakia, Poland and partly Ukraine), obtained from the available domestic and foreign publications and final reports of various geological tasks.

In Fig. 7.10 there are shown the chemical types of mineral waters of selected sites depicted on the structural scheme of the Flysch Zone and the Foredeep of Carpathians compiled by Lexa et al. (2000). The used classification is based on the principle of the prevailing ions; brackets in the title of the chemical type mean contents of a component in the range 10 – 25 meq . l^{-1} % – in this way only chlorides content is shown in Fig. 7.10. Sources of data used on mineral waters of Moravia, Slovakia and Poland are cited in Fig. 7.11., data on the mineral waters of the territory of Ukraine we received from publications Kolodij & Kojnov (1984).

Macrochemical composition of mineral waters of the Flysch Zone and of the Foredeep of the Western Carpathians (Slovakia, Moravia and Poland) is shown in Fig. 7.11. In the chart with a logarithmic scale coefficients $(Na^+ + K^+)/HCO_3^-$ a $(Ca^{2+} + Mg^{2+})/HCO_3^-$ are plotted (Bačová, 2011), calculated from data on ion content expressed in mass concentrations (mg . l^{-1}). The graph provides a comprehensive view of macrochemical composition of mineral waters of the Flysch Zone and of the Foredeep of the Western Carpathians. It also allows to assess the likely participation of different mineralization processes in resulting chemical composition of mineral waters at specific sites – including Cigeľka. The set of hydrogeochemical data contains the results of 234 analyzes of mineral waters.

Gradual change in the chemical composition of water from the Na-HCO_3 type through Na-Cl-HCO_3 and Na-Cl-HCO_3 up to Na-Cl type is shown in Fig. 7.11., expressed by signs colour. Bicarbonate waters are represented by the signs of blue colour and chloride waters or waters with a predominance of chloride in anion composition in shades of green. The TDS of water (Fig. 7.12) is in the range 228 – 126,139 mg . l^{-1}.

The highest TDS have chloride waters of the type Na-Cl and Na-Ca-Cl from the space of the Foredeep of the Western Carpathians – present in the Neogene sediments (Lapczyca) and basement of the flysch nappes of Krosno Group (Fig. 7.10., Devonian, borehole U-3A of the Ustroń Spa in Poland, brine exploited at a depth of 1,318 – 1,728 meters – Rajchel et al., 2007). This are highly mineralized waters to strong brines with TDS more

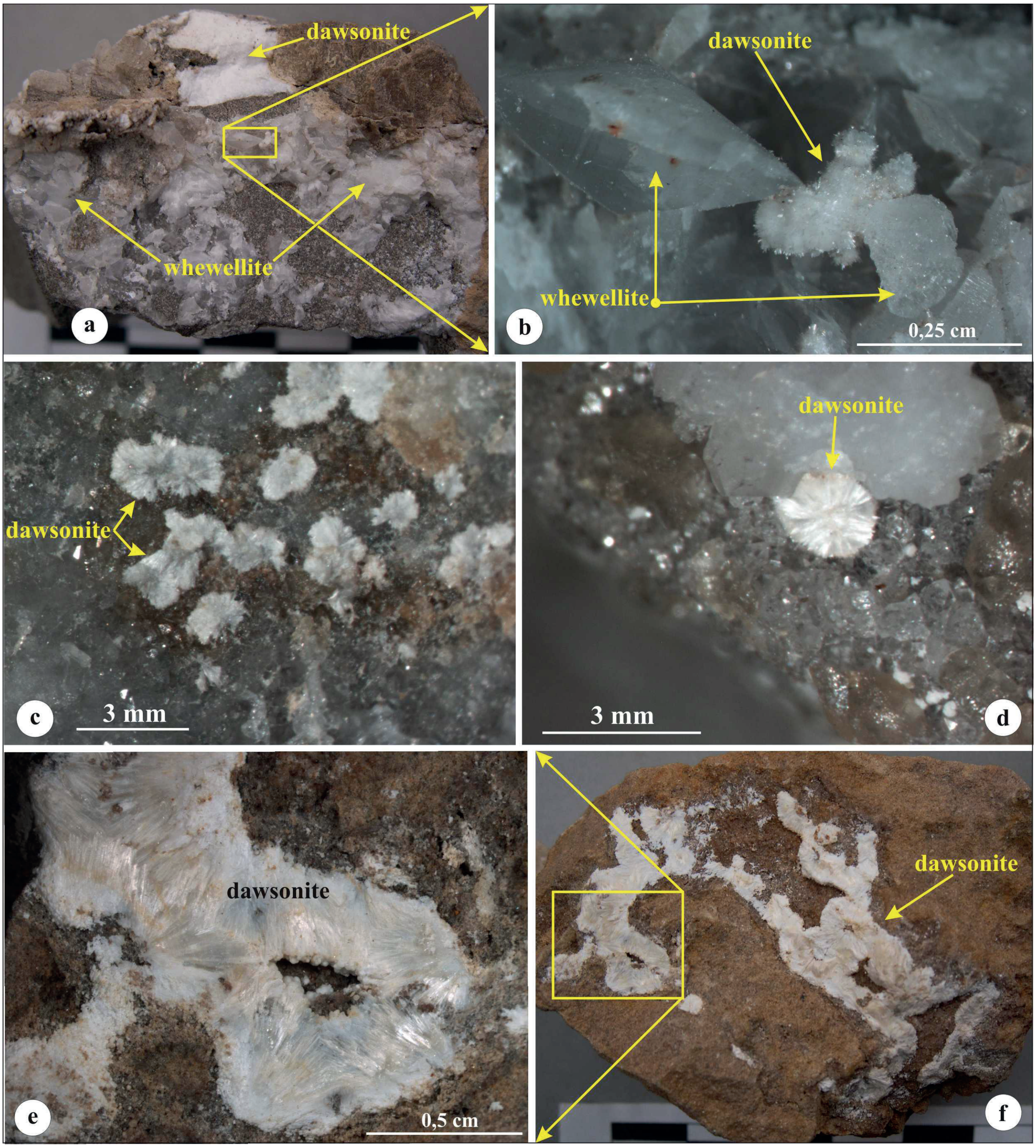

Fig. 7.9 Epigenetic minerals documented in the core recovery of hydrogeological boreholes in Cigeľka. Crystal aggregates of whewellite – Ca (C_2O_4) . H_2O on the wall of crack in sandstone (a), and crystals of whewellite (b) with needle-shaped dawsonite in the borehole V-HC-1/190.6 m. The radial aggregates of dawsonite – NaAl (CO_3) $(OH)_2$ (c, d) in the borehole V-HC-2/42.8 m and radiating thin-needle-shaped aggregates in the sandstone fissure in the valley NW of Cigeľka mineral water plant (e, f). Photo: Bačo.

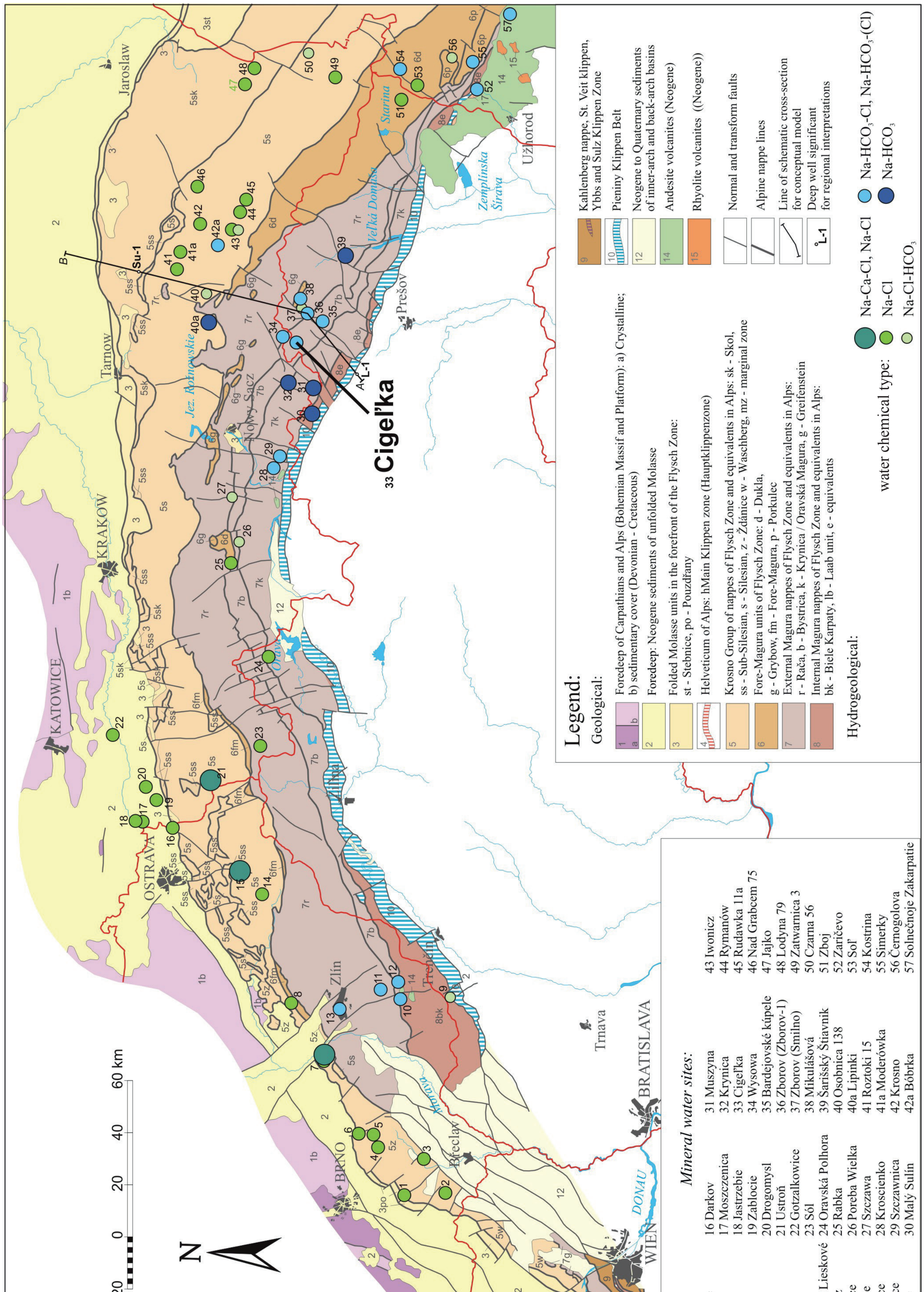

Fig. 7.10 Macrochemical composition of mineral waters of the Flysch Zone and of the Foredeep of Carpathians (Moravia, Slovakia, Poland, partly Ukraine), on the structural scheme (Lexa et al., 2000) – compiled by Bačová, 2013

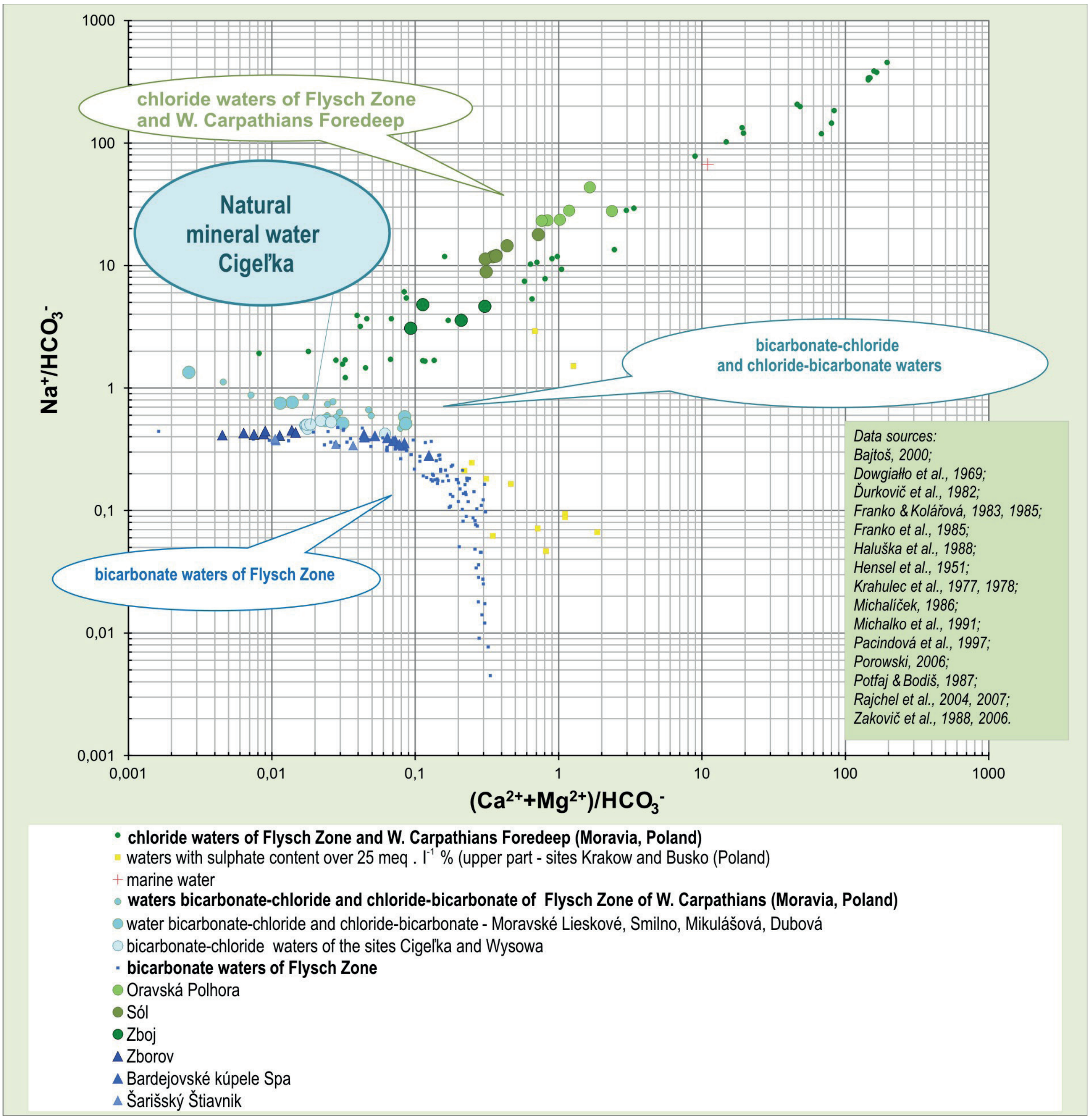

Fig. 7.11 The chemical composition of mineral waters of the Flysch Zone and of the Foredeep of the Western Carpathians, with distinguishing of water types and selected sites

than 100 g . l^{-1} (Fig. 7.10 – dark-green ring no. 21). In Fig. 7.11 the strong brine from the Ustroń location is represented by a group of small dark-green rings with the highest content of sodium and chloride – the top right. Within the Flysch Zone in Slovakia the chemical Na-Cl type posses the brines from sites Zboj (Ďurkovič et al., 1982) and Oravská Polhora (Zakovič et al., 2009). From a genetic point of view they are *sedimentation waters – buried* (Kirjuchin et al. in Švarcev 1996, *fossil marine* according to genetic classification of natural waters compiled by Pačes, 1983). Highly mineralized waters to brines, of the type Na-Cl with thalassogenic mineralization always take up a position to the top of the graph (ratio Na^+ / HCO_3^- is greater than 1).

Sodium chloride (Na-Cl) type of groundwater occurs everywhere in the vertical profile as the thickest hydrogeochemical zone – zone of brines. We encounter it at different depths (in the artesian basins it is present only a few hundred meters below the surface, in the hydrogeological massifs it is present in depths of up to several kilometres), but clearly does not depend on the type of rock environment in which it appears. In general, this is the hydrogeochemical stagnation zone (Macioszczyk & Dobrzyński, 2007). The main source of chloride in groundwater is water of seas and lagoons, buried in the course of formation of sedimentary rocks of marine origin.

Bicarbonate water – from the genetic point of view *of meteoric origin* – is shown in Fig. 7.11. at the bottom of the graph – the coefficient of Na^+/HCO_3^- is always less than 1 (predominantly the value is less than 0.5). This includes mineral waters of the type $Na-HCO_3$ from numerous natural springs of the Flysch Zone of Eastern Slovakia – in the chart particularly in the middle of the left lower quadrant (Fig. 7.11). In the same quadrant in the right side of the body representing concentrated mineral waters with a predominance of calcium and magnesium in the cationic composition, whereas these waters are very weakly to weakly mineralized (most natural mineral water springs in the eastern section of the Flysch Zone). Depending on the factors and the processes of formation of bicarbonate water (the residence time in the rock environment, circulation depth, the action of juvenile CO_2, the intensity of the ion exchange processes, etc.), the chemical composition of this water is changing from $Ca(Mg)-HCO_3$ (bottom right quadrant) to $Na-HCO_3$ type (top left quadrant; Fig. 7.11). Mineralization effect of deep CO_2 is manifested by a shift of signs to the top left. The anion composition of mineral waters of the Flysch Zone of the shallowest circulation, forming the upper part of the zone of active water-exchange, with a total dissolved solids generally less than 1 g . l^{-1} is dominated by bicarbonates, which are a normal component of the groundwater. Kirjuchin (2008) notes that the chemical composition of ordinary hydrogen bicarbonate lime waters is formed by biogenic processes and up to half of the carbon gets into the water from biogenic CO_2. The other half comes from carbonate rocks. Even in the mineral waters of the shallow circulation of the eastern section of the Flysch Zone (especially poorly mineralized) bicarbonates are likely of this origin. As a result of the processes of oxidation of sulphides (pyrite) content of sulphates increases in mineral water, resulting in a change in the type of sulphate and bicarbonate-sulphate-hydrogen-carbonate. Reduction processes of sulphates contribute to emergence of sulphane waters. Another important process of formation of the chemical composition of these mineral waters is the hydrolytic degradation of silicate minerals (enriching water in sodium and silicon).

With increasing depth of circulation and residence time of water in the rock environment increase total dissolved solids and other mineralization processes share.

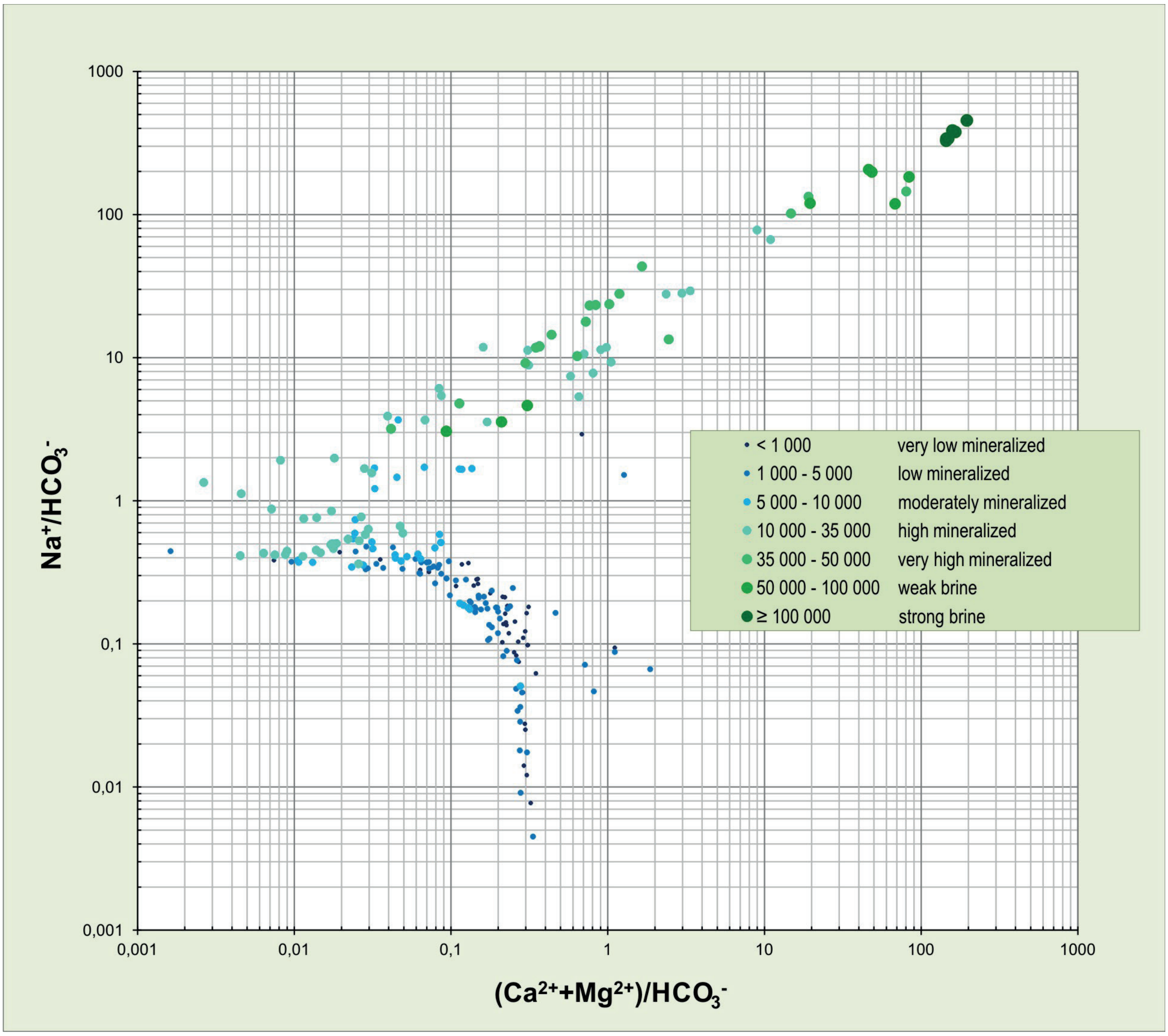

Fig. 7.12 Total dissolved solids (mg . l^{-1}) in mineral waters of the Flysch Zone and of the Foredeep of the Western Carpathians

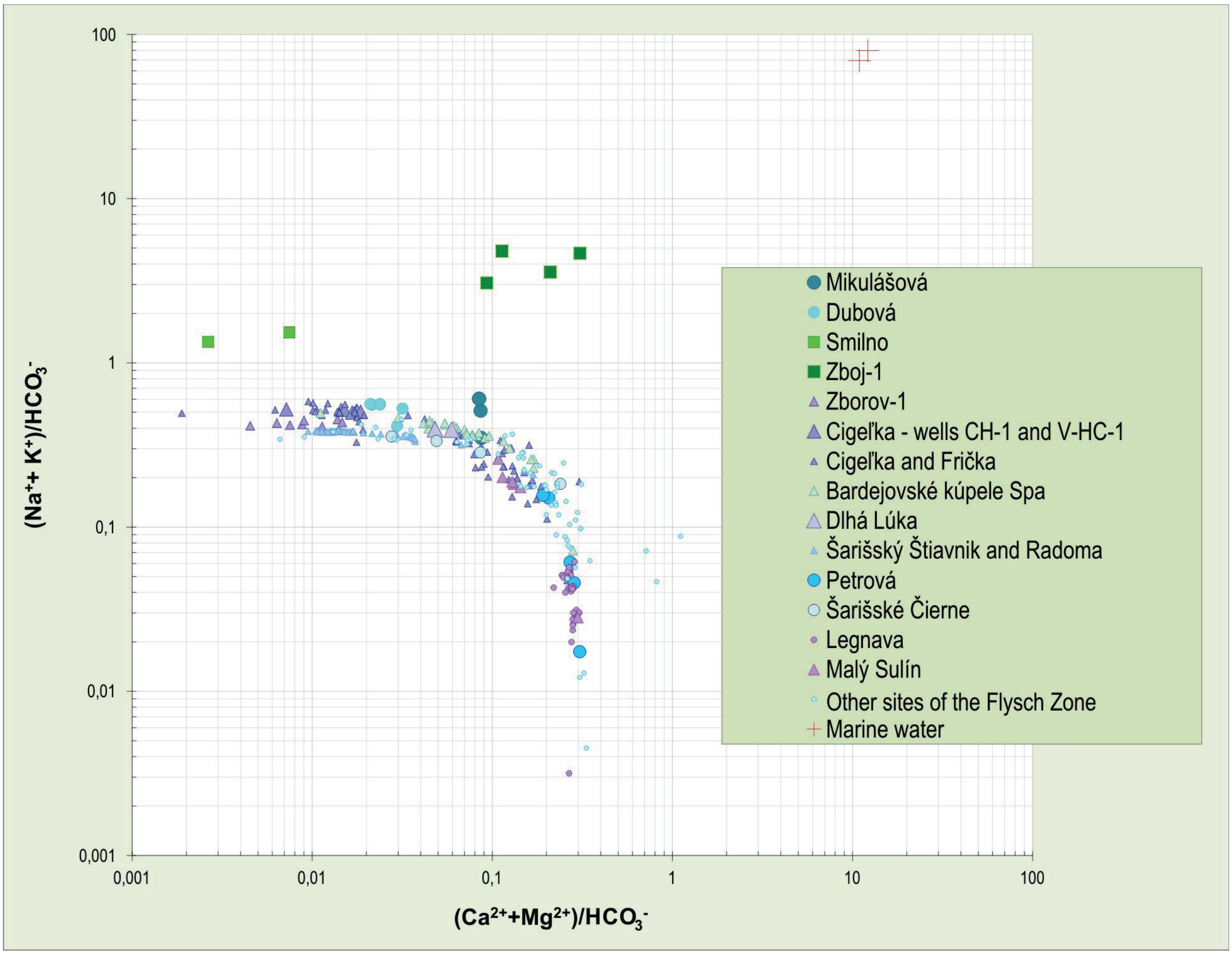

Fig. 7.13 Relationship between coefficients $(Na^{+} + K^{+})/HCO_3^{-}$ and $(Ca^{2+} + Mg^{2+})/HCO_3^{-}$ in the mineral waters of the eastern section of the Flysch Zone

Ion exchange process is becoming important (in claystone complexes), which is manifested by changing the type of water from Ca(Mg)-HCO_3 to Na-HCO_3. The high content of bicarbonates in mineral waters is essentially due to the presence of CO_2 of deep origin.

The values of the coefficient of Na^{+}/HCO_3^{-} in the approximate range from 0.5 to 1.5 have mineral waters of the chemical type Na-HCO_3-(Cl) to Na-HCO_3-Cl known from sites in the inner periphery of the Carpathian arc (Fig. 7.10, for example, Luhačovice, Cigeľka, Wysowa, Szczawa). In the graph (Fig. 7.11.) they are represented by water from boreholes CH-1 and V-HC-1 of the source of Cigeľka and the source Alexander in Wysowa (Poland). This includes bicarbonate-chloride and chloride-bicarbonate water (chemical type Na-HCO_3-Cl to Na-Cl-HCO_3) of the area of Moravské Lieskové (well KLK-1), Smilno (borehole Otto-II) and water from Mikulášová and Dubová (natural mineral springs on northern margin of the Smilno tectonic inlier). Their macrochemical composition is the result of mixing of described above meteoric and sedimentation waters in varying proportions.

Detailed insight into the macrochemical composition of mineral waters of the eastern section of the Flysch Zone provides Fig. 7.13. The sample file of processed data includes analyses of 306 water samples taken so far under various stages of registration of mineral waters, hydrogeological research and exploration of springs, wells and boreholes at known locations. Variable share of sedimentation waters of the Na-Cl type in the chemical composition of mineral waters is reflected in the graph by signs with a significant shift upward. The waters of the type Na-HCO_3-Cl and Na-Cl-HCO_3 surge in natural seeps in major tectonically disturbed zones, or they were detected by boreholes (hydrogeological and deep-structural). These are waters of the sites Mikulášová (Krahulec et al., 1977; Franko & Zakovič, 1980), Dubová (Krahulec et al., 1977 and 1978; Franko & Zakovič, 1980), Bardejovské kúpele and Dlhá lúka (Krahulec et al., 1977 and 1978; Haluška & Petrivaldský, 1988), Cigeľka and Wysowa (Krahulec et al., 1977 and 1978; Malatinský et al., 1984; Pacindová et al., 1997; Dowgiałło et al., 1969, Rajchel, 2012), Zborov (borehole Zborov II – Otto /Franko et al., 1985/). The high content of bicarbonates in them reflects the presence of the deep CO_2.

The waters of the type Na-HCO_3 from the sites Šarišský Štiavnik and Radoma, Šarišské Čierne, Pčoliné are examples of the waters, which TDS is increased mainly due to the action of the deep CO_2 and ion exchange processes (water hydrosilicatogenic mineralization).

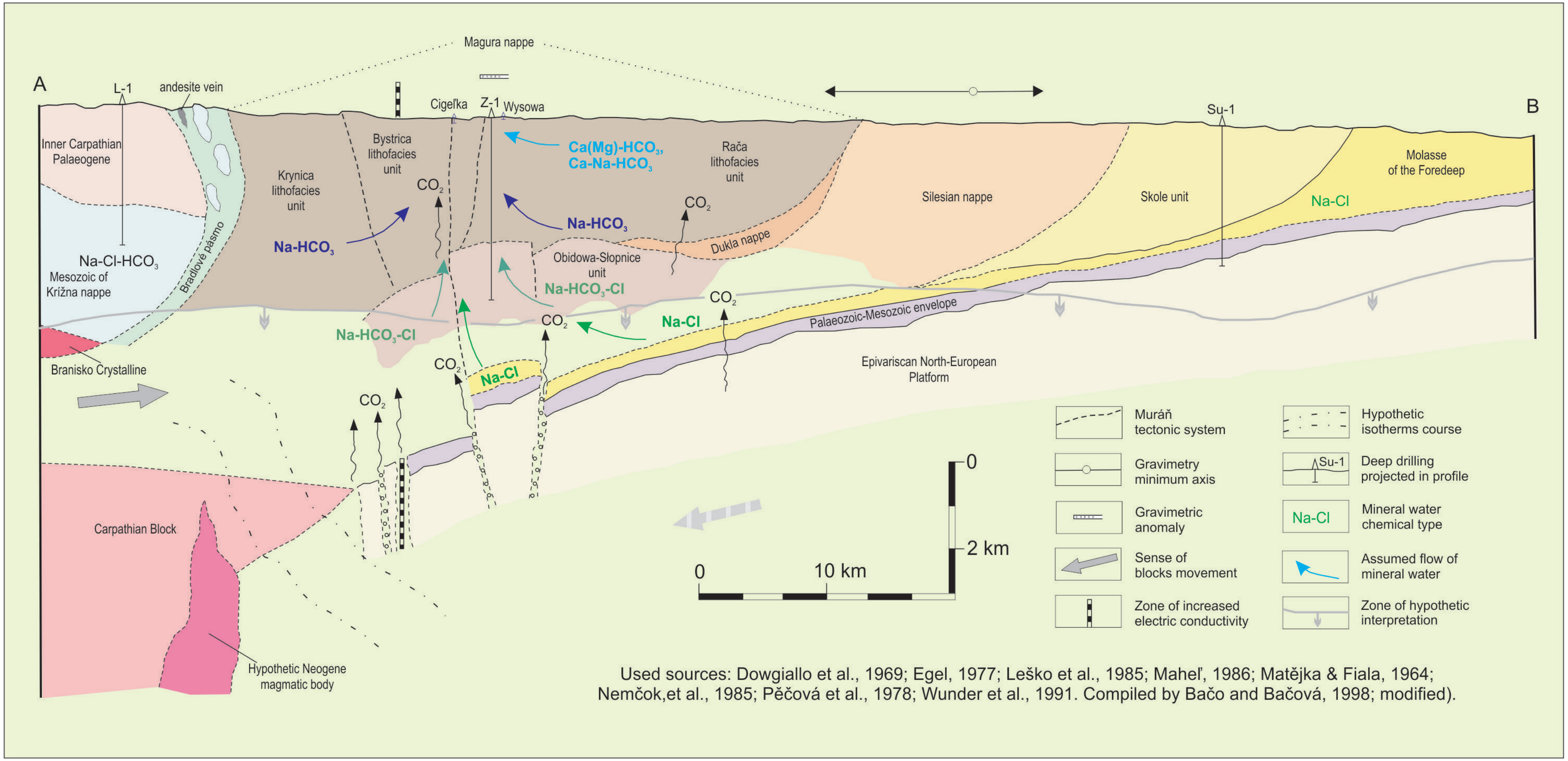

Fig. 7.14 Conceptual model of formation of the chemical composition of the Cigeľka natural mineral water

The Cigeľka natural mineral water (borehole CH-1; 202.5 m), heavily mineralized water from wells Zborov-1 (5,500 m) and Zborov-22 Otto (1,120 m) and weak brine from the well Zboj-1 (5,002 m) have the highest total dissolved solids among previously proven mineral waters of the eastern section of the Flysch Zone. They differ significantly in the content of the dominant macro-components – in chemical type. This stems from differing geological, tectonic and hydrogeological conditions of their formation. The lowest share of the thalassogenic mineralization among them has the well Zborov-1 (hydrogeological and hydrogeochemical results, the content of stable isotopes in the water from a borehole are described in Michalko et al., 1991). In the graph (Fig. 7.13) it is represented by the lowest-lying points on the left, under the signs showing the highly mineralized water from Cigeľka.

The points representing mostly poorly mineralized water with increased content of sulphates and prevailing in anion composition occupy a special position. Bicarbonate-sulphate and sulphate-bicarbonate waters appear at the bottom of the chart to the right (Figs. 7.11 and 7.13). The source of the increased sulphate content in them is the process of oxidation of sulphides (mainly pyrite present in the sandstone-claystone complexes).

According to previously published data on the content of stable isotopes of oxygen ($\delta^{18}O_{H2O}$) and hydrogen (δD_{H2O}) in mineral waters of the Flysch Zone of the Carpathians in Moravia, Slovakia, Poland and Ukraine, it is clear that the isotope heaviest waters are known from sites of the Magura Nappe (Bačová & Michalko, 2007). It allows to express assumption that waters with values $\delta^{18}O_{H2O}$ = 4 ‰ to 6 ‰ (hence Cigeľka, too) are very well sealed from the current meteoric waters by the mighty rock complex of overthrusts of the Magura Flysch.

7.6 The conceptual model formation of chemical composition of the Cigeľka natural mineral water

Knowledge about the discharge area of the Cigeľka natural mineral water, about its chemical composition and its formation, geological and tectonic setting of the area, collected by the geological fieldwork and subsequent processing and interpreting the raw data, resulted in the processing of the conceptual model of formation of this very salty water (Fig. 7.14). The model schematic cross-section is exaggerated in the vertical dimension in order to increase clarity. The intersection plane reflects geological facts that do not occur, de facto.

In the construction of the geological model, we take into account the views of the deep geological structure of this part of the Western Carpathians (especially those that have been graphically expressed) mentioned in the works of the following authors: Leško & Varga (1980), Nemčok et al. (1985), Maheľ (1986), Rudinec (1987) and Wunder et al. (1991).

Surface definition of regional units is adopted and simplified from the maps by Egel (1977) and Nemčok et al. (1985). Position of the Inner-Palaeogene and Mesozoic of the Krížna Nappe (envelope unit in Branisko unit) is interpreted based on the results and interpretation of borehole Lipany-1 (Leško et al., 1982). A method of illustrating the course Klippen Belt primarily took into account the results of the well Hanušovce-1 (Leško et al., 1985). Geological structure in the wider area of Cigeľka is interpreted primarily using the results of the well Smilno-1 (Leško ,1986; Leško et al., 1987) and Zborov-1 (Wunder et al., 1990; 1991) and the deeper subsoil based on the work by Pěčová et al. (1978) and Praus et al. (1984) – Regional geoelectric anomalies, and work by Leško et al. (1979) – Interpretation of the Oligocene-Miocene Molasse. Relationship between the Skola Unit and autochthonous basement – sediments of the Molasse of the Foredeep and northern epi-Variscan platform – we interpreted on the basis of the well Szufnarowa-1 and work by Nemčok et al. (1985).

Views on the formation and origin of mineral water of the Flysch Zone of the Western Carpathians in Poland were published by many authors from the 60's of last Century to the present, with a graphical representation of geological and tectonic conditions in recent years, for example Oszczypko & Zuber (2002) and Zuber & Chowaniec (2009).

The Cigeľka natural mineral water has a chemical composition of the type Na-HCO_3-Cl. In its formation there are involved:

- Meteoric water – formed and accumulated in the environment of the Magura Nappe at greater depth metamorphosed due to ion exchange processes;
- Sedimentation water – probably coming from the basement of the Magura Nappe.

These two components are apparently mixed in the area of conduits to the surface, where they can get from the environment of collector rocks along postorogenic and in this case the transverse only, deep-reaching fault. Penetration of water to the surface in a particular part of this tectonic system is alleviated by local lithological-tectonic conditions.

In the Cigeľka and Wysowa area we assume that they involve:

- Spatial position of the NW border of the longitudinal NW-SE autochthonous elevation of the bedrock – Makovica Ridge – basement of the Smilno tectonic inlier, which in the upper part is probably made up of Oligocene – Miocene Molasse;
- Contrasting arrangement of the basal layers of the Rača lithofacies unit in the Cigeľka area generated by present elevation;
- In the Wysowa area outcrops of Inoceramus layers to the surface;
- The presence of the primary source of mineral water;
- The primary source of gaseous component presence of organic or juvenile origin.

Influence of flysch rock environment upon the chemical composition is manifested not only in a higher sodium content (due to the release of from shales by ion-exchange processes) but also high content of boron, which sources are also Flysch complexes, likely. Chlorine and bromine contents refer to the share of water with thalassogenic mineralization in the chemical composition of the Cigeľka natural mineral water. The high content of bicarbonate is due to the presence of CO_2 of deep origin. The reducing environment in the course of the formation of the chemical composition of the water is reflected in values of Redox potential (Pacindová et al., 1997), and the presence of desulphurisation and ammonisation bacteria. The composition of the gas dissolved in water, does not indicate crude oil or gas bearing capacity of the rock environment. A certain proportion of carbon of organic origin, however, was confirmed by the occurrence of epigenetic mineral of whewellite in Bialowieza sandstone Fm. (in the core recovery of the drill V-HC-1). The high content of stable isotopes ^{18}O and D in water indicates a good sealing of space of water accumulation components from the groundwater of shallower circulation.

In the Magura Nappe of the Flysch Zone of the Carpathians (the area from Moravia to Ukraine) there are three major areas of incidence of moderate to strongly mineralized water of Na-HCO_3 and Na-HCO_3-Cl type (the area of Luhačovice, wider area of Krynica – Cigeľka (Wysowa) – Bardejov Spa, Poľana – Svaľava in Ukraine). These areas are known for the presence of deep-based faults and manifestations of Neogene magmatic activity. Isotopic and chemical composition of the unique Cigeľka natural mineral water points to its deep origin and eventual mixing of water of the Na-Cl type of the Magura Nappe and basement water type Na-HCO_3-(Cl) present at greater depths in the Magura Nappe itself. The high content of bicarbonate is likely mainly due to the presence of presumed deep CO_2 origin [Ukrainian authors (Gucalo et al., 1982) describe an increasing share of depth-based C in bicarbonate mineral waters of the Ukrainian Carpathians in the direction from the Carpathian Foredeep towards the Klippen Belt].

7.7 Conclusions

By summarising the existing knowledge on geological and hydrogeological conditions in the discharge area of the Cigeľka natural mineral water we came to the knowledge of the patterns of occurrence of mineral waters with different types of chemical composition and to create an image of the conduit area of heavily mineralized water to the surface. An important factor, conditioning the output of this precious water to the surface, the presence of CO_2 is likely to be of deep origin, in particular. Figures 7.10 and 7.11 provide a snapshot of the status of mineral waters of Cigeľka in the Flysch Zone of the Carpathians (Moravia, Poland, Slovakia and Ukraine).

When assessing the content of stable isotopes of oxygen and hydrogen the Cigeľka natural mineral water belongs to the heaviest waters of the Carpathian Flysch Zone. From previously published data on the isotopic composition of oxygen ($\delta^{18}O_{H2O}$) and hydrogen (δD_{H2O}) of the mineral waters of the Flysch Zone of the Carpathians in Moravia, Slovakia, Poland and Ukraine, it is clear that isotopically heaviest are the waters from sites representing the area of the Magura Flysch (Bačová & Michalko, 2007). This allows us to express the assumption that waters with the values of $\delta^{18}O_{H2O}$ = 4 ‰ to 6 ‰ (hence Cigeľka, too) are very well insulated from the current meteoric waters by mighty rock complexes of the Magura Flysch Nappes.

7.8 References

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