

Stable isotopes of hydrogen, oxygen and sulphur in the waters of Slovakia

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Abstract. Paper provides a summary of stable isotope (H, O, S) research in different types of water. Precipitation waters were obtained through the monitoring for 10 years at 8 weather stations. Isotope composition of sulphur is characterised by the $\delta^{34}\text{S}$ of snow profiles (March 1996). The waters of the Danube and Morava Rivers are monitored since 1982. In the Žitný ostrov area the Danube River bank infiltration was characterised by isotope composition of oxygen (1992 - 1996). In the Veľká Fatra Mts. the altitudinal effect on $\delta^{18}\text{O}$ (0,1 ‰ per 100 m of the altitude) was estimated. Three main genetic types of groundwater were distinguished by their isotope composition - meteoric waters, fossil sea waters and metamorphic waters. The sources of sulphur in groundwater and the main secondary processes changing its isotope composition are described.

Key words: stable isotopes, precipitation, surface water, groundwater, mineral water, thermal water, oxygen, hydrogen, sulphur, Slovakia

Introduction

The main task of this paper is to offer a brief insight into and basic information about, the state of stable isotope research in Slovakian hydrogeology. This branch of research started in 80ies at the Dionýz Štúr Institute of Geology, at present a part of Geological Survey of Slovak Republic. Such research is an outgrowth of isotope geology studies existing at this Institute since 50ies. Results of this stage of research are summarised by Kantor et al. (1985, 1987, 1988).

Some particular data concerning stable isotope (H, O, S) composition of mineral and thermal waters on the Slovak territory are known (Barnes & O'Neil 1974, Šmejkal et al. 1971, 1981). The main effort was concentrated on the monitoring of precipitation, monitoring of the Danube and Morava Rivers, river bank infiltrating groundwater, and karst waters, and also research on mineral and geothermal waters, their use and protection.

Sample processing

$^{18}\text{O}/^{16}\text{O}$ (water) is measured on CO_2 equilibrated with the water in an equilibration device that is connected on line with a Finnigan MAT 250 mass spectrometer. The unknowns are measured against an internal standard calibrated against SMOW. The reproducibility of the preparation method ($n = 48$) is better than $\pm 0.07\text{‰}$.

Hydrogen gas for isotope analyses is produced by a zinc reduction technique. Approximately 5 μl of a water sample are reduced under vacuum with 150mg of zinc at 490 °C during 30 minutes. At this temperature, zinc reacts quantitatively with H_2O , producing hydrogen gas with an isotopic composition equal to that of water. The hydrogen gas is then measured mass spectrometrically for its deuterium content.

These results are normalised to internationally accepted standards and reported in the usual δ -notation. The standard deviation calculated from replicate δD analyses of a sample is generally better than $\pm 1\text{‰}$.

Sulphate sulphur from waters is precipitated with BaCl_2 (hot, acidified with HCl) as BaSO_4 and converted into H_2S by reaction with a hot mixture of HCl , H_3PO_4 and HI . Any H_2S is purged by nitrogen using zinc acetate, resulting in the precipitation of ZnS . Subsequently, a mixture of ZnS/CuO reacts gradually at temperatures of 320 °C and 770 °C. SO_2 is stored in glass ampoules for measurement. The measurement has reproducibility of $\pm 0.3\text{‰}$. The calibration of the laboratory standard was carried out by IAEA international standards (NZ1 and NZ2) and recommended comparative materials (NBS122 and NBS127).

Samples are measured at Finnigan MAT 250.

Precipitation water

The precipitation is characterised by results of a 10 year (1988 - 1997) monitoring of $\delta^{18}\text{O}$ of the mean cumulative month precipitation at 8 stations (Fig. 1) of the national net of regional stations (Kantor et al. 1989, Michalko et al. 1993, Michalko 1998). The station Chopok belongs to EMEP and GAW/BAPMoN/WMO net; stations Liesek, Stará Lesná and Starina are members of EMEP (MŽP SR & SHMÚ, 1995). A ten year (1988 - 1997) monitoring of the cumulated mean precipitation at 8 stations show that the mean values of $\delta^{18}\text{O}$ (Tab. 1) ranges from -8,70 ‰ (Bratislava Koliba) to -10,44 ‰ (Chopok) and from -6,47 ‰ (July) to -12,73 ‰ (February). The altitudinal effect is minor. More important differences are seen between winter and summer precipitation and these differences greater at stations of lower altitude. At the highest station (Chopok station at 2008 m) these differences are not so important,

probably due to lower temperature differences. The mean $\delta^{18}\text{O}$ is represented by the value $-9,60\text{‰}$. Results are averaged as arithmetic means and they are presented at table 1 and figure 1.

The sulphur isotope composition in precipitation is characterised by the $\delta^{34}\text{S}$ of the snowmelt from 18 localities thorough Slovakia taken in march 1996 (Malík et al. 1997, IAEA 8673/RB project). The $\delta^{34}\text{S}$ values in snowmelt for the complete depth profiles are from $-2,9\text{‰}$ to $+6,7\text{‰}$ with average value of $+4,8\text{‰}$. The dissolved sulphates concentrations are $1,15\text{ mg l}^{-1}$ - $13,50\text{ mg l}^{-1}$, with

an average value of $5,03\text{ mg l}^{-1}$, which is in good agreement with a 15-year monitoring of snowmelt for chemical composition in Slovakia (Gazda & Lopašovský, 1983, Vrana et al. 1989). Two samples ($\delta^{34}\text{S} = -2,9\text{‰}$ Košice and $+2,9\text{‰}$ Ružomberok) are apparently influenced by local industry (Košice iron metallurgy and Ružomberok cellulose processing). The $\delta^{34}\text{S}$ of the rest of samples is uniform in a very narrow range ($+4,0\text{‰}$ - $+6,7\text{‰}$). The seaspray component (PSS) was estimated following Wadleigh et al. (1994) to be $0,93\text{‰}$ - $8,68\text{‰}$, with one exception (Malík et al. 1997).



Figure 1 Monitored stations with their mean $\delta^{18}\text{O}$ [‰] values of precipitation

Table 1 Mean $\delta^{18}\text{O}$ [‰] values of precipitation at 8 stations

Station	Altitude [m.a.s.l.]	Date	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	mean
Bratislava	286	1988 - 1997	-12,03	-11,13	-9,52	-8,68	-5,59	-6,81	-4,64	-8,36	-7,52	-7,76	-10,39	-11,86	-8,70
Chopok	2008	1988 - 1997	-11,57	-11,46	-10,36	-11,12	-8,85	-9,28	-8,76	-9,23	-10,74	-10,69	-11,49	-11,69	-10,44
Liesek	692	1988 - 1997	-12,59	-13,87	-10,90	-10,60	-8,37	-7,61	-7,19	-8,63	-9,86	-9,90	-12,93	-12,68	-10,41
Milhostov	104	1988 - 1997	-13,23	-14,11	-10,42	-8,95	-6,75	-7,28	-5,70	-7,18	-8,04	-8,36	-10,55	-11,60	-9,33
Mochovce	260	1988 - 1997	-11,40	-12,27	-9,24	-9,97	-6,88	-6,47	-5,61	-7,51	-7,82	-8,98	-10,54	-12,36	-9,09
Stará Lesná	808	1988 - 1997	-13,57	-14,11	-10,80	-10,43	-7,57	-6,63	-6,75	-7,70	-9,41	-9,59	-11,76	-13,19	-10,10
Starina	345	1994 - 1997	-12,36	-11,98	-9,56	-9,70	-7,44	-7,00	-7,06	-7,75	-9,30	-8,39	-11,48	-12,76	-9,45
Topolníky	113	1988 - 1997	-11,59	-12,87	-10,16	-9,42	-7,26	-6,34	-6,09	-7,66	-6,94	-8,02	-11,07	-12,06	-9,19
mean			-12,29	-12,73	-10,12	-9,86	-7,34	-7,18	-6,47	-8,00	-8,70	-8,96	-11,28	-12,27	-9,60

Surface waters

Rivers

Based on long term monitoring (from 1982 at least one time monthly), the Danube (at Bratislava) and Morava (at Devínska Nova Ves) Rivers show different characteristics due to the different conditions (climatic, orographic, etc.) in their recharge areas (Fig. 2). The $\delta^{18}\text{O}$ for the Morava River is from -8‰ to -11‰ with lighter water from the snowmelt present in early spring and heavier water of the rain origin, especially in autumn. The

Danube River typically has a higher content of the light oxygen isotope, $\delta^{18}\text{O}$ (usually from $-10,5\text{‰}$, rarely -10‰ , to -13‰) with a typical short duration presence of the very light water in spring - summer due run off from the Alps. In this way the Danube water isotope composition and its behaviour is different from these of local rivers and precipitation. The results are in good agreement with the data - presented by Rank et al. (1991).

The Morava River water influence is detectable on the left bank of the Danube down to Bratislava (Fig. 2) some 8 km from their junction.

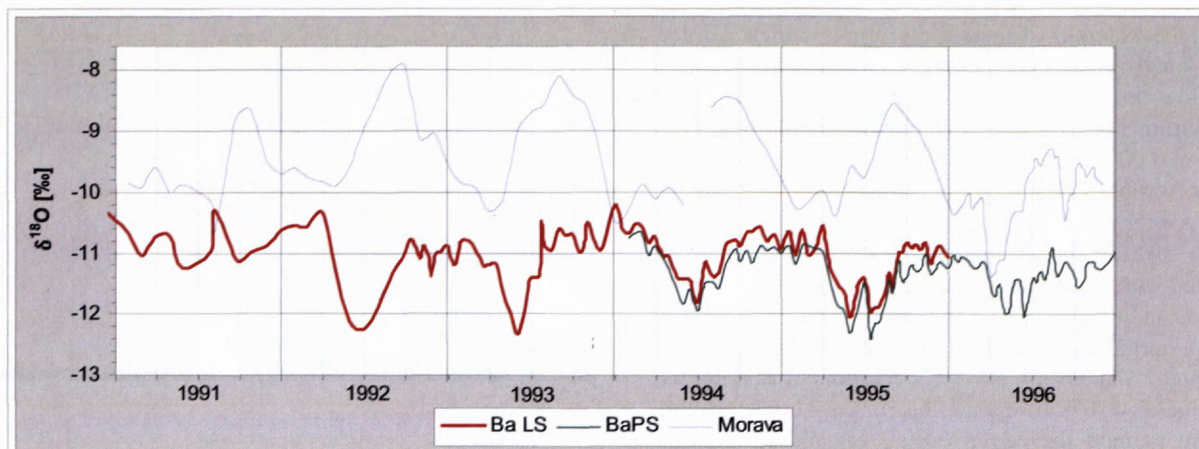


Figure 2 The $\delta^{18}\text{O}$ of Danube and Morava Rivers

BaLS = Bratislava left bank, BaPS = Bratislava right bank, Morava = Morava in Devínska Nová Ves

Lakes

Data on the oxygen, hydrogen and sulphate sulphur stable isotopes from the lakes of the Vysoké Tatry Mts. acquired in the framework of the International Atomic Energy Agency 8675/RB project „Stable isotopes in lakes of High Tatra Mts., Western Carpathians, Slovakia“ represent the first set of this kind information for Slovakia (Michalko et al. 1997). Moreover a complete set of the chemical composition of waters was determined and compared to earlier results, and thereby the contemporary state of acidification was evaluated. Values of the studied chemical compounds correspond to their source - initial precipitation waters and bedrock character, with an influence of biochemical processes. Acidification is due to inactive geological background (granites), high contribution of SO_x and NO_x from atmospheric deposition and low buffering ability of soil. The 1996ies level of acidification of lakes is lower than that of the 1980ies; and it may approach the level before acidification.

Water samples from the Furkotská dolina valley water system (Vyšné Wahlenbergovo pleso lake, Nižné Wahlenbergovo pleso lake, Vyšné Furkotské pleso lake and stream connecting lakes) follow the MWL with natural trend of increasing content of heavy isotopes with lowering altitude. In depth profiles of individual lakes the isotope composition does not change - due to natural conditions during sampling campaigns (spring and fall homothermy?). The water of the Štrbské pleso lake is enriched in heavy isotopes; all samples fit an evaporation line. This could be explained by longer residence time of water or by recharging of water from last phases of snowmelt. The sulphate sulphur isotope ratios from individual lakes are the same and they are identical with those of the snow packs.

Groundwater

Hydrogen and oxygen isotopes

Generally the H and O isotope composition of groundwater in natural circumstances in Slovakia depends mainly on δD and $\delta^{18}\text{O}$ of the precipitation directly or indirectly

through the surface waters (rivers, streams etc.). Groundwaters are cold, so the influence of the rock environment on isotope composition of oxygen is usually negligible.

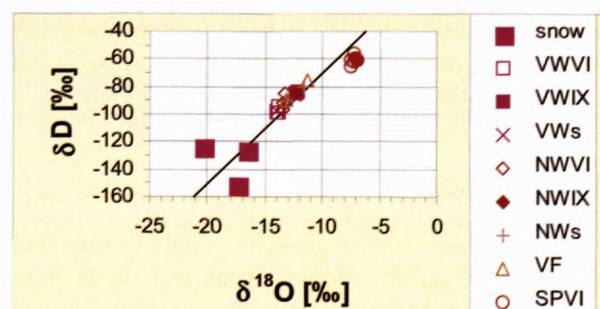


Fig. 3 Hydrogen and oxygen isotopes in snowpack and lakes in High Tatra Mts.

Vyšné Wahlenbergovo pleso - VW, Nižné Wahlenbergovo pleso - NW, stream between VW and NW - VWs, stream under NW - NWs, Vyšné Furkotské pleso - VF, Štrbské pleso - SP, indexes VI - June and IX - September 1996

The groundwater recharge could serve groundwater from Danube river (the right bank down the Bratislava and left bank in the Žitný ostrov area) serve as examples of this problem. The groundwater may be divided into few groups (Ďurkovičová et al. 1993) based on the influence of Danube water and local meteoric waters as end members. In the Kalinkovo area seasonal variations of $\delta^{18}\text{O}$ of Danube water were used to evaluate bank infiltration. Rodák et al. (1995) shows that significant fluctuations of the $\delta^{18}\text{O}$ could be measured in the groundwater within 4 - 6 km of the Danube. Over longer distance the annual fluctuation disappears due to hydrodynamic dispersion. It is not possible to identify the moving front in the aquifer from $\delta^{18}\text{O}$ data alone for more than 2 - 3 years.

A change of $\delta^{18}\text{O}$ as large as 0,1 ‰ with 100 m of mean altitude of recharge area was estimated from 2 years monitoring of 30 karstic springs in Veľká Fatra Mts. (Malík et al. 1993, Mansell 1994, Mansell et al 1995).

The oxygen and hydrogen compositions of Slovak mineral and thermal waters is shown in Fig. 4. The ma-

jority of the waters is of meteoric origin and their oxygen shift is small (generally not larger than 1,5 ‰), mainly due to low temperature. Some of the waters were infiltrated during times of different climatic conditions (^{14}C ages from 6.000 to 28.000 years, Franko et al. 1995) and the light isotopes of hydrogen and oxygen are more abundant.

Most of the saline waters in Western Carpathians is associated with basin areas (Vienna basin, Central depression of Danube basin, Eastern Slovakian Lowland, etc.), or with external flysch and intermontane basins. Anomalous high contents of Na - Cl component are known from mineral waters of crystalline rocks. The saline waters were mainly discovered during oil and geothermal resources prospecting; in natural springs they are scarce. Some of these waters are probably fossil sea waters. These are not plotted in figure 4 due to a lack of δD data. In some tectonic units of the external Carpathian flysch waters are present with a special isotopic composition ($\delta\text{D} \sim 25$ ‰, $\delta^{18}\text{O} \sim +6$ ‰) and their derivatives, due to mixing with local meteoric waters, either recent or older (Corteci & Dowgiallo 1975, Kolodij & Kojnov 1984). These waters are considered to be metamorphic in origin (Lesniak & Dowgiallo 1986, Zuber & Grabczak 1987, Michalko et al. 1991, Pacindová et al. 1997).

Sulphur isotopes

The isotopic composition of the sulphur compound of the groundwater depends mainly on that of the aquifer rock. Sulphur could also be derived from secondary processes; for example, as due to bacterial activity or water mixing. The most important sources of sulphur in Western Carpathians are the sediments of Permian, Triassic (Werfenian and Keuper) and Tertiary ages, ore deposits, or disseminated sulphides of different origin present in the rock. Other sources of sulphur are manmade products such as fertilizers, industrial products, waste, etc.

In some thermal and mineral waters with H_2S primary conditions reconstruction revealed that the sulphur originates from local aquifer rocks (Šmejkal et al. 1971, 1981, Michalko et al. 1994).

The example of the mixing of waters with sulphur of different origin was studied during research of karst - fissure springs of Triassic carbonates rocks of the Krížna and Choč nappes in the Veľká Fatra Mts. (Michalko et al. 1993, Malík et al. 1993). The main sources of sulphur in the area studied are Werfenian ($\delta^{34}\text{S} \sim 25$ ‰) and Keuper ($\delta^{34}\text{S} \sim 16$ ‰) evaporites. These values were found for evaporites from drillholes in the studied area (Michalko et al. 1991, Vrana et al. 1990). They are consistent with world scale (Claypool et al. 1980, Nielsen 1979, Pearson et al. 1991). A third possible source of sulphur in the area is from sediments of Permian age ($\delta^{34}\text{S} \sim 5 - 9$ ‰). The isotope composition of springs with a very low sulphate content (about 20 mg l^{-1}) typically has a $\delta^{34}\text{S}$ value about 5 ‰. In the aquifer rocks of these springs sulphur is not present. These values are very similar to $\delta^{34}\text{S}$ values found for winter precipitation (Malík et al. 1997). A three

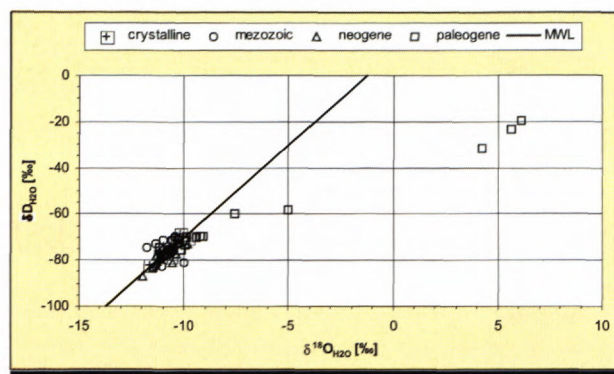


Figure 4 The δD a $\delta^{18}\text{O}$ of mineral and geothermal waters of Slovakia

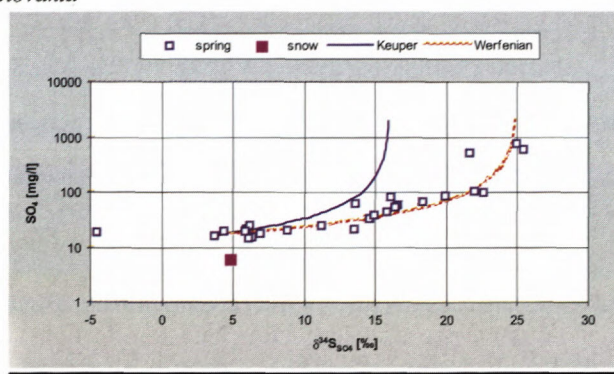


Fig. 5 Mixing sulphur of different origin in Veľká Fatra Mts. springs

snow = „mean snow“ Michalko et al 1997, Keuper, Werfenian = mixing lines of „background“ sulphur ($\delta^{34}\text{S} = 3,7$ ‰, $\text{SO}_4^{2-} = 16,2 \text{ mg l}^{-1}$ data of Salatin IV spring, Malík et al 1993) with hypothetical Keuper ($\delta^{34}\text{S} = 16$ ‰, $\text{SO}_4^{2-} = 2000 \text{ mg l}^{-1}$) and Werfenian ($\delta^{34}\text{S} = 25$ ‰, $\text{SO}_4^{2-} = 2000 \text{ mg l}^{-1}$) endmembers.

component mixing model (Mansell 1994, Mansell et al. 1995) is shown in figure 5; the mean values of „snow“ is plotted as well. The isotope composition of most of investigated springs was formed by the mixing of sulphur from Werfenian shales rich in sulphur and from „background“ sulphur characteristics for aquifers with a low content of sulphur. Only several springs are influenced by Upper Triassic Keuperian sulphur. The involvement of sulphur from Permian sediments is practically excluded due to low concentration of the sulphur component in springs. The source of sulphur in springs with low content of SO_4 and with a negative $\delta^{34}\text{S}$ is unambiguous - possible sources are sulphides or sulphur of organic or manmade origin.

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