

# Beginnings of the Isotope Research of Mineral and Thermal Groundwaters of Slovakia

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**Abstract:** The period from late 60s to mid-eighties of the 20<sup>th</sup> century in Slovak conditions can be regarded in terms of knowledge of the isotopic composition of mineral water as pioneer years. The first data from the turn of the 60/70's come from foreign authors, although the department dealing with the isotope geology at that-time GIDŠ existed since the mid-50s. It was, however, designed to date the K/Ar method and research deposits (isotopes of Pb, S). Oriented research, including mineral waters, has developed after investment into the instrumentation and sample preparation facilities in mid-80's. The results were published just in reports and later only partly quoted by other authors. The article summarizes the state of knowledge of the isotopic composition of mineral water and dissolved substances in them in the mid-eighties of the last century.

**Key words:** mineral waters, O and H isotopes, sulphate, hydrogen sulphide, Slovakia

## 2.1 Introduction

Mineral and thermal waters in Slovakia are an important phenomenon. The complex geological structure of the Western Carpathians with typical tectonic evolution and favourable climatic conditions in the past and now have created conditions for the emergence of a diverse range of hydrogeological structures, and consequently the groundwater sources of different genetic types. The diverse rock environment, often coupled with pervasive CO<sub>2</sub> and higher temperatures creates favourable conditions for the development of mineral and thermal waters with varied chemical composition, often with beneficial effects on the human health. Knowledge of the distribution of stable and radioactive isotopes in the water and the rock environment along with hydrogeology and hydrogeochemistry provide one of the important tools in understanding the characteristics, origin, genesis, time delays and pathways for circulation of mineral water, and thus contribute to improving the protection and use of this natural wealth.

Isotopic research in Slovakia began in the mid-50s of the last century. Workplace built in the predecessors of the SGIDŠ was focused on geochronology (K-Ar method) and research of deposits (isotopes of S and Pb). The first analyses of mineral waters came mainly from foreign authors. Upon the upgrade of the facility and methodological upgrade of the department at the turn of the 70/80's of 20<sup>th</sup> century a considerable attention was paid to the study of stable isotopes (O, H, C, S) in the waters, of course, including the mineral, thermal and geothermal ones. The results are usually published only in reports, which were from time-to-time quoted cited. The article summarizes and illustrates the state of isotope research in the field of

mineral and thermal waters in Slovakia in the mid-80s of the 20<sup>th</sup> century.

## 2.2 Isotope research of waters in Slovakia

Knowledge of the distribution of isotopes in nature and their patterns are closely linked to the development of chemistry, and particularly physics from the late 19<sup>th</sup> century. Since the beginning these lessons were used (directly or indirectly) to solve the problems of geological character. A significant shift in the use of radioactive and stable isotopes in geological practice occurred at the beginning of the second half of the last century when practically usable mass spectrometer was constructed, the necessary theoretical background was compiled and preparation procedures and relevant international standards were prepared.

This trend has also caught SGIDŠ, where since the mid-50s Dr. Ing. Kantor developed Department of Isotope Geology, focusing on the dating of rocks (K-Ar, Pb-Pb) and research in ore deposits (isotopes Pb and S). At the turn of 70/80s, the analytical base was expanded on new mass spectrometer to measure stable isotopes of light elements (Finnigan MAT 250) and methods for measuring the isotopic composition of H, O, S, C (lately N) in different geological materials have been developed including water and substances dissolved therein. Despite repeated attempts measurement of  $\delta^2\text{H}$  using reduction method did not provide results with sufficient reproducibility, and thus data on hydrogen isotopic composition of water are rare. Their measurement was resumed in the second half of the 90s and later, especially after getting analysers LWIA and IR (isotope ratio) of the spectrometer DELTA Advantage. It is now possible to measure the isotopic composition of H, O, C, N, S in water and components dissolved in it, and in other geological materials (sulphides, sulphates, carbonates, shells, gases).

Waters dating based on the activity of tritium was addressed by NRL WRI, <sup>14</sup>C dating by the Department of Nuclear Physics FMFI of Comenius University, Bratislava .

Accurate measurement of isotopes (isotope ratio) in natural substances requires extensive analytical tools, either from the viewpoint of samples adjusting to the measuring environment, or in terms of the measurements of the isotopic composition itself. Also for these reasons, knowledge of isotopic composition in hydrogeological practice in Slovakia was enhanced gradually. Currently, rapid development of technology simplifies and facilitates the acquisition of isotopic data, which consists in the ap-

plication of isotopes of other elements (e.g. He, B, Li, Cl, Ar, noble gases), both in accessibility (decreasing price of analyses) of data from the “classic” sphere. Isotope geology becomes more and more adopted discipline and in many countries collecting data on the isotopic composition of precipitation, surface water, selected sources of mineral, thermal and ordinary groundwaters has become standard part of state monitoring. Since 1961 the International Atomic Energy Agency at UNESCO organizes observation networks for monitoring the isotopic composition of water in the different phases of the hydrological cycle: precipitation (GNIP), rivers and creating further GNIR (air humidity, plants..).

In Slovakia (Department of Isotope Geology at SGIDŠ) the relevant analytical and interpretative base for monitoring the isotopic composition of waters was developed in early 80s, since then the amount of data on the isotopic composition of various genetic types of water, including mineral and thermal water has gradually expanded, and correspondingly increase the amount of respective knowledge. Data on the isotopic composition of water from the previous period is patchy and usually came from foreign authors.

### 2.3 Regional selective characteristics of the isotopic composition of mineral and thermal waters in Slovakia

First knowledge of the isotope composition of mineral and thermal waters in Slovakia are dated back to the turn of 60s of the last century. This includes nationwide selective characteristics of selected sources – to analyse

the isotopic composition by the then-available methodology the authors chose important or most interesting sources of mineral and thermal waters from the entire territory of Czechoslovakia. In that period Slovakia accounted for about one third of the national territory. From geological point of view the whole territory of Slovakia belongs to the Western Carpathians within which the easternmost parts of the Czech Republic fall, as well. In this category of activities in the field of isotope characteristics of mineral and thermal waters in Slovakia notable were works by Barnes & O’Neil in Čadek & Pačes, (1976), Šmejkal et al. (1971 and 1981), Kantor (1985).

The isotopic composition of hydrogen, oxygen and dissolved inorganic carbon (DIC) in selected sources of mineral and thermal waters (32) in California, the Czech Republic and Slovakia was dealt with Barnes & O’Neil in Čadek & Pačes, (1976). From Slovakia 14 sources were sampled from major spas and also geothermal well in Patince (Tab. 2.1). Among the Slovak sources the authors (Barnes & O’Neil in Čadek & Pačes, 1976) included four sources, which are located on the Moravian side of the Carpathians (depicted in Tab. 2.1 by \* and in the Fig. 2.1 by squares). Based on the proximity to a Global Meteoric Water Line (GMWL) almost all investigated waters are derived from local precipitation. The exception are waters from Luhačovice, Napajedla and Bardejov Spa (in Fig. 2.1 they deviate from GMWL), in which they assumed the formation of the final composition as a result of mixing of local groundwater of meteoric origin with metamorphic waters (arrows in Fig. 2.1) with similar composition as a water source Soda Spring in Fort Bragg, California (Fig. 2.1). Currently, the endmember considers water with

Tab. 2.1 Stable isotope data from Slovak mineral and thermal groundwaters. \* sources from part of the Western Carpathians belonging to the territory of the Czech Republic (from Barnes & O’Neil in Čadek & Pačes, 1976)

Locality	$\delta^{13}\text{C}_{\text{DIC}}$ PDB [‰]	$\delta^2\text{H}_{\text{H}_2\text{O}}$ SMOW [‰]	$\delta^{18}\text{O}_{\text{H}_2\text{O}}$ SMOW [‰]	t [°C]	$\text{HCO}_3^-$ [mg·l <sup>-1</sup> ]	Cl <sup>-</sup> [mg·l <sup>-1</sup> ]	Rock environment
Bardejov Spa	-0.5	-61.1	-6.1	11	300	460	Flysch
Korytnica	-3.6	-68.3	-10.3	7	1,200	4	Dolomite
Nosice	-3.8	-69.7	-10.3	11	2,244	81	Flysch
Trenčianske Teplice	-6.9	-71.0	-10.4	40	420	100	Flysch
Vyšné Ružbachy	0.2	-73.5	-10.7	20	1,150	18	Limestone, dolomite
Martin	-2.6	-76.2	-11.0				Lacustrine, underlain by flysch
Liptovský Ján	-1.3	-73.9	-10.9	29	2,060	24	Dolomite
Piešťany	-7.3	-78.3	-11.3	65	260	110	Limestone, dolomite
Kováčová	-9.5	-78.3	-11.3	46	732	4	Dolomite
Sliač	-2.6	-80.4	-11.8	33	1,195	51	Tuff, sandstone
Dudince	-2.5	-80.5	-11.4		3,000	320	Quartzite, limestone
Sivá Brada	-0.2	-82.9	-11.5	12	3,900	290	Flysch
Komárno	-4.2	-88.0	-12.0	48	561	490	Limestone, dolomite
Patince	-9.0	-75.5	-10.8		460	24	Alluvium
Darkov *	-11.3	-42.0	-6.2	12	230	12,200	Flysch
Luhačovice *	1.1	-51.2	-1.9	11	5,100	2,281	Flysch
Napajedla *	3.6	-54.2	-5.4	15	2,700	1,450	Flysch
Teplice nad Bečvou*	-3.8	-71.5	-10.4	22	1,900	39	Greywacke

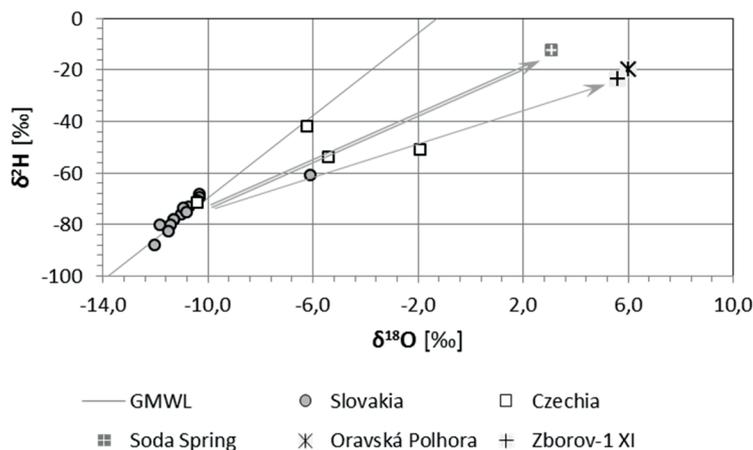


Fig. 2.1 Isotope composition of mineral waters of Slovakia. Data by Barnes & O'Neil in Čadek & Pačes, 1976. The arrows represent mixing line between two endmembers: 1. local groundwater of meteoric origin with  $\delta^2\text{H} \sim -70$  ‰ and  $\delta^{18}\text{O} \sim -10$  ‰ and 2. metamorphic water; a) Soda Spring, California; b) boreholes in Zborov and Oravská Polhora

an isotopic composition similar to the water from the well Zborov-1, (XI<sup>th</sup> horizon) with  $\delta^{18}\text{O} = +5.61$  ‰ and  $\delta^2\text{H} = -23.4$  ‰ or water of the FPJ-1 borehole in Oravská Polhora with  $\delta^{18}\text{O} = +6.08$  ‰,  $\delta^2\text{H} = -19.7$  ‰ (Michalko et al., 1991, Michalko, 1998, Zakovič et al., 2009). The increase in the heavy isotope oxygen in water due to water-rock interaction (oxygen shift) seems to be non-realistic. The apparent increase in the proportion of light isotopes of both elements in mineral waters in the direction from North to South is explained by the impact of rain shadow of high mountains of Carpathian mountain range. Later research has shown that it is more a function of the Mean Residence Time (MRT) and the climate conditions at the time of infiltration.

The total inorganic carbon (DIC) present in water sources investigated was in the range of about  $\delta^{13}\text{C}$  ca -4 ‰ to +4 ‰; the authors (Barnes & O'Neil in Čadek & Pačes, 1976) interpreted the origin from marine carbonates. For samples with isotopically lighter carbon they assume the impact of incomplete dissolution of carbonates accompanied by carbon isotope fractionation.

Relatively much attention was paid in this period to the distribution of sulphur isotopes present in the mineral and thermal waters in different forms. The research resided in the fact that the sources of sulphur present in the rock environment have characteristic isotopic composition, allowing to identify the origin of sulphur present in the water, thus circulation of groundwater and water-rock interaction. Provided, the isotopic composition of sulphur was changed by processes occurring in the groundwater during circulation (redox processes, mixing ..), it is necessary to reconstruct the original initial conditions. By the beginning of the 80s there was completed a perception of the development of the isotopic composition of sulphate (sulphur and oxygen) in the World Ocean (Nielsen & Rieke, 1964, Nielsen, 1979, Claypool et al., 1980). The isotopic composition of sulphur present in the form of sulphide and in sulphatic form in sedimentary rocks in the Western Carpathians was dealt by Kantor & Sládková

1979, Kantor et al. 1982.

Šmejkal et al., 1971 and 1981 dealt with the isotopic composition of sulphur present in the water from selected sources of mineral water in Czechoslovakia. Based on the findings of concentration and isotopic composition of  $\text{SO}_4^{2-}$  and  $\text{H}_2\text{S}$  in water there were reconstructed the relevant characteristics of the initial sulphate – its concentration and isotopic composition of sulphur from the sulphate present in the water prior to bacterial reduction. In the period of 1969 – 1978 there were conducted 41 analyses of this type from 25 mineral water sources across Slovakia (Tab. 2.2, Fig. 2.2). To them should be added 10 analyses from seven sources of thermal water with the circulation bound to the aquifers of the Flysch Zone of the Western Carpathians in Bohemia. The sources originate either from the environment of Mesozoic carbonates of the Central Western Carpathians, or from the Flysch Zone of the Western Carpathians. In the first phase (sampling in 1969) the authors (Šmejkal et al., 1971) used the knowledge and analytical potential of the University of Alberta, Edmonton (postdoctoral fellowship) while primarily focused on the Czech part of the Flysch Zone. Thereafter (1970 – 1978) facilities of the ÚÚG were used, either in Prague or in Brno (Šmejkal et al., 1981).

The water of sources studied (Šmejkal et al., 1971, 1981) contains  $\delta^{34}\text{S}$  of the present sulphate ranging from -25.7 ‰ to +34.1 ‰,  $\delta^{34}\text{S}$  of coexisting  $\text{H}_2\text{S}$  from -71.1 ‰ to +17.1 ‰ at sulphate concentrations of 11 mg · l<sup>-1</sup> to 1,431 mg · l<sup>-1</sup>, sulphane from 0.8 mg · l<sup>-1</sup> to 600 mg · l<sup>-1</sup>. The exemption constitutes a source of Šaratica, wherein the hydrogen sulphide is not present (reduction does not take place), and sulphate concentration is 13,000 mg · l<sup>-1</sup>. The degree of reduction reaction – the conversion of the initial sulphate to sulphide – is moving in a range from 0.1 % to 97 %, while the successive samplings for each source are not always the same. This fact depends on the activity of the bacteria, i.e. slightly changing living environment, especially on food sufficiency, which constitutes carbon present in water in organic form. This fact Šmejkal et al. (l.c.) attributed also to differences in the degree of conversion of the sulphur in the sources related to the Flysch Zone – in units (Rača and Magura) rich in organic matter it is high, the external units where the organic carbon content in water is low, the conversion occurs on a small scale. In the isotopic composition of sulphur in immediate sulphate groups for both basic sources, there are systematic differences; depleted sulphur is typical for sulphate in water bound to flysch (mean =  $\delta^{34}\text{S}$  2.5 ‰), while sulphate present in Mesozoic water sources is characterized by average value  $\delta^{34}\text{S} = 25.5$  ‰. This difference is even more pronounced for upgraded initial isotopic composition of sulphate, i.e. the original composition of sulphate present in the water prior to bacterial reduction. The average value for water flysch is  $\delta^{34}\text{S} = -10.9$  ‰;  $\delta^{34}\text{S}$  of the initial sulphate in water sources bound to Mesozoic

is 22.9 ‰. The sulphate is present in the rock environment of an aquifer. Šmejkal et al. (1981) assumes the origin of enriched sulphur corresponding to the development of the World Ocean (Claypool et al. 1980) in the evaporites of the Mesozoic Ocean, particularly of Middle Triassic age (Röt, Oberer Bundsandstein, Werfenian). Source of very light sulphur present in the flysch rocks ( $\delta^{34}\text{S}$  to -25 ‰) they assume in sulphides which (most likely) originated from (bacterial?) reduction of marine sulphate of an of ocean respective age.

Kantor (1985) interprets the results of the analysis (by Rybár, 1971) of the isotopic composition of sulphur in the sulphate present in the water of 35 sources of mineral water (Tab. 2.3, Fig. 2.2). Precipitation of hydrogen sulphide present in the water of some sources was not successful at sampling, so it was not possible to reconstruct the original composition of sulphur – as a direct result of water-rock interaction. However, in most sources the sulphate reduction does not take place (and if any, so at a very low level), and thus it is possible to characterize the original source of sulphur directly. Relevant data on the chemical composition Kantor (1985) takes from Franko (1975) and Krahulec et al. (1977, 1978; Tab. 2.3). The examined sources were selected to characterize the significant structures. The bulk of the sources are located in the central zone of the Western Carpathians and is bound to Mesozoic carbonate complexes of Tatricum, Fatricum and Hronicum with a characteristic alternation of collector rocks and aquicludes and with complex tectonic structure. In the selected set, there are also several mineral water sources sampled by Šmejkal et al. (1981); the values  $\delta^{34}\text{S}_{\text{SO}_4}$  are similar, mostly within the analytical error range.

Differences in reported values are rather attributable to the dynamics, or to the temporal time changing of the course of bacterial reduction. Studied mineral waters were of variable composition either in terms of sulphate content (from 98 mg · l<sup>-1</sup> to 4,366 mg · l<sup>-1</sup>) as well as the isotopic composition – determined  $\delta^{34}\text{S}_{\text{SO}_4}$  ranged from -11.18 ‰ to 33.23 ‰.

The acquired data yielded knowledge on the origin of sulphur, and also the genesis and mutual relations of the mineral waters. Based on the isotopic composition of sulphur in the water of dissolved sulphate Kantor (1985) distinguished three basic sources of springs with several sub-groups. In the first group there are sources of mineral water with sulphur derived from the dissolution of evaporites of marine origin characterized by a higher representation of the heavy isotope of sulphur. The original isotopic composition of evaporites has been preserved or was only

minimally altered as a result of reduction. The second group consists of mineral water sources, which sulphur cannot be derived from evaporites of marine origin. High share of light isotope of sulphur,  $\delta^{34}\text{S}$  values are around 0 ‰ and are often (highly) negative. They originated from the oxidation of pyrite present in the sediment. The third main group is mineral water, in which in the formation of sulphate sulphur both sources are involved. As an ex-

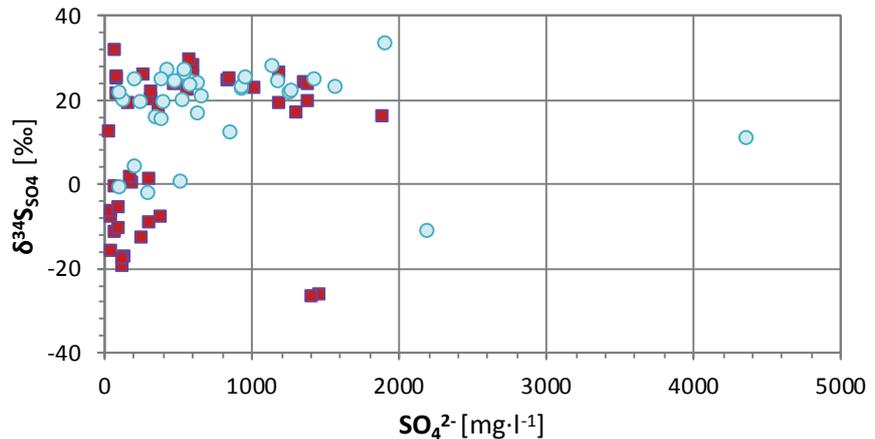


Fig. 2.2 Dependence of isotope composition of sulphur of dissolved sulphate on sulphate concentration. In groundwater with co-existing hydrogen sulphide reconstructed values are used (tab.2.2) for original initial sulphate. There are two main groups of sulphur sources in groundwater – Triassic Ocean evaporites with characteristic heavy sulphur ( $\delta^{34}\text{S} \sim 20$  ‰) and pyrite present in sediments (in one case sulphide of hydrothermal origin) with depleted sulphur ( $\delta^{34}\text{S}$  from ca -20 ‰ up to ca 0 ‰). Sulphate with extremely heavy sulphur ( $\delta^{34}\text{S} > 30$  ‰) represents residual sulphate after reduction. Data by Šmejkal et al (1971, 1981) and Kantor (1985), Tabs.2.2, 2.3.

amples Kantor (l.c.) points to the water from Solivar with  $\delta^{34}\text{S} = 10.97$  ‰. He assumes a presence of the sulphate of Neogene Sea ( $\delta^{34}\text{S} \sim 23$  ‰) and the sulphate formed by oxidation of sulphide sulphur present in the sediment in the form of pyrite. This process is likely to be applied already at sedimentation, because Kantor & Sládková (1979) demonstrated the increased amount of light isotopes of sulphur in the sulphate sulphur of Karpatian sediments from this area.

The sources with marine sulphate he subdivided in line with the evolution of the isotopic composition of marine sulphate (Claypool et al., 1980, Balderer in Pearson ed., 1991) according the age to springs with sulphur derived from evaporites of Late Triassic age (Keuper), Permian-Early Triassic age and evaporites with high presence of heavy isotopes of sulphur of the upper part of the Early Triassic (+ equivalents of Röt, Werfenian). Representatives of the first group are two springs from Valča with a sulphur  $\delta^{34}\text{S} = 16.63$  ‰ and 15.24 ‰. Light sulphur ( $\delta^{34}\text{S} = 12.40$  ‰) of the spring in Rovné derived from evaporites (Permian) – Early Triassic complexes (Kantor & Sládková, 1979 Kantor, 1982). The largest representation have springs with sulphur derived from the higher parts of evaporites of the Early Triassic (+ equivalents of Röt, Werfenian) which are characterized by  $\delta^{34}\text{S}$  values > 20 ‰ to 28 ‰. In some sources (e.g. Sivá Brada) the enrich-

Tab. 2.2 Data of isotope composition of dissolved sulphate in mineral water and co-existing hydrogen sulphide. Reconstruction of original characteristics of primary sulphate. Data from Šmejkal et al. (1971, 1981), original characteristics recalculated by author. \* Springs in Western Carpathians territory belonging to the Czech Republic.

N°	Locality	Source	Date	Instantaneous sulphate					Con- version [%]	Original sulphate	
				SO <sub>4</sub> [mg·l <sup>-1</sup> ]	H <sub>2</sub> S [mg·l <sup>-1</sup> ]	δ <sup>34</sup> S <sub>SO<sub>4</sub></sub> [‰] CDT	δ <sup>34</sup> S <sub>H<sub>2</sub>S</sub> [‰]	Con- version [%]		δ <sup>34</sup> S <sub>SO<sub>4</sub></sub> [‰] CDT	SO [mg·l <sup>-1</sup> ]
<b>Mesozoic carbonates</b>											
1.	Banská Bystrica		BB-10	1970	1,011.0	2.8	23.1	n	0.8	ca 23	1,018.9
				1971	941.0	0.8	24.2	n	0.1	ca 24	943.3
2.	Belušké Slatiny	kúpeľný	PB-3	1971	301.0	4.6	22.1	-24.0	4.1	20.2	314.0
		kúpeľný	PB-3	1975	308.0	2.4	23.2	-28.1	2.1	22.1	314.8
3.	Dudince	S-3	ZV-70	1970	557.0	7.0	26.4	-16.2	3.4	24.9	576.7
		S-3	ZV-70	1975	598.0	5.2	28.4	n	2.4	n	612.7
3.	Lipovce	S-2	PV-100	1971	77.0	4.8	25.1	n	15.0	n	90.5
		S-2	PV-100	1972	n	4.8	26.7	-26.6	n	n	
		S-2	PV-100	1975	147.0	4.5	23.9	-29.7	8.0	19.6	159.7
4.	Liptovské Sliače	Čertovica	LM-67	1970	469.0	2.8	23.8	n	1.7	ca 23.5	476.9
5.	Liptovský Ján	B-2	LM-46	1971	836.0	1.2	24.7	n	0.4	n	839.4
		B-2	LM-46	1972	840.0	1.2	25.6	-28.3	0.5	25.4	843.4
6.	Malinovec Santovka	B-3	LE-15	1970	571.0	8.2	27.5	-12.8	4.0	25.9	594.1
		B-3	LE-15	1975	600.0	7.5	27.7	n	3.4	n	621.1
7.	Mýto pod Ďumbierom		BB-58	1972	67.0	1.1	34.1	-12.4	4.4	32.0	70.1
8.	Patince	SB-1	KO-4	1975	71.0	3.5	25.6	-4.5	12.2	21.9	80.9
9.	Piešťany	Trajan	TR-4	1969	525.0	11.0	24.4	-6.3	3.0	23.5	556.0
		Trajan	TR-4	1971	528.0	11.0	25.1	-15.6	5.0	22.8	559.0
		Trajan	TR-4	1975	n	6.5	26.4	-16.8	n	n	
10.	Plavecký Peter	SE-18	SE-18	1975	184.0	28.0	33.6	8.8	30.0	26.1	262.9
11.	Sivá Brada		SNV-5	1970	1,178.0	1.2	26.6	-1.5	0.3	26.5	1,181.4
12.	Sliač	Spring A	ZV-8	1970	1,350.0	1.7	24.3	n	0.3	ca 24.1	1,354.8
13.	Slovany, Smrdutá voda		TM-15	1975	353.0	2.6	19.7	-36.0	2.0	18.6	360.3
14.	Smrdáky	Jozef I	SE-20	1969	35.0	450.0	21.8	17.1	97.0	17.2	1,303.5
		Jozef I	SE-20	1975	192.0	600.0	21.2	15.8	90.0	16.3	1,883.3
15.	Sobrancecké kúpele	kúpeľný	ML-8	1971	556.0	220.0	32.9	7.3	53.0	19.3	1,176.2
		kúpeľný	ML-8	1975	505.0	24.0	32.8	8.6	12.0	30.0	572.7
16.	Stankovany	medokýš	LM-124	1971	1,373.0	2.5	24.2	-33.5	0.5	23.8	1,380.0
		medokýš	LM-124	1972	n	3.3	24.2	n	n	n	
17.	Trenčianske Teplice	V-3	TE-54	1971	1,362.0	4.5	20.3	-33.5	0.9	19.7	1,374.7
		V-3	TE-54	1975	n	4.0	20.0	-28.4	n	n	
<b>Flysch rock environment</b>											
18.	Hruštín		DK-5	1971	37	1.5	-3.3	-44.1	10.3	-7.5	41.2
19.	Keľča		HN-7	1971	130	60.0	27.6	-36.6	56.5	-8.7	299.1
			HN-7	1975	178	70.0	25.8	-38.0	52.6	-7.7	375.3
20.	Malá Poľana		HN-8	1971	93	32.0	24.8	-24.8	49.2	0.4	183.2
			HN-8	1975	100	24.0	19.3	-24.4	40.4	1.7	167.7
21.	Oravská Polhora			1975	25	6.0	-2.4	-11.6	40.4	-6.1	41.9
22.	Osadné		HN-11	1971	11	1.1	-0.6	n	22.0	n	14.1
23.	Šarišský Štiavnik			1972	36	9.0	-0.6	-25.8	41.3	-11.0	61.4
24.	Vrchpredmier Klokočov			1971	28	2.6	-9.7	-37.5	20.7	-15.5	35.3
25.	Vyšný Orlík		BV-80	1971	41	28.0	20.9	-39.8	65.8	-19.0	119.9
			BV-80	1975	114	48.0	19.9	-40.1	54.3	-12.7	249.3
27.	* Čejč			1969	250	18.0	6.9	-24.3	16.9	1.6	300.7
28.	* Kladeruby			1970	110	1.0	0.6	n	2.5	n	112.8
29.	* Napajedla	Slanica		1969	57	12.8	-1.7	-23.9	38.8	-10.3	93.1
		Slanica		1975	37	7.5	8.5	-15.4	36.4	-0.2	58.1
30.	* Šaratica			1978	13,000	0.0	-19.6	n	0.0	-19.6	13,000.0
31.	* Šitbořice			1970	1,431	7.1	-25.3	-68.1	1.4	-25.9	1,451.0
				1975	1,384	6.0	-25.7	-71.1	1.2	-26.2	1,400.9
32.	* Vizovice	Dudík		1969	82	15.3	-6.3	-37.7	34.5	-17.1	125.1
		Švajda		1975	59	13.0	6.5	-24.3	38.3	-5.3	95.6
33.	* Želechovice			1969	91	7.7	-13.2	-35.6	19.3	-17.5	112.7

Tab. 2.3  $\delta^{34}\text{S}$  data of sulphate dissolved in mineral water. Data by Kantor (1985), analyses of  $\delta^{34}\text{S}$  carried out by Rybár (1971)

Nº	Locality	Source	Groundwater type	t [°C]	TDS [g·l <sup>-1</sup> ]	SO <sub>4</sub> [mg·l <sup>-1</sup> ]	H <sub>2</sub> S [mg·l <sup>-1</sup> ]	$\delta^{34}\text{S}_{\text{SO}_4}$ CDT [‰]
1.	Baldovce	Deák	HCO <sub>3</sub> -SO <sub>4</sub> -Ca-Mg	10.0	5.67	421.8	0.0	27.04
2.	Banská Bystrica	Altánka	HCO <sub>3</sub> -SO <sub>4</sub> -Ca-Mg	17.4	3.48	937.8	0.0	22.54
3.	Budiš	B-1				660.1		20.95
4.	Buzica	crossing	HCO <sub>3</sub> -Cl-Na	17.2	10.62	630.8	0.0	24.11
5.	Dudince	S-3	HCO <sub>3</sub> -Na-Ca	28.0	5.34	549.8	9.0	26.05
6.	Jánovce	Spa spring	HCO <sub>3</sub> -SO <sub>4</sub> -Ca-Mg	23.2	3.66	960.4	0.0	25.47
7.	South-Slovakian coal basin	borehole PS				98.4		-0.63
8.	Kalinčiakovo	Ilona	HCO <sub>3</sub> -SO <sub>4</sub> -Ca-Mg	25.5	0.96	241.6	0.0	19.30
9.	Kalinka					202.1		4.20
10.	Korytnica	Jozef	SO <sub>4</sub> -HCO <sub>3</sub> -Ca-Mg	6.5	3.47	1,421.7	0.0	24.70
11.	Kováčová	Borehole at a house	SO <sub>4</sub> -HCO <sub>3</sub> -Ca-Mg	46.2	2.78	1,262.5	0.6	21.51
12.	Lipovec	Solivar	HCO <sub>3</sub> -Na-Ca	6.0	2.99	102.3	0.0	21.73
13.	Lúčky	Helena	SO <sub>4</sub> -HCO <sub>3</sub> -Ca-Mg	25.5	2.84	1,174.8	0.0	24.58
14.	Eupčianska dolina Valley					1,277.3		22.35
15.	Michaľany	Borehole at railway station	HCO <sub>3</sub> -Cl-Na	10.0	21.30	1,907.7	0.1	33.23
16.	Pôtor					300.4		-2.30
17.	Rovná					855.9		12.20
18.	Santovka	B-6	HCO <sub>3</sub> -Ca-Na	16.2	3.46	349.8		15.71
19.	Santovka Malinovec	B-3	HCO <sub>3</sub> -Na-Ca	27.5	5.60	577.8	0.6	24.56
20.	Sivá Brada		HCO <sub>3</sub> -SO <sub>4</sub> -Ca-Mg	12.3	7.19	1,146.9	0.8	28.09
21.	Slatina					396.3	9.5	19.63
22.	Slatina	Prameň pri MNV	HCO <sub>3</sub> -Na-Ca	14.0	3.13	123.0	0.0	19.93
23.	Sliač	Spa spring	SO <sub>4</sub> -HCO <sub>3</sub> -Ca-Mg	33.0	3.89	1,574.4	0.0	23.05
24.	Sobrance	Spa spring	Cl-Na	13.9	9.86	548.1	23.9	27.24
25.	Solivar	brines				4,366.4		10.97
26.	Šindliar		HCO <sub>3</sub> -Ca	9.0	2.62	213.6	0.0	24.70
27.	Šošár (Želovce)	spring Slaná voda				517.3		0.70
28.	Švermovo	Šťavica	HCO <sub>3</sub> -SO <sub>4</sub> -Ca-Mg	13.0	2.99	382.7	0.3	24.93
29.	Tisovec		HCO <sub>3</sub> -SO <sub>4</sub> -Ca-Mg	10.0	2,332.20	583.9	0.0	23.53
30.	Turčianske Teplice	Červený bazén	SO <sub>4</sub> -HCO <sub>3</sub> -Ca-Mg	37.5	1.34	530.0	0.0	19.83
31.	Valča	Smrdutá voda (Sloviansky p.)				638.2		16.68
32.	Valča	Creek below Smrdutá voda				384.8		15.24
33.	Vyšný Sliač	spring Čertovica	HCO <sub>3</sub> -SO <sub>4</sub> -Ca-Mg	20.2	3.05	476.9	2.0	24.56
34.	Zbudský Rokytov					2,192.9		-11.18
35.	Železnô					936.7		23.19

ment can be attributed to low bacterial reduction intensity. The importance of isotopically light sulphur ( $\delta^{34}\text{S} \sim 5$  ‰), so-called background sulphur present in springs with low sulphate concentration when mixing pointed out Malík & Michalko (2002). The result of mixing of large quantities of groundwater with this sulphur and the groundwater with sulphur derived from marine evaporites of Werfenian age ( $\delta^{34}\text{S} \sim 25$  ‰) is the sulphate with values of  $\delta^{34}\text{S}$  characteristic for the Late Triassic Ocean sulphate derivatives, which can lead to misinterpretation.

High proportion of heavy isotopes of sulphur in mineral waters from the Neogene sediments of the Eastern Slovakia Lowland (Sobrance, Michaľany) Kantor (1985)

attributed to the effect of recent (bacterial reduction) and syngenetic processes. Kantor & Sládková (1979) and Kantor et al. (1982) demonstrated the sulphur enrichment in Badenian evaporites of subincumbent and basal parts of salt deposits. In both cases (sulphur enrichment of Badenian Sea and vice versa, the depletion of sulphur in sulphate of Karpatian Sea) the processes were probably of supra-regional character.

Group of mineral waters with sulphate originating from the oxidation of sulphide sulphur present in the collector rock environment Kantor (1985) divided by the origin of sulphate into three groups. Sources with depleted sulphur derived from pyrites from rocks of the Flysch

Zone represents the spring in Zbudský Rokytov with  $2,193 \text{ mg} \cdot \text{l}^{-1} \text{ SO}_4^{2-}$  with  $\delta^{34}\text{S} = -11.18 \text{ ‰}$ . The sulphate of the sources from the Neogene sediments of the South-Slovakian coal basin (Pôtor, Slaný prameň in Želovce and well PS) with sulphate concentration of  $93 \text{ mg} \cdot \text{l}^{-1}$  to  $517 \text{ mg} \cdot \text{l}^{-1}$  as  $\delta^{34}\text{S} = -2.30 \text{ ‰}$  to  $0.70 \text{ ‰}$ ; it also comes from the oxidation of sulphide, probably syndimentary sulphur. In contrast, water from a gallery for noble sulphur in Kalinka (sulphate concentration  $202 \text{ mg} \cdot \text{l}^{-1}$  and  $\delta^{34}\text{S} = 4.20 \text{ ‰}$ ) represents a group of mineral waters in which sulphate comes from the oxidation of sulphides of hydrothermal origin.

## 2.4 Regional and local targeted research

In the early period, in addition to work aimed at general reviews of isotope pattern of mineral water sources nationwide the acquisition of knowledge of the isotopic composition of water and/or dissolved compounds was a relevant part of the work aimed at solving specific problems of origin, protection and utilization of mineral water in local or regional scales. This group of works carried out in the mid-80s can include studies of the isotopic composition of geothermal waters of the Central Depression of the Danube Basin, research in mineral waters of the crystalline of the Nízke Tatry Mts. and the solution of the genesis of geothermal waters of the Vienna Basin.

The first indication of the isotopic composition of water from a geothermal well from Slovakia brought Barnes & O'Neil in Čadek & Pačes, (1976), who on the basis of the values  $\delta^{18}\text{O} = -10.8 \text{ ‰}$  and  $\delta^2\text{H} = -75.5 \text{ ‰}$  of the water in the well in Patince defined its origin from precipitation (Tab. 2.1). They assumed for inorganic carbon ( $\delta^{13}\text{C} = 9.0 \text{ ‰}$ ) the impact of incomplete dissolution of carbonates.

The first data on the isotopic composition of geothermal water from the Central Depression of the Danube Basin in terms of isotopes of hydrogen and oxygen are the result of activities of the organization VIKÚV. Analysis of seven water wells in 1976 provided Franko & Bodiš (1989), after their rearrangement Michalko (in Franko et al., 2000; Tab. 2.4). Based on isotopic data ( $\delta^2\text{H}$  ranges from  $-68.2 \text{ ‰}$  to  $-96.0 \text{ ‰}$  and  $\delta^{18}\text{O}$  from  $-9.8 \text{ ‰}$  to  $-13.8 \text{ ‰}$ ) meteoric origin of waters can be assumed.

An acknowledged fact that the mineralization and temperature of geothermal water of the Neogene sediments of

Tab. 2.4 First isotope data from geothermal wells of Central Depression of the Danube Basin. Unpublished data from 1976 (VIKÚV) in Franko & Bodiš (1989), rearranged after Franko et al. (2000)

Locality	Source	$\delta^{18}\text{O}_{\text{H}_2\text{O}}$ SMOW [ ‰]	$\delta^2\text{H}_{\text{H}_2\text{O}}$ SMOW [ ‰]
Diakovce	Di-1	-13.8	-96.0
Topoľníky	FGT-1	-12.8	-90.8
Kráľová pri Senci	FGS-1/A	-11.1	-77.2
Chorvátsky Grob	FGB-1/A	-11.5	-82.0
Galanta	FGG-1	-11.1	-78.0
Čalovo	Č-1	-9.8	-68.2
Dunajská Streda	DS-1	-10.9	-77.0

the Central Depression of the Danube Basin increase with depth has been confirmed and supplemented by data on oxygen isotopic composition of these waters. Kantor (1985), in collaboration with Bodiš indicates  $\delta^{18}\text{O}$  of geothermal water from 16 wells, of which one was from the edge of Levice marginal block (Po-1 in Podhájska) and Komárno elevated block (M-3 in Komárno), the other fourteen from the Central Depression of the Danube Basin (Tab. 2.5, Fig. 2.3). Wide range of  $\delta^{18}\text{O}$  values (from  $-1.98 \text{ ‰}$  to  $-13.18 \text{ ‰}$ ) of geothermal waters demonstrates the varied and complex conditions of their origin and formation. For depleted water Kantor (l.c.) assumed a meteoric origin, whereas he excludes recent precipitations as their source by comparing the average rainfall in Vienna (annual average of  $-9.4 \text{ ‰}$   $\delta^{18}\text{O}$  to  $-10.3 \text{ ‰}$ ). As a source of depleted meteoric water he doesn't exclude meteoric water from glaciation periods; he considers a source of water brought by the Danube River into the Danube Plain from the Alps. The data provided observations of the isotopic composition of the Danube, Morava and Váh, and also knowledge of the isotopic composition of groundwater from overlying Quaternary sediments in piezometer PZ-I in Šamorín. Kantor (l.c.) determined the presence of isotopically depleted water from the Danube River bank infiltration to a depth of 154 m,  $\delta^{18}\text{O}$  ranging from  $-10.59 \text{ ‰}$  to  $-11.82 \text{ ‰}$  what corresponds to the average composition of the Danube water. In support of this interpretation is also increase in the light isotope of oxygen from peripheral to central part of the basin in profile Chorvátsky Grob, Kráľová pri Senci, Diakovce,  $\delta^{18}\text{O}$  from  $-11.25 \text{ ‰}$  through  $-11.93 \text{ ‰}$  to  $-13.18 \text{ ‰}$ . In the marginal parts of the Basin he assumed meteoric origin of water infiltrated from the Malé Karpaty Mts.

Geothermal water of borehole Kol-3 in Nesvady with high presence of heavy oxygen isotope ( $\delta^{18}\text{O} = -1.98 \text{ ‰}$ ) captured in the Pannonian sediments is considered to be a fossil marine water. Gradual changes in favour of the light isotope with decreasing depth of wells of tapped Pontian aquifers manifest changes in the isotopic composition – from Sarmatian to Quaternary – gradual turning from sea through brackish and finally lacustrine water. The second option is mixing among seawaters and depleted waters of meteoric origin (according to Kantor l.c. of Danube origin) present either in sandy Dacian sediments in the well Di-1 ( $\delta^{18}\text{O} = -13.18 \text{ ‰}$ ), or Pontian – drilling FGa-1 in Gabčíkovo ( $\delta^{18}\text{O} = -12.51 \text{ ‰}$ ) and FGT-1 Topoľníky ( $\delta^{18}\text{O} = -12.09 \text{ ‰}$ ), or in the Quaternary gravels. In favour of idea about alpine origin of depleted constituent, is the presence of large volumes of these waters in the overlying Quaternary gravels and gravels/sands. This assumption was preferred by Franko (2001) and the followers, despite the already known data on the MRT of the majority of geothermal water wells (the first tens of thousands of years; Franko et al., 1995). Therefore the isotopically light water dates back to the cold climate. In water derived from precipitation in the area of the Alps and brought by the then Danube it can be assumed increased presence of the light isotope of oxygen (and hydrogen) compared to today. The Danube water effect (of unknown age) on the formation of geothermal waters is conceded the central part of the Basin.

Tab. 2.5 Basic and isotope composition data of geothermal wells in Podunajská panva (Danube) Basin water (Data by Kantor, 1985)

Locality	Source	Hydrogeological structure	Well depth [m]	Watered section [m]		Age	Lithology	Sampling date	t [°C]	Q [l·s <sup>-1</sup> ]	d <sup>18</sup> O <sub>H<sub>2</sub>O</sub> [‰] SMOW	TDS [g·l <sup>-1</sup> ]	Cl <sup>-</sup> [mg·l <sup>-1</sup> ]	
				from	to									
Diakovce	Di-1	Central Depression of Danube Basin	3,303	720	810	Dacian	sands	30.03.1983	38.0	4.0	-13.18		3.5	
Diakovce	Di-2		1,551	1,416.5	1,535.5	Pontian	sands	30.03.1983	68.0	12.0	-11.40	2.10	290.0	
Dunajská Streda	DS-1		2,500	2,183	2,432	Pontian	sands	30.03.1983	91.5	15.2	-7.31	6.90	2,440.0	
Dvory nad Žitavou	FGDŽ-1		2,500	1,024	1,616	Pontian	sands	30.03.1983	62.0	7.2	-9.10	3.40	1,515.0	
Gabčíkovo	FGGa-1		2,582	1,122	1,926	Pontian	sands	30.03.1983	52.0	1.0	-12.51	1.10		
Horná Potôň	FGHP-1		2,500	1,364	1,963	Pontian	sands	30.03.1983	68.0	20.0	-10.03	4.70	1,443.0	
Chorvátsky Grob	FGB-1/A		500	276.21	299.67	Pontian	sands	30.03.1983	24.0	3.5	-11.25	0.49	33.0	
(Nesvady)	Kol-3								30.03.1983			-1.98		5,184.0
Komárno	M-2		1,060	771	1,025	Pontian – Pannonian	sands	30.03.1983	42.0	4.5	-10.95	0.51	915.0	
Kráľová pri Senci	FGS-1/A		1,500	910	1,235	Pontian	sands	30.03.1983	52.0	13.0	-11.93	7.70	1,379.0	
Topoľníky	FGT-1		2,501	1,394.4	2,043	Pontian	sands	30.03.1983	74.0	23.0	-12.09	2.20	250.0	
Tvrdošovce	FGTv-1		2,406	587	1,362	Pontian	sands	30.03.1983	70.0	20.0	-11.34	15.00	123.0	
Veľký Meder	Č-1		2,502	2,289	2,380	Pontian	sands	30.03.1983	92.0	7.6	-8.77	5.10	2,090.0	
Vincov les	FGG-1		1,990	1,212.5	1,470	Pontian	sands	30.03.1983	62.0	15.0	-10.97	3.20	316.0	
Vlčany	FGV-1		2,500	1,244	1,852	Pontian	sands	30.03.1983	62.6	10.0	-11.83	2.10		
Komárno	M-3		1,184	1,139	1,184	Triassic + Jurassic	dolomites, limestones	30.03.1983	51.0	5.0	-12.58	3.10		
Podhájska	Po-1	1,900	1,155	1,740	Badenian Triassic	clastic dolomites, quartzites	30.03.1983	80.0	53.0	-6.63	19.60		9,536.0	

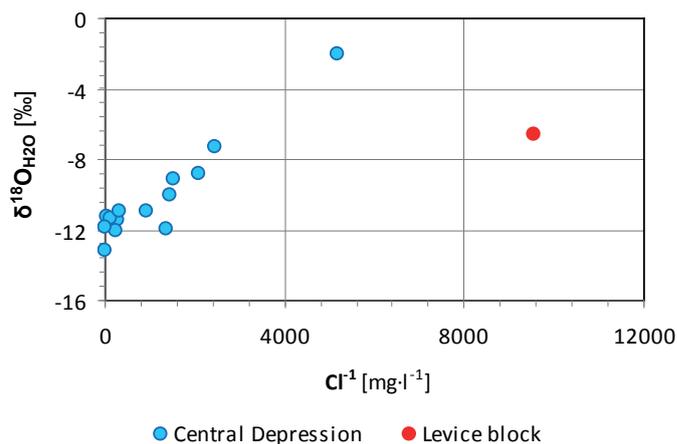


Fig. 2.3 Geothermal water of Central Depression of the Podunajská panva Basin; relationship between  $\delta^{18}\text{O}_{\text{H}_2\text{O}}$  /  $\text{Cl}^-$  concentration

The idea of the origin of water in local rainfall, in transport by rivers of the higher altitudes of the Western Carpathians, but also about its penetration to the Basin from the marginal mountains is evidenced by higher residence time (and hydraulic properties of aquifer rocks), and also by the fact that in shallow Neogene horizons they were documented in more than 20 wells with confined groundwater level meteoric water (Bottlik et al. 2013; Michalko et al. 2015). Their  $\delta^{18}\text{O}$  isotopic composition ranged from -11.16 ‰ to -13.90 ‰, with mean value -12.75 ‰, apparently of glaciation age. In formation of geothermal waters in the Danube basin area there are involved different constituents. Evident is share of the water of marine origin; (Fig. 2.3) however, a sea is progressively substituted by brackish environment, so chemical and isotopic composition change over time. The other constituent is isotopically light water coming from precipitation of the cold period – it gets in the Basin area from surrounding mountains or by palaeoflows. Large amounts of isotopically light meteoric water mainly from the Alpine delivers – and delivered – the Danube River. In cases where the final composition of geothermal water was affected by water of marine origin, the determined  $^{14}\text{C}$  ages have to be perceived as the mixed ones. This fact was not taken into account by Franko (2001) and subsequently Franko et al. (2008), Povinec et al. (2010a, 2010b). The need to determine the criteria to distinguish different kinds of waters and estimate their share in the final composition of the geothermal waters was pointed out by Kantor (1985).

Tab. 2.6 Isotope composition of the incrust from the borehole Po-1 in Podhájska

Layer N°	Mineral	$\delta^{13}\text{C}$ [‰] PDB	$\delta^{18}\text{O}$ [‰] PDB	$\delta^{18}\text{O}$ [‰] SMOW
1	Aragonite – brown coloured from Fe component	1.60	-11.28	19.23
2	Calcite – brown coloured from Fe component	1.08	-13.49	16.95
3	Aragonite – first white non-coloured layer	1.34	-14.90	15.50
4	Aragonite – white colour	1.15	-15.08	15.23

According Kantor (1985) the conduits for depleted water present in carbonates of the Komárno elevated block in borehole M-3 at depth of 1,139 – 1,184 meters ( $\delta^{18}\text{O} = -12.58$  ‰) creates the system of Komárno faults; however he did not exclude its origin in local precipitation waters during glaciations. For its source are now considered karst waters infiltrating from the South. Problematic seems to be isotopically heavier water ( $\delta^{18}\text{O} = -10.95$  ‰) tapped in the borehole M-2 in overlying Pontian sands.

In water ( $\delta^{18}\text{O} = -6.63$  ‰) tapped in the borehole Ro-1 in Badenian clastic rocks and Triassic dolomites the author (l.c.) assumes a significant proportion of marine

water. At this site the author (l.c.) upgraded the research on study of the isotopic composition of incrust (Tab. 6). The incrust is composed of calcite and aragonite lamina. There were sampled four lamina; brown-coloured aragonite and calcite near the base were likely affected by turbulent conditions at the time of their origin.

On the basis of the relevant data obtained from the two white aragonite lamina (Tab.2.6) and the assumed steady state Kantor (l.c.) determined precipitation temperature of 65 °C and 68 °C. In fact, the well water at the collar reaches 80 °C, which is justified by non-reaching of steady state. Carbonates are also isotopically markedly different from carbonates of marine origin.

As part of a detailed hydrogeochemical research of mineral waters of crystalline of the Nízke Tatry Mts. (Rapant 1991, 1994, Rapant et al., 1986) there were applied findings of the isotopic composition of oxygen (and hydrogen) of water (Tab. 2.7). Two pieces of information about the isotopic composition of sulphur are coming from nationwide surveys by Šmejkal et al. (1981) and Kantor (1985) (Fig. 2.1, Tab. 2.2). Based on the findings of  $\delta^{18}\text{O}_{\text{H}_2\text{O}}$  Kantor (1985) attributed the waters of all monitored sources meteoric origin; the isotopic composition of hydrogen he didn't specified (Tab.2.7). The data come from the archives of the former Department of Isotope Geology SGIDŠ (Michalko, 1998). Large differences in the distribution of oxygen isotopes Kantor (l.c.) attributes to differences in altitudes of catchments, or the effect of precipitation of cold and warm periods. Based on the identity of the values  $\delta^{18}\text{O}$  he supposes homogenization for springs in Malužiná (LM-96, LM-97), and thus a longer residence time, or deeper circulation. The share of fossil water of Neogene Sea in the composition of the water of these springs and spring Boženy Němcovej in Bacúch characterized by a high chloride content, he referred to only as a theoretical possibility. He considered these waters to be of clearly meteoric origin (Fig. 2.4). Thus, the presence of rich spectra sporomorphs of Neogene age in water of several springs (Planderová, Rapant reportedly in oral Kantor, 1985, Rapant et al., 1986, Rapant, 1991, 1994) he explains by the interaction of mineral water with the sediments of the Neogene age.

In evaluating the chemical composition and genesis of geothermal waters of the Slovak part of the Vienna Ba-

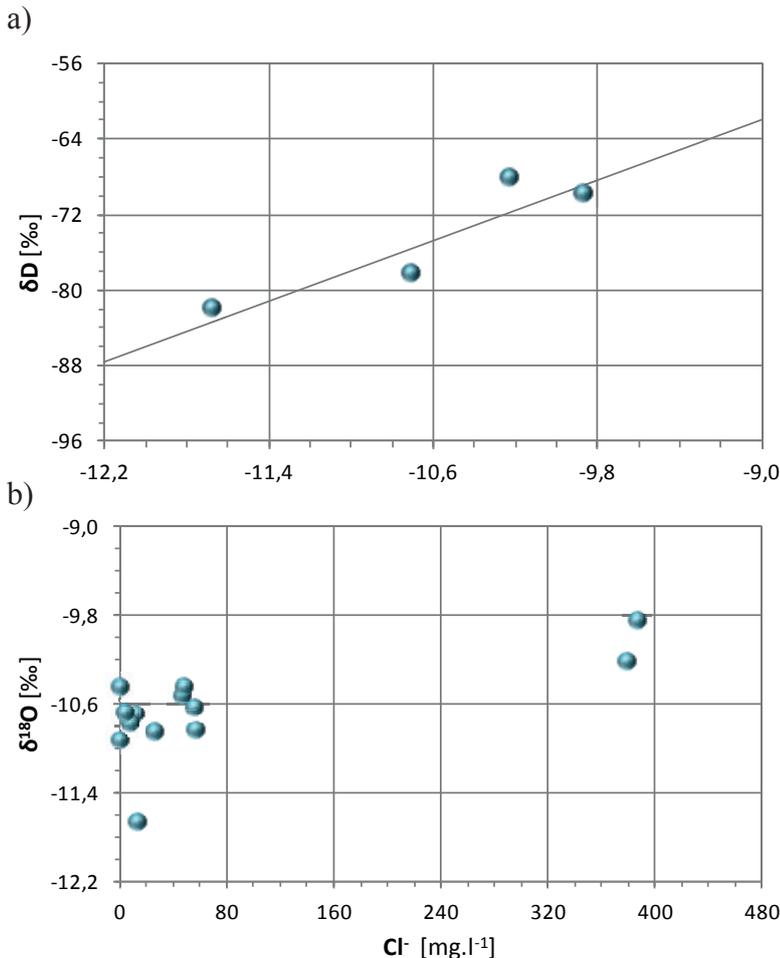


Fig. 2.4 Mineral waters from crystalline environment of the Nízke Tatry Mts.; a) isotope composition of O and H, b) relationships between  $\delta^{18}O_{H_2O}$  and  $Cl^-$  concentration

sin (Bodiš in Remšík et al., 1985) the hydrogeochemical data provided the basis, along with the knowledge of the geological setting of pre-Neogene bedrock and Neogene itself, the characteristics of evaporites and isotopic analyses. Based on the factor analysis of hydrogeochemical data there were allocated three factors, namely the so-called “marine”, in which positive factor scores achieved  $Na^+$ ,  $K^+$ ,  $Cl^-$ ,  $Br^-$ ,  $I^-$ ;  $SO_4^{2-}$  was significantly negative. The second factor (“metamorphosis II”) with significant correlation between bicarbonates and sulphates represents infiltration degradation, or interaction water-anhydrite. The third factor “metamorphosis I” represents the water-rock interaction and is characterized by a positive saturation of magnesium, calcium, chloride, sodium, and the TDS. Results of the analysis were interpreted in real environs of hydrogeological structures.

In the hydrogeological structure of the Láb-Malacky elevation with adjacent sunken blocks there are present in the Mesozoic basement strong brines of distinct sodium-chloride type with TDS 90 – 128 g . l<sup>-1</sup>. Low sulphate concentrations, although in the rock environment anhydrite presence is evidenced, result from inhibitory action of  $CaCl_2$ , which blocks the dissolution of anhydrite. Ion-exchange processes increase the total dissolved solids and  $CaCl_2$  content. After reaching a steady state in a closed

system the reaction does not take place at present. Probably in the Early Karpathian penetrated in the emerged area of elevation the sea lagoons; their brines infiltrated into Triassic carbonates. However, evaporation due to the contribution of meteoric water into the lagoon had not taken place up to a degree of precipitation of salts, as it is evidenced by isotopic composition ( $\delta^{18}O = -2.5$  ‰, Buzek in Remšík et al., 1985) of brine from the horizon from 2,873 to 2,877 m of drilling Láb-120.

In Závod-Studienka sunken zone marinogenic waters have been found, degraded to some degree, of distinct sodium-chloride type with TDS in the range of 15 – 25 g . l<sup>-1</sup>. The degree of degradation decreases with depth.

In the hydrogeological structure of Šaštín elevation (Bodiš in Remšík et al., 1985) and adjacent sunken zones waters of indistinct sodium chloride character are present with TDS 7 – 15 g . l<sup>-1</sup>. The waters are bound to aquifer constituted by Eggenburgian clastics and Triassic dolomites of the Choč Nappe. The structure is characterized by the differentiation of water in the depth and lateral direction (SW-NE). In the Šaštín area significant interaction with anhydrite is involved in the formation of the water. In the well Šaštín-12 Kantor et al. (1982) provided Late Triassic characteristic values  $\delta^{34}S$  from 14.4 ‰ to 17.0 ‰ for the anhydrite present in the Haupt Dolomite (overlying Lunz Mb., 10 samples from a depth of 4,193–4,953 m). The anhydrites from the base of the Lunz Mb. (two samples from a depth of 5,700 – 5,830 meters) referred to as the upper part Oponice Limestone (Němec & Kocák, 1982, in Kantor, 1982) are significantly enriched in the heavy isotopes of sulphur –  $\delta^{34}S = 22.5$  ‰ and 22.8 ‰. The waters are rich in sulphates and hydrogen sulphide, although at present its formation does not take place. Bodiš (in Remšík et al., 1985) assumes start-up of the biological processes responsible for the formation of  $H_2S$  by mixing of waters of marine and meteoric origin, their termination at the subsidence of Inner-Carpathian units and subsequent increase in temperature to nearly 100 °C.

In Lakšárska Nová Ves elevation there are two basic types of water. At greater depths (well LNV-7) marinogenic waters are present with TDS from 34.7 to 43.8 g . l<sup>-1</sup>. Bodiš (in Remšík et al., 1985) considers them represent infiltrated marine waters affected by reaction with the surrounding geological environment, especially anhydrites. They have preserved thanks to the presence of impermeable Lunz Mb. Anhydrites from a depth of 6,043 – 6,400 m (4 samples) showed the isotopic composition of sulphur ( $\delta^{34}S$  from 15.6 to 17.2 ‰) characteristic for evaporites of the Late Triassic (Kantor, 1982). In the basal Eggenburgian clastics and upper parts of Inner-Carpathian units

Tab. 2.7 Isotope composition of O and H in mineral waters of the Nízke Tatry Mts. (data by Kantor, 1985)

Locality	Source	Source labeling	Type	$\delta^{18}\text{O}_{\text{H}_2\text{O}}$ SMOW [‰]		$\delta^2\text{H}_{\text{H}_2\text{O}}$ SMOW [‰]	Cl <sup>-</sup> [mg·l <sup>-1</sup> ]	$\delta^{34}\text{S}_{\text{SO}_4}$ [‰] CDT
				08.12.84	05.06.85			
Bacúch	spring B. Němcovej	BB-1	HCO <sub>3</sub> -Cl-Na	-10.22		-68.3	380.7	
Jarabá		BB-45	HCO <sub>3</sub> -SO <sub>4</sub> -Ca-Mg	-10.59				
Jarabá	Bachláč	BB-46	HCO <sub>3</sub> -SO <sub>4</sub> -Ca-Mg		-10.70	-78.4	13.2	
Jarabá	Kumštová	BB-48	HCO <sub>3</sub> -Ca-Mg-Na		-10.64		57.2	
Jarabá	Predjasienok	BB-47	HCO <sub>3</sub> -Ca-Mg		-10.46		2.0	
Jarabá	Husárka, vrt H-1	BB-50	HCO <sub>3</sub> -Ca-Na-Mg		-11.67	-82.1	13.8	
Jarabá	Kyslá	BB-49	HCO <sub>3</sub> -Ca-Mg		-10.78		9.2	
Liptovská Lúžna	Banské	LM-61	HCO <sub>3</sub> -Ca-Mg		-10.69		5.4	
Malužiná	Main spring	LM-96	SO <sub>4</sub> -HCO <sub>3</sub> -Ca-Mg	-10.53	-10.44		48.0	
Malužiná	Kadlub	LM-97		-10.45	-10.44		48.9	
Mýto pod Ďumbierom		BB-57	HCO <sub>3</sub> -Cl-Na		-9.86	-69.9	387.5	
Mýto pod Ďumbierom		BB-58	HCO <sub>3</sub> -Cl-Na	-9.81				32.0
Pohronský Bukovec		BB-61	HCO <sub>3</sub> -Na	-10.84			58.0	
Vyšná Boca		LM-146			-10.86			
Vyšná Boca	Behind Church	LM-136	HCO <sub>3</sub> -Ca-Mg	-10.86			27.3	
Železnô	Ž-1	LM-101			-10.93		1.2	23.2

Tab. 2.8 Isotope data from sources of mineral water in Slovak part of Vienna Basin. Data by Kantor in Remšík et al. 1985. All numbers for original sulphate recalculated by author. <sup>1</sup>Data by Šmejkal et al., 1981 (Tab.2.2) used by Bodiš in Remšík et al., 1985, <sup>2</sup>Data by Bodiš in Remšík et al., 1985, <sup>3</sup>(Mean data Kantor in Remšík et al., 1985)

Locality	Source	Watered section [m]	Sampling date	$\delta^{18}\text{O}_{\text{H}_2\text{O}}$ SMOW [‰]	$\delta^2\text{H}_{\text{H}_2\text{O}}$ SMOW [‰]	Instantaneous sulphate				Original sulphate	
						SO <sub>4</sub> [mg·l <sup>-1</sup> ]	H <sub>2</sub> S [mg·l <sup>-1</sup> ]	$\delta^{34}\text{S}_{\text{SO}_4}$ [‰] CDT	$\delta^{34}\text{S}_{\text{H}_2\text{S}}$ [‰] CDT	SO <sub>4</sub> [mg·l <sup>-1</sup> ]	$\delta^{34}\text{S}_{\text{SO}_4}$ [‰] CDT
<sup>1</sup> Plavecký Peter			1975			184.0	28.0	33.6	8.6	262.9	26.1
<sup>1</sup> Smrdáky	Jozef I		1969			35.0	450.0	21.8	17.1	1,303.5	17.2
			1975			192.0	600.0	21.2	15.8	1,883.3	16.4
	RGL-1	1,242 – 1,322	03.02.84	-10.90		<sup>2</sup> 1,372.6	<sup>2</sup> 234.2	43.09	2.33	2,032.8	29.9
		1,242 – 1,322	08.02.84	-10.76	-74.2						
		1,242 – 1,562	29.03.84	-10.91	-81.0	<sup>3</sup> 1,371.4	<sup>3</sup> 222.6	44.15	2.17	1,998.9	31.0
		1,100 – 2,100	02.04.84	-10.95	-77.1						
		1,100 – 2,100	18.04.84			<sup>3</sup> 1,371.4	<sup>3</sup> 222.6	43.69	2.89	1,998.9	30.9
Kuklov	Kuklov-3	2,900	02.02.84								23.39

sodium-chloride waters are present with TDS = 5 – 7 g · l<sup>-1</sup>. In view of the isotopic composition of H and O the meteoric origin of waters is probable (Kantor in Remšík et al., 1985), and their composition is the result of the water-rock interaction. The Na-Cl component originates from reaction with overlying Neogene sediments; sulphates emerged thanks to anhydrite dissolution. On the basis of the water from well RGL-1 (Tab. 2.8) reconstructed sulphate features high enrichment in heavy isotope of sulphur, which is characteristic of Rôt and its equivalents. Sulphuric acid

with trivalent Fe oxides is the result of (bacterial) oxidation of pyrite. Kantor (in Remšík et al., 1985) reports that for achieving the isotopic steady state, fractionation in the system of dissolved sulphate – gaseous hydrogen sulphide should correspond temperatures of 140 °C – 150 °C, in the system bisulphate – hydrogen sulphide the temperature of 110 °C.

Springs of mineral waters with hydrogen sulphide are located along the NW edge of the Malé Karpaty Mts. are considered to represent natural seepages of groundwater

from the Lakšárska Nová Ves elevation (Bodiš in Remšík et al., 1985). In favour of this idea is the isotopic composition of sulphur in their water solutes (Tab. 2.8), which can hardly come from Neogene of the Vienna Basin. For gypsum present in these sediments in Devín, Devínska Nová Ves, Stupava Kantor (1982) found  $\delta^{34}\text{S}$  in the range of -13.0 ‰ to -31.5 ‰ and thus it can not be considered synsedimentary mineral. Similarly differing are the values characteristic for the marine evaporites of Neogene Sea in terms of the isotopic composition of oxygen  $\delta^{18}\text{O}_{\text{SO}_4}$  which ranges from -3.48 ‰ to +6.15 ‰. The crystallization water in gypsum is not of marine origin, as well. Based on data on the isotopic composition ( $\delta^{18}\text{O}$  from -6.1 ‰ to -7.0 ‰ of 3 samples) the water from which the gypsum precipitated had isotopic composition  $\delta^{18}\text{O} = -9.6$  ‰ to -10.5 ‰, which corresponds to the composition of the current precipitations (Kantor et al., 1982). Knowledge of the isotopic composition of pyrite present in the sediment ( $\delta^{34}\text{S} = -6.6$  ‰ to -46.1 ‰) confirms the idea of Květ (Bodiš in Remšík et al., 1985) that the formation of gypsum in the Neogene of the Vienna Basin is due to the reaction of sulphuric acid with carbonates. The acid along with trivalent Fe-oxides is the result of (bacterial) oxidation of pyrite.

## 2.5 Conclusions

Knowledge of the isotopic composition of mineral water in Slovakia achieved in mid-eighties of the last century consisted of two nationwide thematic publications of foreign authors and a number of specialized SGIDŠ studies to address specific problems of the genesis of mineral water in selected regions. The research focused on the knowledge about isotopic composition of hydrogen and oxygen in the water and also in the isotopic composition of water-dissolved constituents, especially sulphur present in sulphate and also sulphide forms.

Based on knowledge of isotopes representation in the basic components of the water molecule the meteoric water origin was confirmed without a doubt in substantial part of the investigated sources of mineral water. The isotopic composition of oxygen and hydrogen in most mineral waters followed the global line of meteoric water and corresponded to precipitations. Water with increased representation of unusually light isotopes H and O in the sedimentary infill of the Central Depression of the Danube Basin of Neogene age were considered either meteoric waters brought by the Danube River from the Alps, or for meteoric waters coming from colder periods. They could be brought into the Basin by local palaeo-streams or due to transfer from the surrounding mountains. In the deep levels of the sedimentation space, some geothermal wells uncovered waters whose isotopic composition is close to the isotope composition of ocean water. Transitional composition was considered to represent either direct composition of brackish water gradually depleted Neogene Sea, or the result of the mixing of fossil seawater with groundwater of meteoric origin. It was raised and discussed the question of the appropriate criteria to address these problems. Mineral waters enriched in the heavy isotopes of H and O in some mineral waters from the Palaeogene Flysch Zone

sediments were considered a result of mixing between the (then hypothetical) water source of metamorphic origin with groundwater coming from local precipitation. Mineral waters of the Nízke Tatry Crystalline have meteoric origin and their chemical composition and the presence of Neogene sporomorphs has to be explained by contact with rocks of appropriate age. Large differences in the distribution of oxygen are considered to be a result of different altitudes of infiltration areas, or the result of circulation. For sodium-chloride waters present in the shallower aquifers of the Lakšárska Nová Ves elevation of the Slovak part of the Vienna Basin meteoric origin has been demonstrated.

Inorganic carbon present in the water sources investigated in the range of from about  $\delta^{13}\text{C}$  ‰ -4 to +4 ‰ comes from the dissolution of marine carbonates. The increased presence of light carbon isotope in some mineral waters is explained by incomplete dissolution of carbonates with isotopic fractionation of carbon.

Thanks to the available analytical and sizing techniques the research in constituents dissolved in water components was aimed at the study of sulphur present in the water in various forms. The mineral waters, in which due to the ongoing bacterial reduction coexist  $\text{SO}_4^{2-}$  and  $\text{H}_2\text{S}$  there was characterized level of the ongoing reaction and the conditions were also reconstructed (concentration and isotopic composition of sulphur) of sulphate present in the water prior to the start of activity of the bacteria. Based on knowledge of the isotopic composition of sulphur in sulphate (and possibly hydrogen sulphide) there were determined two main sources of sulphur. Isotopically heavy sulphur comes from the dissolution of evaporites of marine origin. In the case its isotopic composition was not affected by other processes (mixing, oxidation-reduction processes, sorption, adsorption ...), based on the ratio of isotopes of sulphur (and oxygen) in sulphate we can estimate the age of marine sediments with which the water was in contact. In our conditions this involves distinction among the Permian-Early Triassic, Early-Middle Triassic, or Late Triassic and Neogene sediments. Sulphate extra-enriched in sulphur ( $\delta^{34}\text{S} > 30$  ‰) is regarded as the residual sulphate after reduction. Highly depleted sulphur present in some waters bound to rock complexes of Flysch Zone is the result of (at least) two-stage reduction of the original sulphate of Palaeogene Sea. During the first stage the enriched residual sulphate was degraded; resulting isotopically light sulphide has been preserved in the sediment in the form of pyrite. This light sulphur in the sulphide form becomes part of the groundwater due to the water-rock interaction in which as a result of bacterial reduction particularly isotopically depleted hydrogen sulphide is formed. Analogously isotopically enriched (heavy) sulphate in the mineral waters that surge out in the Neogene filling of the Vienna Basin – rich in pyrite and gypsum with a very light sulphur – is considered a consequence of transfer of mineral water with heavy sulphur from the deeper layers of the Basin deposits.

For the interpretation of findings of great importance was ongoing and in parallel research into isotopic composition of rivers, ordinary groundwater, later on precipitations, isotopic composition of carbonate rocks and shells,

as well as sulphides and sulphates present in the rock environment.

The results obtained in the initial stages of isotope research in the field of mineral water have contributed to the knowledge on the formation of the mineral waters in the Slovak Republic and created conditions for a wider application of isotope geology in this area.

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