ENVIRONMENTAL ISOTOPES IN GROUNDWATERS OF LEVOČSKÁ KOTLINA BASIN

J. MICHALKO and M. FENDEK

Štátny geologický ústav Dionýza Štúra, Mlynská dolina 1, 817 04, Bratislava 11, Slovakia

Abstract: Main sources of geothermal and mineral waters were characterised according to the content of environmental isotopes in Levočská kotlina basin. Waters are meteoric in origin and do not contain any Tritium. The ^{14}C ages (18 ma - 28 ma) should be verified. Sulphate sulphur comes mainly from werfenian evaporites, mixing between this heavy ($\delta^{34}S$~25 ‰) and light ($\delta^{34}S$~5 ‰)"background" sulphur occurs in some sources. $^{87}Sr/^{86}Sr$ ratio seems to offer robust criteria for individual aquifers.

Key words: Geothermal and mineral waters, δD, $\delta^{18}O$,$\delta^{34}S$, $^{87}Sr/^{86}Sr$, Slovakia

Introduction

Research of environmental isotopes in natural waters was carried out mainly as a part of hydrogeological research solved by the Geological Survey of Slovak Republic (GSSR), as well as by the studies carried out as a part of research contracts with IAEA Agency in Vienna (Fendek - Michalko, 1997, Malík et al., 1997).

Study of environmental isotopes contents give the basic data to solve the problem of groundwater genesis and interrelationships. Stable isotope ratios of oxygen, hydrogen, sulphur and carbon were measured at GSSR at Finnigan MAT 250 mass spectrometer with reproducibility for $\delta^{18}O$ better than ± 0,07 ‰, for δD ± 1 ‰, for $\delta^{34}S$ ± 0,3 ‰ (Rúčka 1998). Calibration of internal standards was carried out by international standards (V-SMOW, NZ 1, NZ 2, NBS 122 and NBS 127). $^{87}Sr/^{86}Sr$ ratio was measured at Polish Academy of Sciences, Warsaw. It is normalized to $^{87}Sr/^{86}Sr$ = 0,1194, NBS SRM987 with true $^{87}Sr/^{86}Sr$ = 0,710248 Tritium concentrations were measured at VUVH Bratislava with reproducibility 5 %. 14C activity was measure at Commenius University Bratislava, the "age" is calculated with correction factor k = 0,85 (Šivo et al 1995).

Geological settings

The Levoča Basin is located in the north-eastern part of the Slovak Republic. It is separated by faults from the Klippen Belt in the north and northeast, and borders the Tatry in the northwest as well as eastern tracts of the Nízke Tatry, Slovenské rudohorie and Čierna hora Mts. in the south. Western branch of Hornád fault separates it from the northern part of Košice Basin. The Vikartovský chrbát Ridge extends from the Nízke Tatry eastward to the Levoča Basin. The ridge is confined by a conspicuous E-W-trending fault in the south. The Branisko horst confined by faults in the west and east stretches from the Slovenské rudohorie northward also into the Levoča Basin. Ružbachy inlier rises from the substratum of the Paleogene between the Spišská Magura and Levočské vrchy Mts. In the southeast, the inlier is lined by a fault representing a continuation of Subtatric fault.

The basin is filled with the Inner Carpathian Paleogene composed of a several-tens-of-metres-thick basal conglomerate formation and an overlying flyschoid formation up to 4000 m in thickness.

The geologic structure of the pre-Tertiary substratum includes all tectonic units of the Inner West Carpathians. The Gemeric Paleozoic and Mesozoic complexes of the Galmus and Stratenská hornatina Mts. extend into the southern tract of the Spiš Basin below the Paleogene. The Vikartovský chrbát Ridge consists of the Ipoltica Group of the Hronicum. To the north the pre-Tertiary substratum consists of a wide belt of the Choč nappe which stretches as far as north of the Branisko. Tertiary rocks of the Šarišská vrchovina rest on the Permian-Mesozoic envelope.

Groundwaters in the area flow out to the surface in natural springs at Gánovce, Baldovce and Vyšné Ružbachy. The springs at Baldovce (including Sivá Brada) are recharged from carbonates of the Choč nappe, the Tatric and Veporic envelope units, those at Vyšné Ružbachy from Krížna nappe carbonates, and those at Gánovce and Lipovce from Choč nappe carbonates. The existence of waters at these localities has been proven by shallow wells. Waters from springs and shallow wells are 13.6 - 26.7 °C warm and those from deep wells 19 - 107 °C.

As far as the chemical composition of groundwaters is concerned, it is dependent on the type of aquifer, depth of circulation and length of contact time with the rock environment. Waters hosted by Vernár nappe carbonates are of Ca(Mg)-HCO_3 type with T.D.S. 0.61 - 1.28 $g.l^{-1}$ and those bound to Choč nappe carbonates discharged by shallow and deep wells alike are of Ca(Mg)-HCO_3 type with T.D.S.

2.85 - 3.29 $g.l^{-1}$. Waters bound to Krížna nappe carbonates discharged by natural springs are of $Ca(Mg)$-HCO_3 type with T.D.S. 1.85 $g.l^{-1}$ and those from deep wells are of Na-HCO_3, Na-$Ca(Mg)$-HCO_3-Cl-SO_4 and Na-Cl types with T.D.S. 8.67 - 11.95 $g.l^{-1}$. Waters hosted by carbonates in the Tatric and Veporic envelope units are of $Ca(Mg)$-HCO_3 type with T.D.S. 3.49 - 7.92 $g.l^{-1}$. Genetically, the waters are atmospherogenic with petrogenic mineralization. Waters from all wells (Lipany-2 and Plavnica-1, Šariš-1), except for those at Gánovce and Vyšné Ružbachy, which tapped natural springs, have a marinogenic component seeped from a Paleogene sea.

Environmental isotopes

Environmental isotope data were collected to characterise main sources of the geothermal and mineral waters in Levočská kotlina basin and groundwater in main aquifers groundwater and in this region. Presented data (Table 1) were collected in 1994, 1996 and 1998 (Daniel et al. 1998, Fendek et al. 1997, Franko et al. 1995, Fendek et al, 1996, Michalko et al. 1995, Michalko & Zakovič unpublished data, Šivo et al. 1995.

The introducing of the hydrogen isotope method at GSSR were accompanied by analytical problems and samples from 1994 and 1996 were re-measured few times; now the "best possible" results are presented (Rúčka, Wiegerová, personal communication 1998). Due this, the existence of "older meteoric water line" (Michalko et al. 1995, Fendek et al. 1997) later published by Franko & Melioris (2000) as W_3MWL should be though out once again. Sulphate $\delta^{34}S$ results from 1998 are generally lower than older results and this is probably due to the different processing during field precipitation (this was not done by GSSR specialist). Dubious (δD and $\delta^{34}S$) data are marked by ! in the Table 1 and generally are not used in figures. Isotopes $\delta^{34}S$ and $\delta^{18}O$ of sedimentary evaporites (Fendek et al, 1996, Daniel et al. 1998) are shown in Table 2.

Oxygen and hydrogen isotopes

All studied groundwater are meteoric in origin and they generally follow the MWL. They are (with exception of some fresh waters) stable in time in their isotope composition. Oxygen shifts are not large due to low temperatures. Array could be explained by spatial (altitudinal), temporal and regime differences.

Tritium activity is under the 1,7 TU what is detection limit of method and groundwaters are submodern. Fresh water from Nové Okno source represents probably mixture of submodern and modern recharge or modern recharge (to 10 years). Real ages of groundwaters should be checked by independent method due to complex hydrogeochemistry.

Isotope composition of sulphate

The main sources of sulphur in groundwater are sedimentary evaporites, mainly permian and lower Triassic with $\delta^{34}S \sim 5$ - 15‰, werfenian with $\delta^{34}S \sim 25$ ‰, keuper with $\delta^{34}S \sim 16$ ‰ and Tertiary with $\delta^{34}S \sim 20$ - 23 ‰ (Claypool et al. 1980, Pearson et al. 1991), and minerals in Table 2. Michalko et al. (1993) defined "background" sulfur $\delta^{34}S \sim 5$ ‰, witch correspond with $\delta^{34}S$ (~ 4,7 ‰) of winter precipitation at Slovak territory (Malík et al. 1997). Light sulphur is present in pyrites from Paleogene sediments or could have antropogenic origin (here probably two samples from PD-64 and PD-72 sources, Tab. 1). Application of mixing model (Mansell et al 1995) with using werfenian, keuper and background sulphur (here used spring Tri studničky) as end members is presented at Fig. 2. From the graph is evident domination of werfenian heavy sulphur in sulphate majority of studied groundwaters, likewise in HKJ-3 in Gemeric unit. Sulphate sulphur of second representant of this unit (HKJ-4) seems to originate from lower Triassic evaporates.

Isotopes of strontium

Strontium isotopes ratio in groundwater is controlled mainly by water-rock interaction and important role has the solubility of minerals and mixing of groundwaters as well. The data about $^{87}Sr/^{86}Sr$ of rock are from the Western Carpathians territory scarce and from studied area we have none. Ratio of $^{87}Sr/^{86}Sr$ of all samples is in the 0,708 to 0,7092 frame and is stable in time at least for source VR-2. $^{87}Sr/^{86}Sr$ ratio is very characteristic for groundwater present in individual stratigrafic-tectonic units, Table 1. Groundwater in Choč nappe aquifer is characterized by six samples in narrow range 0,708222 – 0,708300 and one with 0,708383, Krížna nappe groundwater by one sample with 0,70868, Gemeric unit groundwater by two samples 0,708979 and 0,709015 and Paleogene groundwater by one sample with 0,709143.

$\delta^{34}S$ and $^{87}Sr/^{86}Sr$ ratio represent two independent characteristic of the water-rock interaction, their relations are presented at fig. C. Very similar array one can see at graphs of $^{87}Sr/^{86}Sr$ versus Sr content and $^{87}Sr/^{86}Sr$ versus Sr/Ca*1000 factor, here not shown.

Conclusion

According to δD and $\delta^{18}O$ results all waters are generally follow the MWL line - waters should be thought as meteoric in origin. They are (with exception of some fresh waters) stable in time in their isotope composition. Oxygen shifts are not large due to low temperatures. Generally waters are in low temperature range, with temperature up to some 50 °C. Oxygen shift due to low temperature is small even if aquifers are carbonate with exclusion these of basement (crystalline) and flysch (Paleogene). So, differences in hydrogen and oxygen isotope composition are mainly due to differences of recharge areas.

Sulphate in groundwater originates in little part from precipitation, soil and human activities, main part is due to solution of sulphur present in sulphatic or sulphidic form in aquifers. Very low $\delta^{34}S$ in two springs could be explained by dissolving of sedimentary pyrite usually present in flysh sediments or sulphur has an antropogenic origin. Isotopically "heavy" sulphur present in other sources should be derived from sedimentary gypsum of see origin. Values with $\delta\ ^{34}S$ about 20 ‰ could be explained like middle Triassic values, or by mixing with heavy werfenian rich in sulphur source with background "light" and low in sulphur endmember. Situation is documented by Fig. 2 where sources are plotted in SO_4 content versus $\delta\ ^{34}S$ diagram.

$^{87}Sr/^{86}Sr$ ratio values enabled to divide studied localities into single tectonic-stratigraphic units. Groundwaters in Choč nappe aquifers are characterized by six samples in narrow range 0,708222 – 0,708300 and one with 0,708383, Krížna nappe groundwaters by one sample with 0,70868, Gemeric unit groundwaters by two samples 0,708979 and 0,709015 and Paleogene groundwaters by one sample with 0,709143.

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Tab. 1. Isotope composition of natural groundwaters of Levočská kotlina basin. (data from Daniel et al. 1998, Fendek et al. 1997, Franko et al. 1995, Fendek et al, 1996, Michalko et al. 1995, Michalko & Zakovič unpublished data, Šivo et al. 1995). G - geothermal water, M - mineral water, FW - fresh groundwater

Tab. 2. Isotope composition of the evaporites from Levočská kotlina basin (data from Daniel et al. 1998, Fendek et al, 1996)

Fig. 1. $\delta D/\delta^{18}O$ relations in groundwaters of Levočská kotlina basin

C94, 96: crystalline sampled1994, 96
CH94,96,98: Choč nappe sampled 1994,96,98
P94,96,98: Paleogene sampled 1994,96,98
G94,96,98 Gemeric unit sampled 1994,96,98
K94,96: Krížna nappe sampled 1994,96

Fig. 2. $\delta^{34}S$ of dissolved sulphate and sulphate concentration relations. Mixing model

Fig. 3. $^{87}Sr/^{86}Sr$ and $\delta^{34}S_{SO4}$ relationship in groundwaters

Locality	Source	Tectonic-stratigraphic unit	Water type	Date	$\delta^{18}O_w$ [‰] SMOW	δD_w [‰] SMOW	$\delta^{34}S_s$ [‰] CDT	$\delta^{18}O_s$ [‰] SMOW	$^{87}Sr/^{86}Sr$ norm.	error	T [TU]	$\delta^{13}C$ [‰] PDB	^{14}C [p.m.c]	Age [m.a.]
Arnutovce	HKJ-3	Gemeric unit	G	1994	-11,2	-82,1	24,3					-4,1	4,1±0,3	25
	HKJ-3		G	1996	-11,1	-78,7	23,4							
	HKJ-3		G	1998	-11,06	-81,5	21,4!	14,84	0,708979	0,000011				
Baldovce	BL-1	Choč nappe	M	1994	-10,36	-83,5								
	BL-1		M	1996	-10,23	-77,1	27,9							
Forbasy	PD-07	Paleogene	M	1996	-10,15	-75,7								
Gánovce	PD-20	Choč nappe	G	1994	-11,28	-79,1	25,8					-0,2	3,3±0,3	26.9
	PD-20		G	1996	-11,36	-81,3	26,3		0,708247	0,000009	<1,7			
Kamienka	PD-39	Paleogene	M	1996	-11,12	-78,5	7,6							
Letanovce	HKJ-4	Gemeric unit	G	1998	-11,23	-80,8	12,5	12,83	0,709015	0,000011				
Nová Ľubovňa	LZ-6	Paleogene	M	1996	-10,63	-75,6	10,1		0,709143	0,00001	<1,7			
Podbanské	Tri studničky	Crystalline	FW	1996	-12,91	-91,9	5,3							
Poprad	PP-1	Choč nappe	G	1994	-11,01	-78,1	25,4					-4,2	6,8±0,3	20.9
	PP-1		G	1998	-11,04	-80,8	21,4!	16,5	0,708222	0,000011				
Sivá Brada	Sv. Kríž	Choč nappe	M	1994	-11,59	-81,5	28,3					3,4	2,9±0,3	27.8
	Sv. Kríž		M	1996	-11,48	-83,3	28,3		0,708383	0,000011	<1,7			
Slovenská Ves	PD-64	Paleogene	M	1996	-13,39	-77,7!	-15,3							
Spišská Teplica	Nové Okno	Choč nappe	FW	1994	-10,89	-76,2	11,4							
	Nové Okno		FW	1996	-10,93	-79.0	10,4				4,2			
Stará Lesná	FGP-1	Paleogene	M	1995	-11,16									
	FGP-1	Choč nappe	G	1996	-11,05	-82,4								
	FGP-1		G	1996	-11,04	-81,2	25,2		0,708225	0,00001				
	FGP-1		G	1996	-11,06	-83,3								
Starý Smokovec	PD-72	Crystalline	M	1994	-11,19	-75,9								
	PD-72		M	1996	-11,14	-77,5	-8,3							
Tatranská Kotlina	Studienka	Choč nappe	FW	1994	-10,52	-72,4	8,2							
	Studienka		FW	1996	-10,56	-72,5								
Toporec	PD-87	Paleogene	M	1996	-10,51	-75,4	6,2							
Veľká Lomnica	PD-90	Paleogene	M	1996	-9,68	-70,2								
Vyšný Slavkov	Spring	Choč nappe	FW	1994	-10,68	-79,4	7,8							
	Spring		FW	1996	-10,51	-76,8	4,8							
Vojňany	PD96	Paleogene	M	1994	-10,30	-67,9								
	PD-96		M	1996	-10,1	-75,4								
Vrbov	VR-1	Choč nappe	G	1994	-11,59	-78,5	24,1					-7,5	3,6±0,3	26,1
	VR-1		G	1998	-11,43	-86,8	22,7!	16,13	0,7083	0,000009				
	VR-2	Choč nappe	G	1994	-11,43	-83,6	23,8					0,9	3,2±0,3	27,1
	VR-2		G	1996	-11,37	-85,2	24,1		0,708267	0,000011	<1,7			
	VR-2		G	1998	-11,24	-86,2	17,5!	15,69	0,708255	0,000015				
Vyšné Ružbachy	Izabela	Krížna nappe	G	1994	-10,83	-80	20,8					-3	9,3±0,3	18,3
	Izabela		G	1996	-10,8	-77,1	20,7							
	VR-5	Krížna nappe	G	1996	-10,79	-77	25,5		0,70868	0,00001	<1,7			
Výborná		Paleogene	M	1994	-10,12	-66,4								

Tab. 1

Locality	Source	Depth	Tectonic - stratigraphic unit	mineral	$\delta^{34}S_{SO4}$ [‰] CDT	$\delta^{18}O_{SO4}$ [‰] SMOW
Stratená	981	166,8	Upper Paleozoic of Gemeric unit	Anhydrite	11,5	15,72
Danišovce	DH-1	921		Anhydrite	11,7	16,70
Danišovce	DH-1	918		Anhydrite	10,7	16,99
Šafárka	Ša-1			Anhydrite	10,8	16,66
Stará Lesná	FGP-1	3247,0	Choč nappe	Anhydrite	25,4	
Stará Lesná	FGP-1	3246,5		Gypsum	24,9	
Stará Lesná	FGP-1	3250,0		Gypsum	25,0	

Tab. 2

Fig. 1

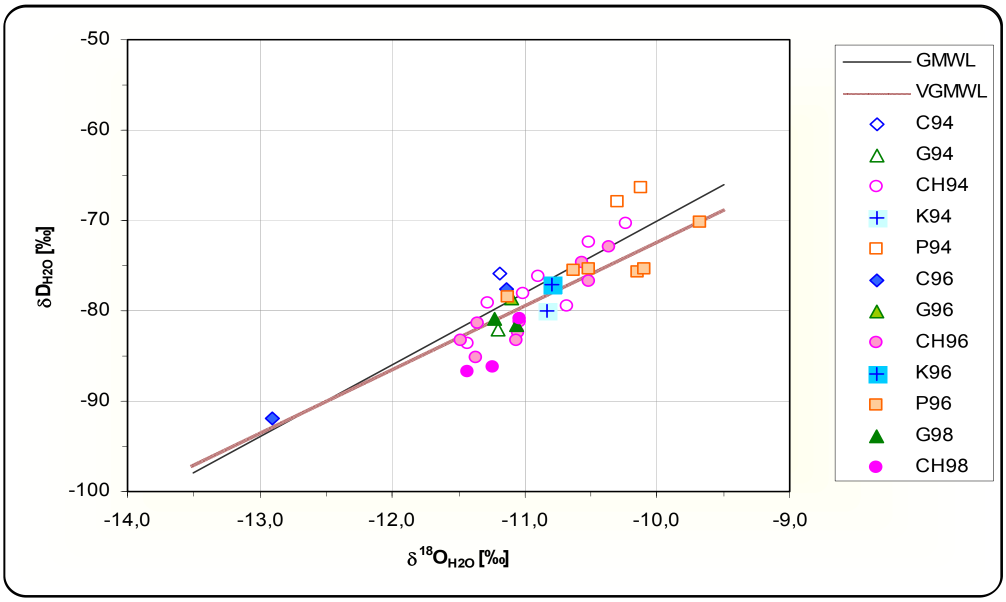

Fig. 2

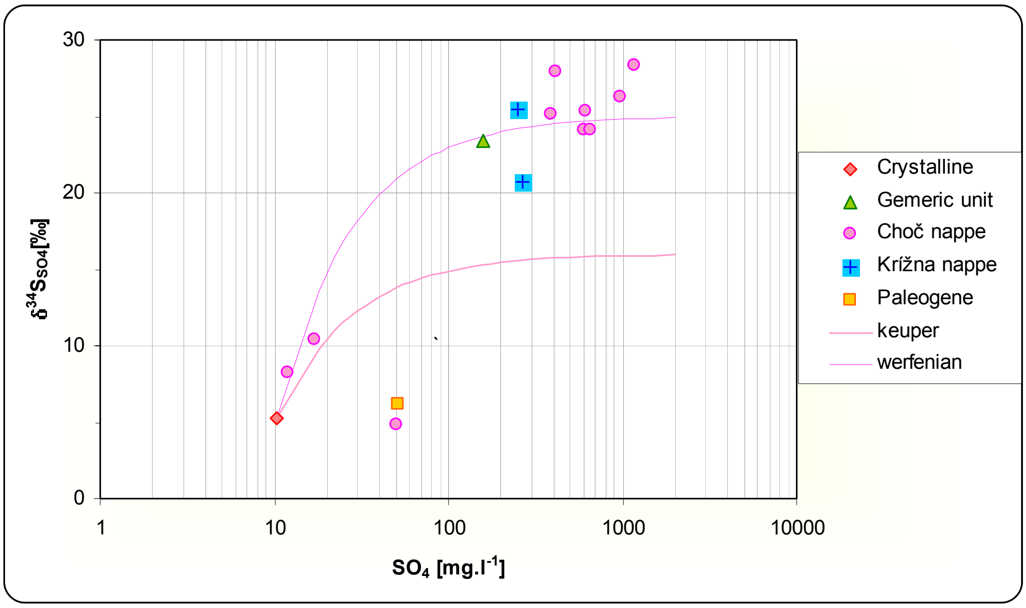

Fig. 3