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**ISOTOPIC COMPOSITION OF GROUND WATER IN THE SW PART OF  
THE UPPER SILESIA COAL BASIN WITHIN TERRITORIES OF POLAND AND  
CZECH REPUBLIC**

IZOTOPOVÉ SLOŽENÍ PODZEMNÍCH VOD V JIHOZÁPADNÍ ČÁSTI HORNOSLEZSKÉ  
UHELNÉ PÁNVE NA ÚZEMÍ POLSKA A ČESKÉ REPUBLIKY

**Abstract**

Interpretation of the origin of groundwater, sampled and analysed in 2002-2003, in the SW part of the USCB – at the borderland of Poland and Czech Republic, has been performed being based on chemical and isotopic analyses. Mine water from Carboniferous aquifers (Poland) was identified as belonging to the following genetic types: the oldest type of Permian hot climate, paleoinfiltrated Tertiary water types of pre-Badenian and post-Badenian age, and Quaternary water types. Several mixed types of the above-mentioned ones were also ascertained. Recent natural (or technological) waters mix together with waters of the deeper parts of the rock massif. Miocene water from the Czech part of the USCB may be derived from Miocene seawater mixed with water types of another origin. Cumulative mine water from the Ostrava and the Petřvald parts of USCB basin (troughs) are formed by water from the coarse clastic Lower Badenian aquifer (“detrit”) mixed with recent infiltration.

**Abstrakt**

Interpretace původu podzemních vod z jihovýchodní části hornoslezské uhelné pánve v příhraničních oblastech Polska a České republiky byla provedena na základě chemických a izotopových analýz vod, vzorkovaných a analyzovaných v letech 2002-2003. Důlní vody z karbonských zvodní (Polsko) přísluší k následujícím genetickým typům: nejstarší vody horkého klimatu, paleoinfiltrované terciární vody pre- a postbadenského stáří a vody kvartéru. Byly zjištěny i některé směsné vody těchto typů. V hlubinných dolech se nachází směs recentních přírodních (nebo technologických) vod s podzemními vodami terciéru nebo karbonu. Miocénní vody z české části hornoslezské pánve pochází z mořských vod, někdy smíšených s vodami jiného původu. Vody v zatopené ostravské a petřvaldské dílčí pánvi jsou směsnými vodami vod hrubozrnných klastik spodního bádenu („detrit“) a infiltrovaných vod recentních.

**Key words:** groundwater, stable isotopes, mining drainage, the Upper Silesian Coal Basin.

**Introduction**

Over 200 years of mining activity in the SW part of the Upper Silesian Coal Basin (USCB), enabled local hydraulic contacts between main aquifers in this region: Quaternary sandy aquifers, groundwater horizons of Lower Badenian and Carboniferous aquifers. On the other hand, this part of the USCB is an area where valuable balneological waters occur. Mining drainage, reaching the depth of 1200m, caused partial depletion of the groundwater resources, and in consequence led to changes of their chemical composition. Groundwater types

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of the examined area might be often considered as mixtures of waters from different aquifers, sometimes with some participation of technological fluids. Interpretation of the origin of brines occurring in the USCB, based on chemical and isotopic analyses, was the subject of numerous published works, eg.: Buzek, Michaliček (1996), Różański (1985), Różkowski, Przewłocki (1974), Różkowski (1999), Zuber, Grabczak (1985), Pluta, Zuber (1995), Pluta (2003). This paper presents results of our original study on isotopic composition of groundwater, sampled and analysed in 2002-2003, in the SW part of the USCB – at the borderland of Poland and Czech Republic.

## Sampling and analyses

The sampling covered groundwater from inflows into mine workings, from underground boreholes and from balneological water intakes; the localities of interest are shown in Fig 1 and Fig 2. Examination of physico-chemical parameters was performed by means of in situ techniques, in compliance with obligatory procedures (Witczak, Adamczyk, 1995). Chemical analyses were carried out, using standard methods, by the Laboratory of the Institute of Water and Wastewater Engineering of Silesian University of Technology in Gliwice. Isotopic composition of water was analyzed by the Laboratory of Faculty of Physics and Nuclear Techniques of the Academy of Mining and Metallurgy in Cracow. The results of spectrometric analyses (Finnigan Delta-S apparatus) are presented as compared with Standard of Mean Ocean Water (V-SMOW). Error of single analyze (including sample preparation) equals to  $\pm 0,1\%$  and  $\pm 1\%$  in case of delta  $^{18}\text{O}$  and delta  $^2\text{H}$  respectively.

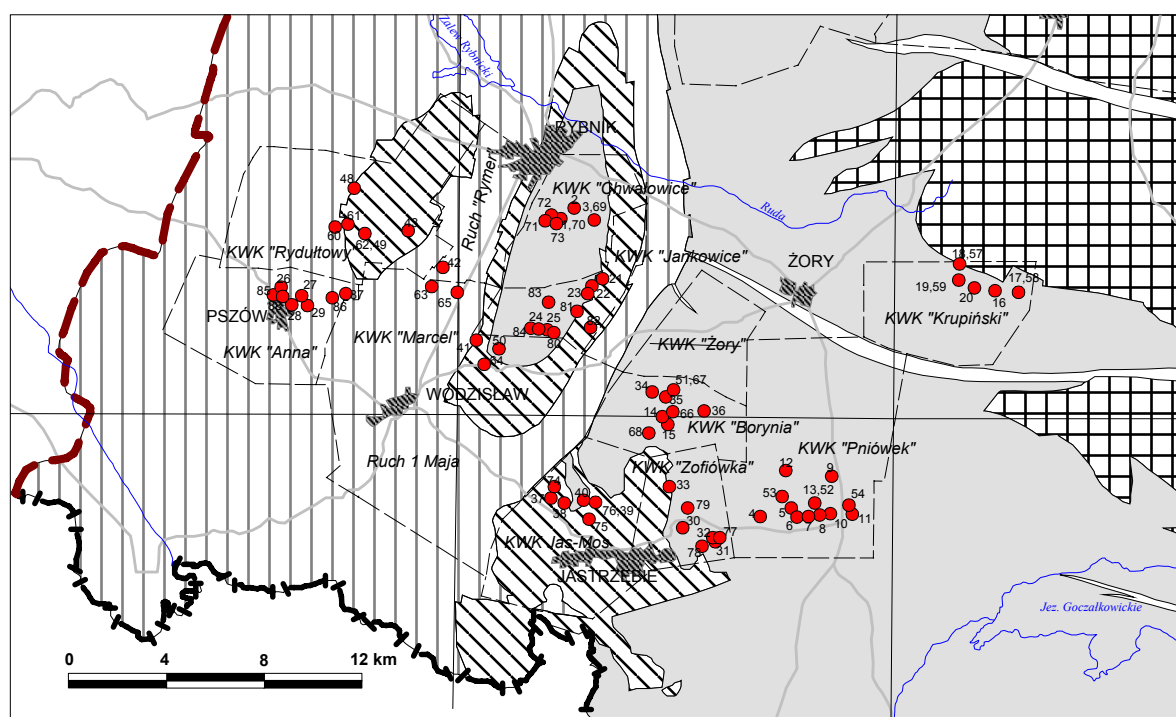


Fig. 1. Sampling in the Polish part of the USCB:  
 1 – Cracow Sandstone Series; 2 – Mudstone Series; 3 – Upper Silesian Sandstone Series; 4 – Paralic Series.  
 Sample numbers as follows in the text.

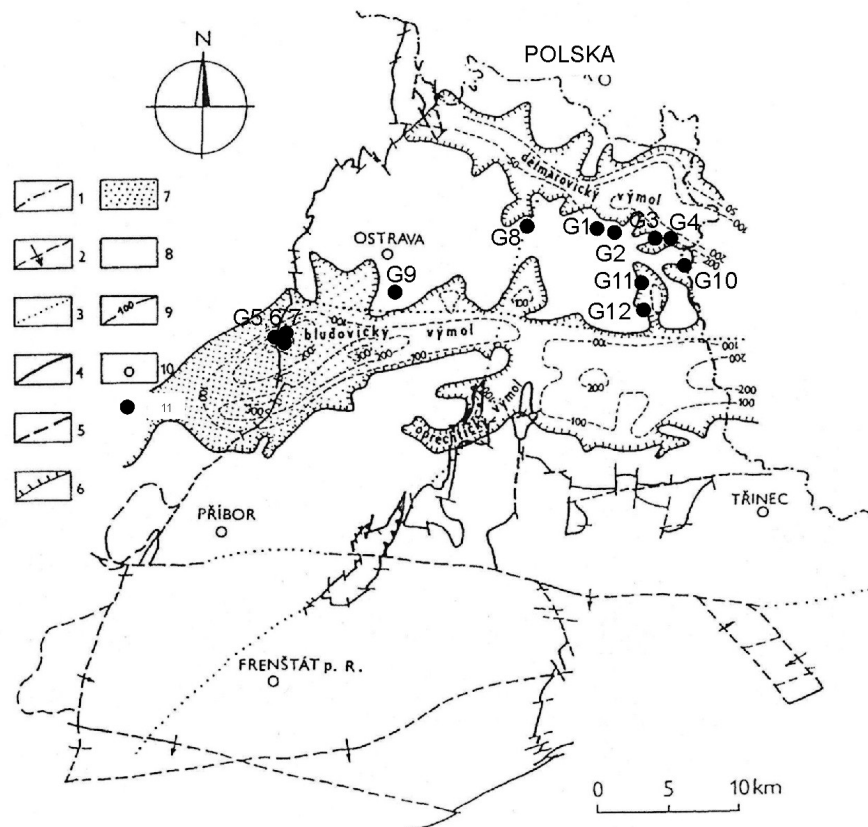


Fig. 2. Sampling in the Czech part of the USCIB.

Explanations: 1 – state border; 2 – main faults, 3 – prospective areas limits; 4 – The USCIB border; 5 – probable border of the USCIB; 6 – occurrence limits of Lower Badenian coarse clastic sediments; waters of the type: 7 -  $\text{HCO}_3\text{-Na}$ ; 8 -  $\text{Cl-Na}$ ; 9 – isolines of thickness of Lower Badenian coarse clastic sediments; 10 – cities; 11 – sampling points

## Interpretation

In order to describe the examined waters, we have adapted genetic classification, published by Pluta & Zuber (1995), distinguishing the following types: connate water of the Miocene sea formations (M), the oldest paleoinfiltration brines of a hot Permian climate (P), waters of Tertiary infiltration of the last hydrogeologic cycle – between the last transgression and the beginning of Quaternary (T), Quaternary infiltration (Q), brines of a pre-Badenian hot climate recharge:  $\text{SO}_4$ -rich (Us) and  $\text{SO}_4$ -free (U), and mixed waters: QP, QT, QU, PQ i PU. Interpretation of groundwater origin was performed also with exploitation of other published works that are listed in the introduction.

For interpretation of isotopic analyses, it appeared helpful to take into account also hydrochemical parameters and to divide analysed population into 4 groups, based on sulfates contents and values of Cl/Br ratio: group I -  $\text{SO}_4 > 600$  mg/l; group II -  $600 > \text{SO}_4 > 10$  mg/l and  $\text{Cl/Br} > 300$ ; group III -  $600 > \text{SO}_4 > 10$  mg/l and  $\text{Cl/Br} < 300$ ; group IV -  $\text{SO}_4 < 10$  mg/l. Graphs of analysed parameters relationships are presented in Figs 3 to 9 (Figs 5 to 8 depict the parameters relationships, analysis of which was performed in order to support the isotope data interpretation). Waters from the Tertiary formation of the Czech part of the USCIB were at first interpreted on the background of the Polish ones. Next their isotopic and hydrochemical parameters were analysed independently, assuming that they may represent separate hydrochemical environments.

### Groundwater of the group I - $\text{SO}_4^{2-} > 600$ mg/l

Concentrations of chlorides are well correlated to  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  values in waters of the Ist group. Points 27, 29, 61 and 86 are located on a straight line. They represent waters sampled at the depths of 800 and 1000 m (coal mines "Anna" and "Rydultowy"), featured by values:  $\text{rNa/Cl}$  0,74 - 1,38 and  $\text{Cl/Br}$  230 – 270. Taking into account their mineralization from 9,5 up to 46,1 g/l and iodine concentrations below 1,0 mg/l, they should be

classified into the mixed water types – QP. By this, the presence of the youngest infiltrative waters at great depths is reflected. This might be caused by admixtures of technological waters or by the role of mining activity in opening paths for shallow groundwaters migration. Linear arrangement of the mentioned points leads to an alternative hypothesis that one of the end members (apart from the P type) of such mixtures might be water of QT or QU type. This is supported by the higher concentrations of SO<sub>4</sub> in lighter (in sense of isotopic composition) and less mineralised samples.

Samples 1, 2 and 3, from the "Chwałowice" mine, have: δ<sup>18</sup>O and δ<sup>2</sup>H values about -5‰ and from -35 to -40‰ respectively, mineralisation 65 - 81 g/l, rNa/Cl 0,75 - 0,8, and Br/I 6 – 27. High values Cl/Br: from 390 to 780, indicate a certain role of evaporites leaching in forming of the groundwater, and allow to classify them into the PT type.

δ<sup>18</sup>O - δ<sup>2</sup>H relationship for SO<sub>4</sub>-rich samples: 48, 60 ("Rydułtowy"), 65 ("Marcel") and 85 ("Anna") suggest their mixed origin. Samples 65 and 85, both highly mineralized (100 and 120 g/l respectively), with similar sulfates concentration (3200 mg/l) and Cl/Br value - about 330, despite the change in isotopic composition, may be classified as the PQ type water types.

Sample 65 is represented at the δ<sup>18</sup>O - δ<sup>2</sup>H diagram, rather below the zone of the oldest paleoinfiltration (P), while the sample 85 (from the Chrobry shaft – the "Anna" mine) is shifted towards lighter isotopic composition. Presence of Quaternary waters in the sample 65 suggests disturbance of impermeable cover of Carboniferous formation within the "Marcel" mining area, or impurities of technological waters in this sample.

Samples 48 and 60 were classified into the QP type. However, the sample 48 has a lighter isotopic composition, lower mineralization and lower SO<sub>4</sub> contents. Cl/Br and Br/I values are equal to 330 and 11 (sample 48), and 300 and 68 (sample 60), indicating a possible admixture of Tertiary infiltration (T) in sample 48.

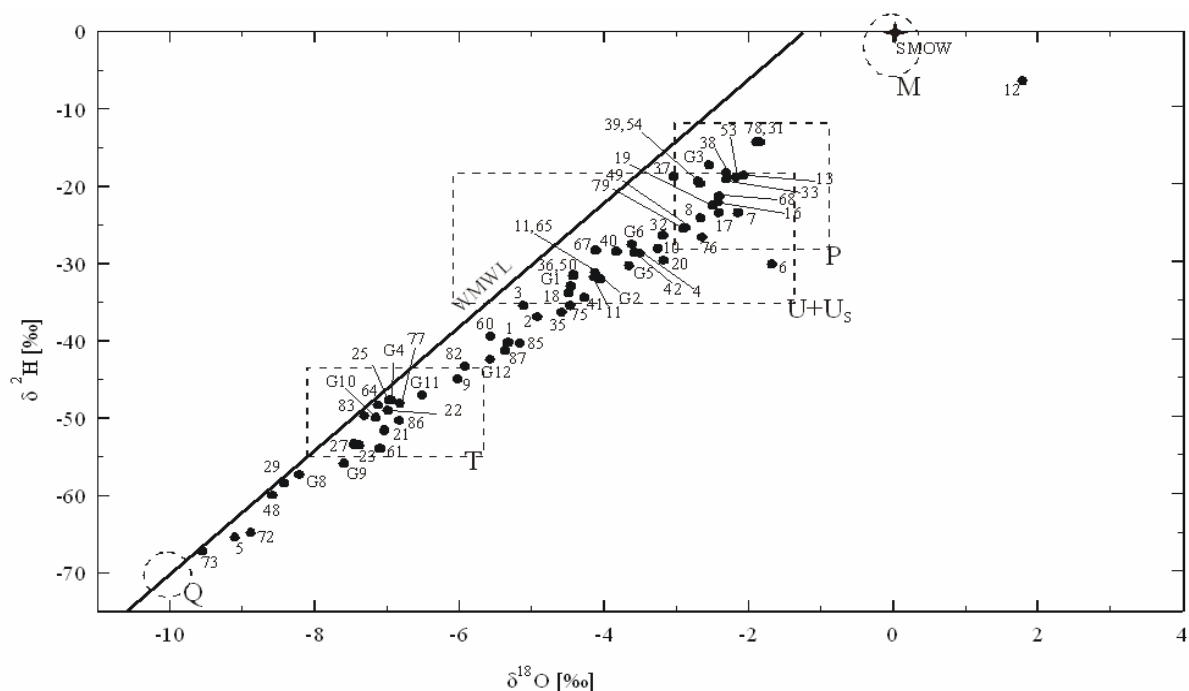


Fig. 3. δ<sup>18</sup>O - δ<sup>2</sup>H relationship

Explanations: SMOW – Ocean water standard; WMWL – meteoric line; M - connate water of the Miocene sea formations, P - the oldest paleoinfiltration brines of a hot Permian climate, T - waters of Tertiary infiltration of the last hydrogeologic cycle – between the last transgression and the beginning of Quaternary, Q - Quaternary infiltration, U+U<sub>s</sub> - brines of a pre-Badenian hot climate recharge. Ranges of δ<sup>18</sup>O and δ<sup>2</sup>H values for respective water types after Pluta & Zuber (1995).

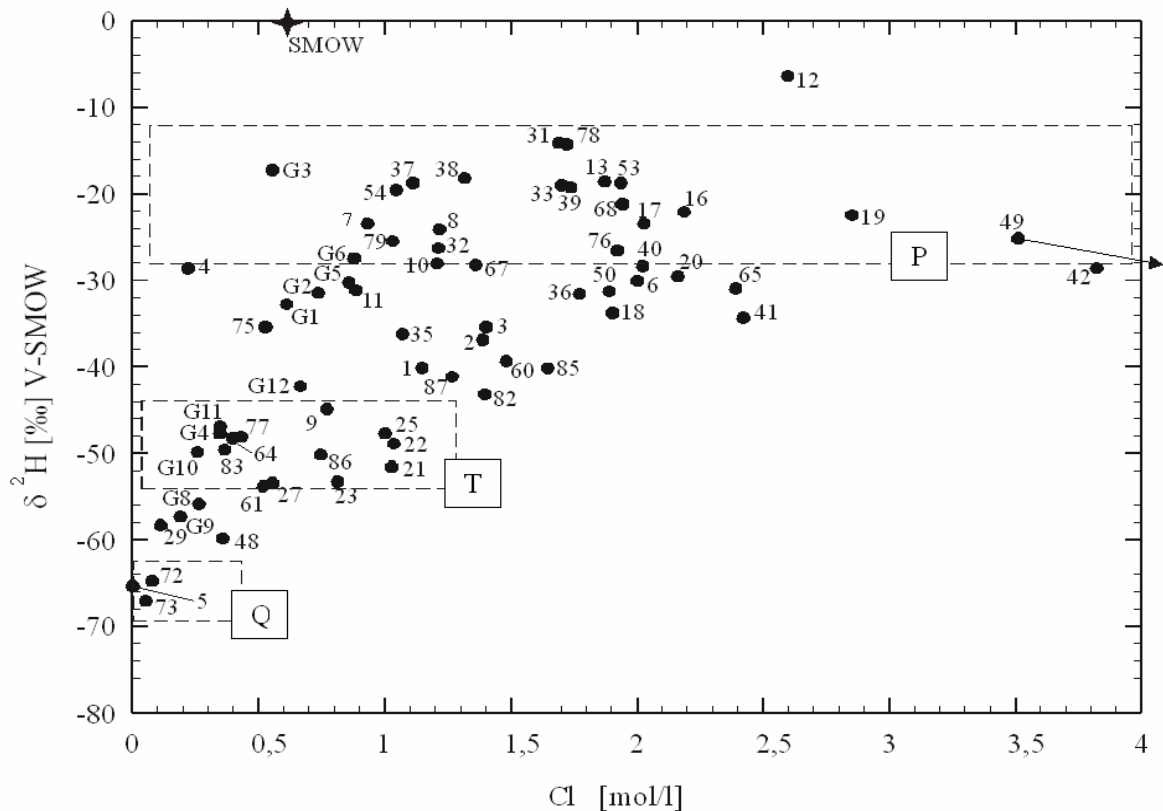


Fig. 4.  $\delta^2H$  – Cl relationship in the whole population of analysed waters  
 Explanations: SMOW – Ocean water standard; P - the oldest paleoinfiltration brines of a hot Permian climate, T - waters of Tertiary infiltration of the last hydrogeologic cycle – between the last transgression and the beginning of Quaternary, Q - Quaternary infiltration. Ranges of Cl and  $\delta^2H$  values for respective water types after Pluta & Zuber (1995) – slightly modified.

#### Groundwater of the group II - $600 > SO_4^{2-} > 10$ mg/l and $Cl/Br > 300$

The following samples were classified into the group II: 72, 73 ("Chwałowice"); 18, 20 ("Krupiński") and 21, 22, 82, 83 ("Jankowice"). Samples 72 and 73 (QT type) were taken from shafts at the depth of about 50 m. By their parameters and situation on the  $\delta^{18}O$  -  $\delta^2H$  diagram (shift from the present infiltration water towards the heavier ones) their genesis connected with mixing between the Q and the T types of water is indicated. An alternative explanation of their origin is also possible: the sample no 72 represents probably evaporated recent water mixed with a small amounts of higher mineralized water of unknown origin. Isotopic composition of the sample no 73 approaches most closely the one of Holocene water in the examined area.

In case of 20 and 82 samples, low  $SO_4$  concentrations and values of  $Cl/Br \sim 330$ ,  $Br/I \sim 45$  (higher than typical for waters of the U type), allow to classify such water to the mixed type – PQ.

By isotopic composition and value of  $Cl/Br \sim 580$  of the sample no 83, it is indicated that it belongs to the T type. This sample however has too low mineral content and a low  $SO_4^{2-}$  content, and therefore it was classified as a mixed type - QT with some admixture of the P type water.

High mineralization (110 g/l) of the sample no 18, absence of  $SO_4$ , low value of  $Br/I \sim 6$ , and  $Cl/Br \sim 480$  - indicative for possibility of evaporites leaching, it is possible to interpret this water as being connected with pre-Badenian recharge – of the U type.

Mineralization of about 59 g/l, absence of  $SO_4$ , relatively high values of  $Cl/Br$  (about 440) and  $Br/I \sim 21$  allow to classify samples 21 and 22 to the mixed types – P+U. Slight shift towards the lighter isotopic composition might be attributed to an admixture of recent water (Q).

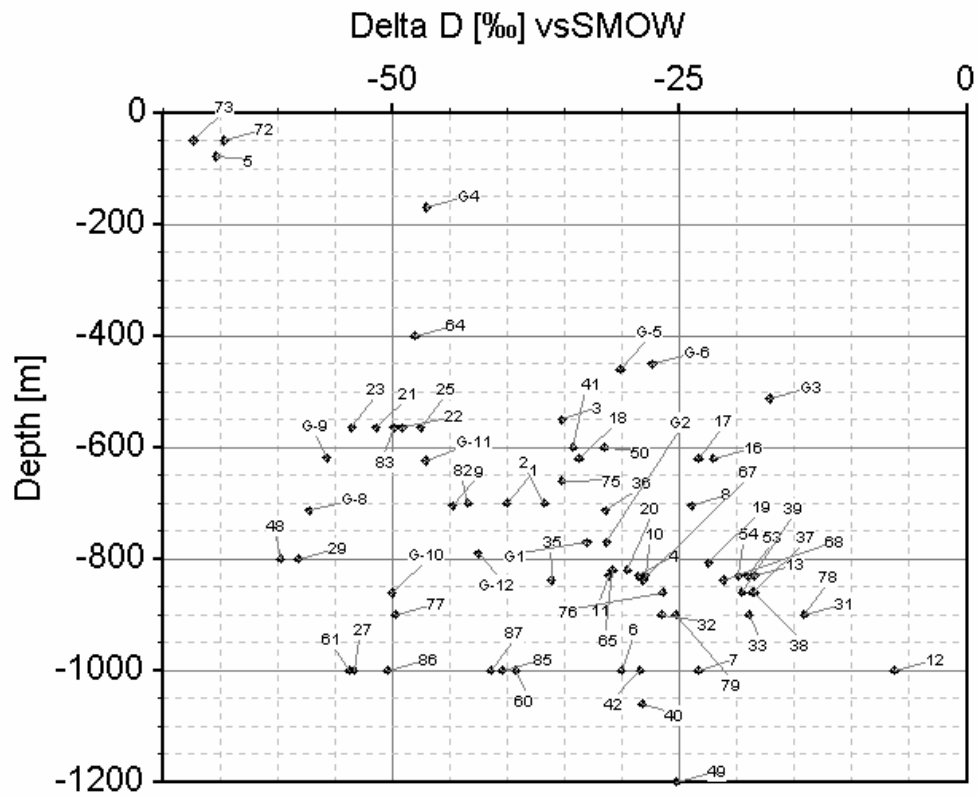


Fig. 5. Relationships between  $\delta^2H$  (Delta D) and the depth at which waters occur

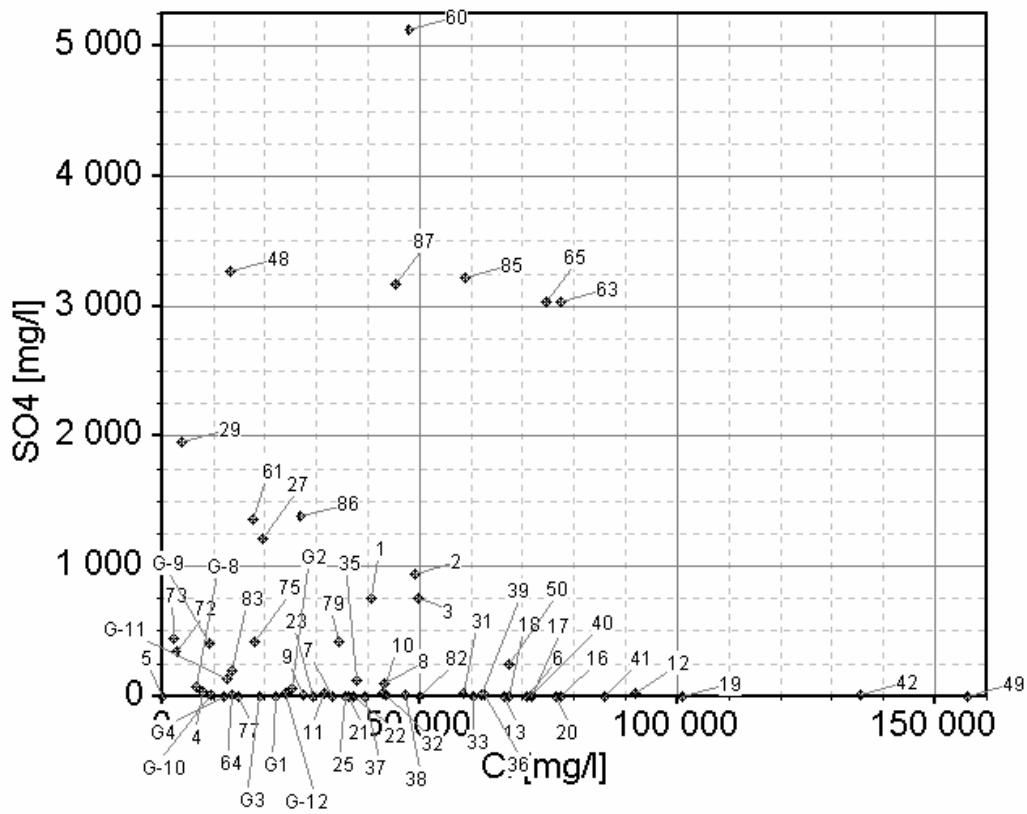


Fig. 6.  $SO_4^{2-}$  - Cl relationship in the whole population of analysed waters

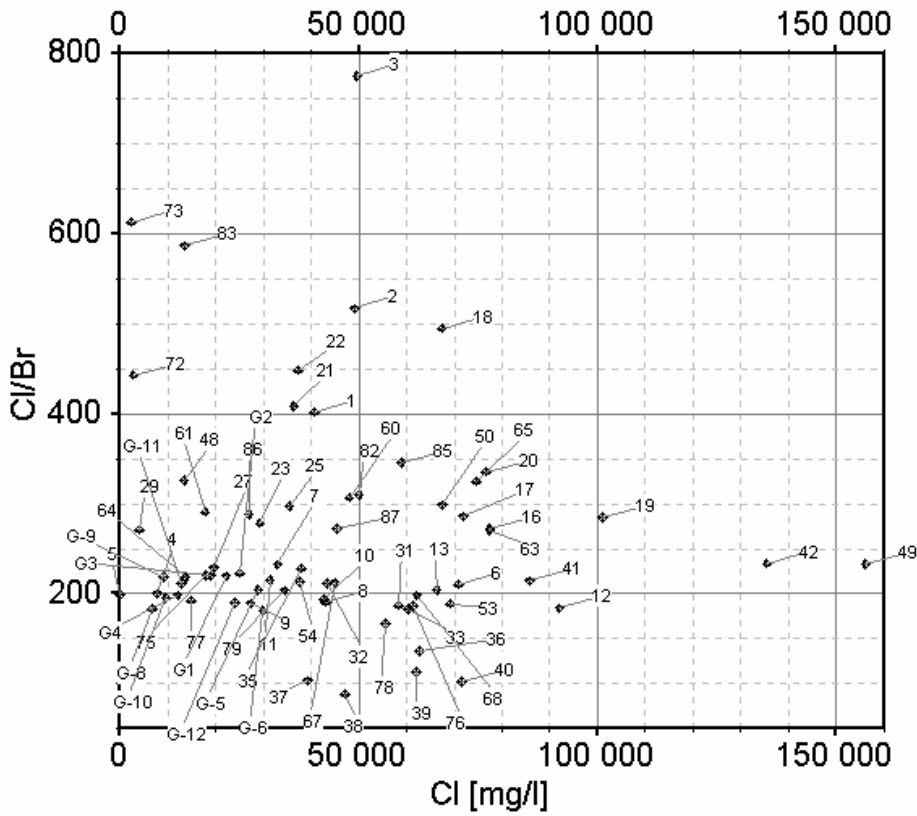


Fig. 7. Cl/Br – Cl relationship in the whole population of analysed waters

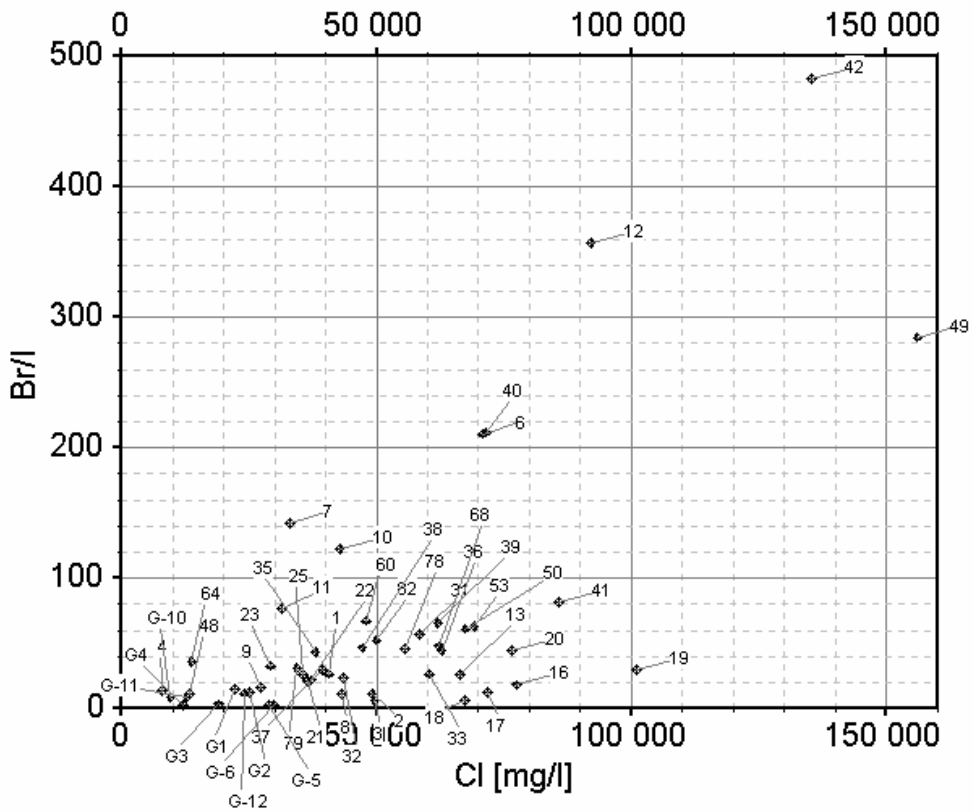


Fig. 8. Br/I – Cl relationship in the whole population of analysed waters

### **Groundwater of the group III - $600 > \text{SO}_4 > 10 \text{ mg/l}$ and $\text{Cl/Br} < 300$**

Water types of the group III were sampled within the depth interval between 400 to 1060 m. Their isotopic composition indicates the P type (the oldest paleoinfiltration brines of a hot climate) or mixed types (containing the P and the Q end members).

The following samples were classified as being of the P type: 4, 7, 8, 10, 13 ("Pniówek"); 16, 17, 19 ("Krupiński"); 31, 32, 79 ("Zofiówka"); 38, 40 ("Jas-Mos"), and 42 ("Marcel"). High Ba concentrations were recognized in samples of 40 and 42 – about 1500 mg/l.

Water types derived from mixing of P and Q end components were represented by samples: 9, 11 ("Pniówek"); 23, 25 ("Jankowice"); 35 ("Borynia"); 75 ("Jas-Mos"), and 50, 64 ("Marcel").

Samples 6 and 12 ("Pniówek") were taken from the depths of 1000 and 1100 m respectively. They are shifted towards positive values of  $\delta^{18}\text{O}$  and they belong also to the group III ( $600 > \text{SO}_4 > 10 \text{ mg/l}$  and  $\text{Cl/Br} < 300$ ). They were formed due to effect of evaporation of the P type, under conditions of low humidity and intense air flowing (water sampled from inclined drift airway and from a pool in a drift). Sample no 5 ("Pniówek" – leakage from behind the Shaft II walling at the depth of 78 m) represents recent water (Q), evaporated at humid conditions.

Typical paleoinfiltration brines of a hot climate (P) of isotope values:  $\delta^{18}\text{O}$  ranging between 3,6‰ to -1,0‰, and  $\delta^2\text{H}$  between -28,0‰ to -12,0‰, are featured by strong differentiation of Cl contents, low variability of  $\delta^2\text{H}$ , and decrease of iodides with rising chlorides concentrations.  $\text{SO}_4$  concentrations in water of this type do not exceed some dozens of mg/l, except for the sample from abandoned workings of the "Zofiówka" mine – no 79 (421 mg  $\text{SO}_4/\text{l}$ ).

### **Groundwater of the group IV - $\text{SO}_4 < 10 \text{ mg/l}$**

Waters of the group IV, sampled at the depths from 600 to 1200 m, have isotopic composition specific for paleoinfiltration brines of a hot climate (P). They were represented by the following samples: 33, 78 ("Zofiówka"); 36 (inflow from the "Żory" liquidated mine to the "Borynia" mine); 67, 68 ("Borynia"); 37, 39, 76 ("Jas-Mos"); 49 ("Rydułtowy"); 41 ("Marcel") and 53, (KWK "Pniówek").

Samples 77 ("Zofiówka") and 87 ("Anna") should be classified into the PQ type, with little contribution of Quaternary water, which at the deeper working floors, might be connected with the technological water.

By the barium concentration level of 400mg/l in the sample 36 (inflow from the "Żory" liquidated mine) a termination or delay in barite precipitation process is indicated, which was reported for this locality by Pluta (2000).

### **Water from the Czech part of the USCB**

All of the samples were taken either from Badenian aquifers, that are present in the overburden of Carboniferous series, or contain substantial fraction of water of such an origin. The water is being exploited for balneological purposes, they are also influenced by mine drainage in underlying Carboniferous complex.

Samples G1 and G2 (the OKD, a.s. Důl ČSA, o.z. Karviná = "ČSA" mine) and G10, G11 and G12 (the ČMD, a.s. Důl ČSM, o.z. Doubrava = "ČSM" mine) were primarily identified as inflows from coarse clastic sediments on the base of lower Badenian (so called "detrit"). This must be stressed however, that the samples may contain some part of water of other origin.

The G3 and G4 were sampled from balneological water exploitation wells in the Darkov health resort. They represent waters of the upper sandy horizon of lower Badenian (situated above "detrit"). G5 and G6 obtained from the exploitation wells in the Klimkovice health resort, represent water of the lower sandy horizon (lower Badenian), which is present within the structure of the Polanka upon the Oder river.

G8 and G9 are samples of cumulative waters from the liquidated mining areas of the Ostrava Trough and the Petřvald Trough respectively. These waters are considered to contain components mainly of quaternary and waters of the lower Badenian basal clastics.



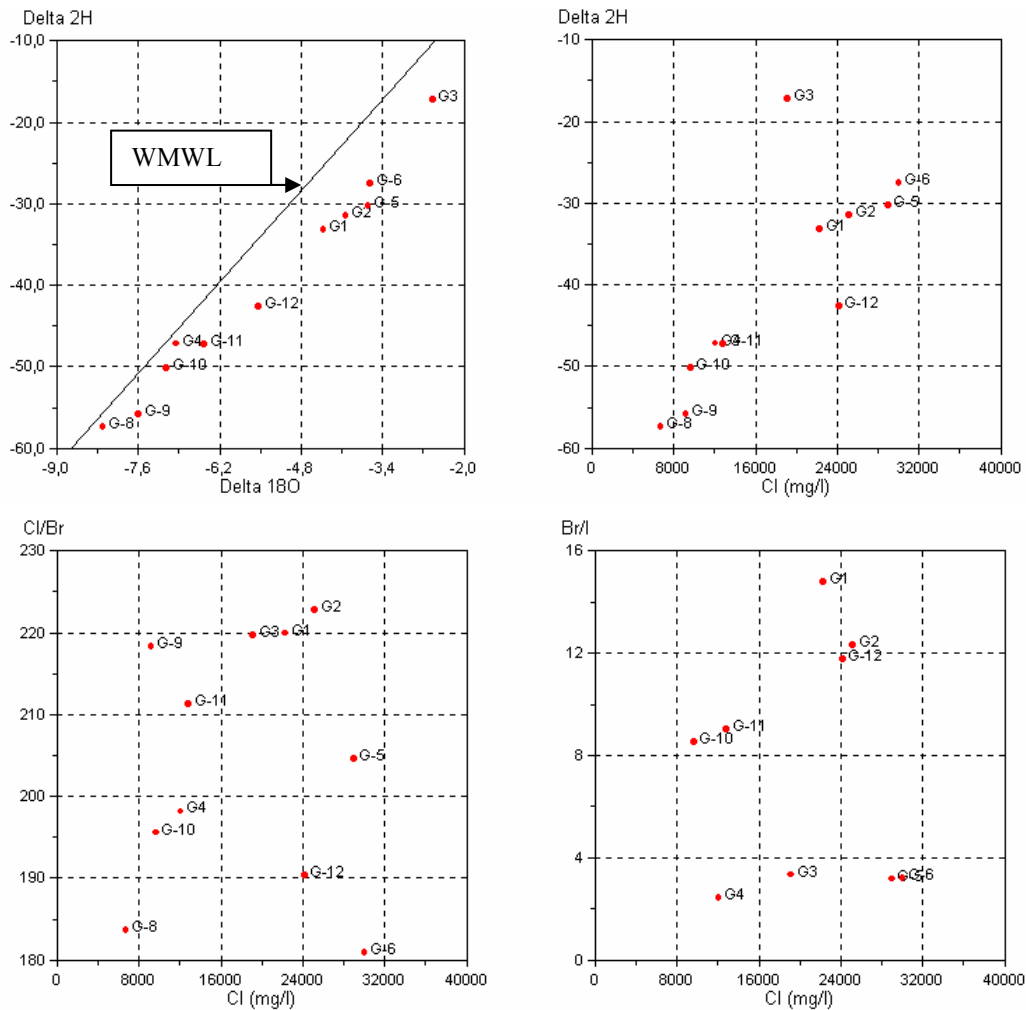


Fig. 9. Relationships of  $\delta^{18}O - \delta^2H$ ,  $\delta^2H - Cl$ ,  $Cl/Br - Cl$ , and  $Br/I - Cl$  in waters from the Czech part of the USCB

If waters of the Lower Badenian pelitic facies were of marine origin (Grmela, 1997; Hufova, 1971; Tylčer, 1977), the value of  $Cl/Br \sim 289$  ( $rBr/Cl = 1,54 \cdot 10^{-3}$ ) and isotopic composition approaching closely to the SMOW (Zuber, 1986) should be expected in case of our samples (with exception of G8 and G9). The analyzed water however, have isotopic compositions different from the one determined in fossil marine waters of Miocene, known from Dębowiec and Zabłocie, in the territory of Poland.

The samples G1 and G2 are very similar to each other, taking into account their isotopic composition, physico-chemical parameters, and also  $Cl/Br$  and  $Br/I$  values (Fig. 9.). By  $\delta^{18}O - \delta^2H$  relationship, the G1 and G2 samples are ranked apparently among the  $SO_4^{2-}$ -free brines of a pre-Badenian hot climate recharge – the U type. However, by low values of  $Cl/Br$  ratio, indicating rather a seawater evaporation, such a genesis is excluded. It is possible that such water types belong to a separate type and they were derived from evaporated seawater (M) mixed with other water of a lighter isotopic composition. As the  $Cl/Br$  value in the assumed mixed water is relatively high, chemical composition of the lighter waters might be formed due to evaporates leaching. Some participation of the P type in the mixed water should not be excluded; due to sampling conditions in the mine workings.

Location of samples G10 and G11 in  $\delta^{18}O - \delta^2H$  diagram is very similar – their points fall into the area of the T type waters. Such a situation is a little bit misleading, as the waters contain undoubtedly a fraction of waters from “detrit”, which should be isolated from infiltration in post-Badenian period. The G12 sample is shifted towards the waters of heavier isotopic composition. It should be pointed out here that higher mineralised waters have lower  $\delta^{18}O$  and  $\delta^2H$  values (this refers also to G1 and G2). Chloride-bromide ratio in case of all the three samples from the “ČSM” (G10-12) mine does not directly confirm the genesis attributed to evaporates leaching. The most straight interpretation connects their genesis with mixing phenomena, similarly as in the case of G1 and G2, but with a greater participation of the recent water, and water of the P type in sample G12.

Samples G3 and G4 (Darkov) are situated on  $\delta^{18}\text{O}$  -  $\delta^2\text{H}$  and Cl -  $\delta^2\text{H}$  diagrams on the mixing line of recent seawater and light (in sense of isotopes) infiltration water. Values of Cl/Br (about 200-220) and Na/Cl (about 0,8) are lower than in the seawater. Chemistry of the higher mineralized sample - G3, approximates SMOW more than G4 does. Sample G4 (the "Helena" well), as it from a smaller less depth, may contain some part of the recent water.

Physico-chemical parameters of G5 and G6 (samples from Klimkovice), and their locations in  $\delta^{18}\text{O}$  -  $\delta^2\text{H}$  and Cl -  $\delta^2\text{H}$  diagrams are very similar. Slight differences are observed in Cl/Br values - about 205 for sample G5, and for G6 - 181 mg/l approx. Considering that G3, G4, G5 and G6 are representing sandy aquifers of lower Badenian, any significant differences in isotopic composition of the waters should have not been expected. It appears however, that G5 and G6 are shifted towards the heavier water and vary rightwards from the meteoric line - WMWL on the  $\delta^{18}\text{O}$  -  $\delta^2\text{H}$  diagram. This suggest some fraction of evaporated seawater in their composition. Both G5 and G6 were taken in the Moravian Gate territory, where the water of "detrit" series contain elevated concentrations of geogenic  $\text{CO}_2$  (Grmela, 1997). Hence, if there were any hydraulic connections between sandy and "detrit" aquifers of the area, we should rather expect a shift of G5 and G6 towards left from the WMWL line. This origin shift - resulting from isotope exchange between juvenile  $\text{CO}_2$  and oxygen of water (described eg. in. Ciężkowski, 1990) - is absent in mentioned samples, what proves their isolation from the  $\text{CO}_2$ -reach waters of the "detrit".

Therefore, the absence of so called origin shift in samples G5 and G6 - origin shift resulting from isotope exchange between juvenile  $\text{CO}_2$  and oxygen of water (described eg. in. Ciężkowski, 1990) - proves a lack of connections of these waters with  $\text{CO}_2$ -reach waters of the "detrit". This phenomena could be connected with intense evaporation.

Parameters and position of samples G8 and G9 on  $\delta^{18}\text{O}$  -  $\delta^2\text{H}$  and Cl -  $\delta^2\text{H}$  diagrams are similar and participation of the most recent waters (Q) in their composition is evident. A significant fraction of cumulative water in this area derives also from the drainage of the "detrit" sediments of lower Badenian (Grmela, 2003). Interpreting chemical and isotopic composition of waters represented by samples G8 and G9, it should be stated then, that these waters are formed by recent infiltration water mixed with smaller quantities of water from the "detrit" aquifer.

## Conclusions

The interpretation of isotopic composition of examined water samples is based on genetic classifications, published by different authors; Pluta & Zuber (1995) among others. Additionally, considering the basic hydrochemical constituents of the water, we divided the analysed population into groups, based on sulfates contents and values of Cl/Br ratio. Then it was established that examined mine water from Carboniferous aquifers (Polish part of the SW fragment of the USCB) belong to the following genetic types: the oldest water of hot climate (P), paleoinfiltration Tertiary water of pre-Badenian (U) and post-Badenian (T) ages, and Quaternary water (Q). Several types derived from mixing of mentioned end-members were also ascertained.

Mining drainage impact is manifested by the vertical extent of the intensive infiltration zone to the observed depth of 800 m below the surface. However, the isotopic analyses indicate that recent natural water (or technological water) mixes together with water from deeper aquifers. Admixtures of water from Tertiary aquifers were ascertained in the mine water within depth range of 565 m to 800 m below the surface.

Isotopic composition of Lower Badenian waters from the Czech part of the USCB is different to the one determined in fossil marine waters of Miocene, known from the territory of Poland. Samples G1 and G2 (the OKD, a.s. Důl ČSA, o.z. Karviná mine) possibly belong to a separate type and they are derived from evaporated seawater (M), mixed with other water (formed due to evaporates leaching) of a lighter isotopic composition. They also contain some admixture of the P type water. Samples G10-12 (the ČMD, a.s. Důl ČSM, o.z. Doubrava mine) were probably formed in a similar mixing processes, but with a greater participation of the recent waters than in the case of G1 and G2.

Samples G3 and G4 (Darkov) are situated on the diagrams on the mixing line of recent seawater with light - Quaternary infiltration water. Sample G4 ("Helena" well) may contain some part of the recent waters. Samples G5 and G6 (Klimkovice), representing sandy aquifers of lower Badenian, are shifted towards the heavier waters and leftwards from the WMWL line on the  $\delta^{18}\text{O}$  -  $\delta^2\text{H}$  diagram. By this, some portion of evaporated seawater in their composition is indicated. G8 and G9 (cumulative water from the Ostrava and the Petřvald Troughs) were formed by mixing of water from the "detrit" aquifer with water of recent infiltration.

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## Resumé

V letech 2002-2003 bylo provedeno vzorkování přírodních zdrojů důlních vod v České a Polské části hornoslezské pánve, vzorkování fosilních mořských vod písčitéch poloh spodního bádenu, vod detritové zvodně a karbonských zvodní (Polsko). Lokality jsou zobrazeny na obr. 1 a 2. Vzorky z české části pánve jsou předznačeny písmenem G. Izotopové složení ( $\delta^{18}\text{O}$  a deuteria  $\delta^2\text{H}$ ) bylo analyzováno v laboratoři Wydziału Fizyki i Techniki Jądrowej AGH Kraków (Polsko).

Pro interpretaci byl dále použit hydrogeochemický rozbor těchto vod a vypočtené koeficienty z hydrogeochemických rovnováh. Vody byly rozděleny podle obsahu  $\text{SO}_4^{2-}$  do tří skupin s hranicemi 600 mg/l a 10 mg/l. Skupina vod s obsahem <10, 600> mg/l byla ještě rozdělena podle poměru Cl/Br s hranicí na hodnotě 300.

- Skupina I : vody o hodnotách  $\text{SO}_4^{2-} > 600$  mg/l,  
Skupina II : vody o obsahu  $600 > \text{SO}_4^{2-} > 10$  mg/l a Cl/Br > 300,

Skupina III : vody o obsahu  $600 > \text{SO}_4^{2-} > 10$  mg/l a  $\text{Cl}/\text{Br} < 300$ ,  
Skupina IV : vody o obsahu  $\text{SO}_4 < 10$  mg/l.

Toto rozdělení bylo postaveno na dosavadních znalostech základních typů zdrojů důlních vod v oblasti hornoslezské pánve (vody kvartéru, písčitych poloh sp. bádenu, detritu a případně vod karbonských) a na základě multiparametrické analýzy souboru dat vod ze spodního bádenu a karbonu v české části pánve. Shlukovací analýza byla provedena při akceptaci stanovených parametrů  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+ + \text{K}^+$ ,  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{HCO}_3^-$  a celkové mineralizace.

Základem interpretace vzorků pro stanovení izotopového složení byly vztahy charakteristických parametrů: koncentrace  $\text{rNa}/\text{Cl}$ , obsahy  $\text{Cl}/\text{Br}$  a  $\text{Br}/\text{I}$  a celková mineralizace. Výsledky jsou porovnány se standardem recentních mořských vod (SMOW – Ocean water standard).

V genetickém rozdělení podzemních vod jsme se přidrželi dělení a označení provedeného v práci Pluta, Zuber (1995): M ... miocénní mořské vody; P ... nejstarší solanky aridního klimatu; T ... terciární infiltrační vody; Q ... vody kvartéru; U (Us, U) ... vody předbádanského horkého klimatu (vnitřně rozdělené podle obsahu  $\text{SO}_4^{2-}$ ) a vody směsné z těchto základních grup (QP, QT, QU, PQ a PU).

Vztahy jednotlivých sledovaných parametrů jsou graficky zobrazeny v grafech na obr. č. 3 až 9.

Převážná většina vzorků vod skupiny I náleží zjevně k vodám mořského typu s různým stupněm zahuštění výparem (s nepřekročením bodu krystalizace halitu) a v různém stupni počáteční biodegradace některých iontů. Vzorky vod ze skupiny III a IV (silně odchýlené od teoretické linie evaporační krystalizace solí mořské vody) reprezentují smíšené vody mezi mořskými vodami (SMOW) a rezidui solanek po krystalizaci halitu, opět s různým stupněm biodegradace některých iontů.

Analýza výsledků hydrogeochemických rozborů dále prokazuje, že fosilní vody bádenu a vody z hlubších úrovní karbonského masívu v základních iontech  $\text{Na}^+$ ,  $\text{K}^+$  a  $\text{Cl}^-$  jsou natolik geochemicky rezistentní, že procesy jejich degradace se prakticky v čase neprojevují.

$\text{Br}^-$  podobně jako  $\text{Cl}^-$  se v době evaporace mořské vody chová konservativně. Jeho nabohacení nad SMOW nepovažujeme však za pouhý produkt rozkladu organických látek z mikroorganismů (Fisher, Boles, 1990; Cai et al, 1997), ale je zde pravděpodobný i značný podíl primárního obsahu tohoto iontu v terciárním moři (Worden, 1996). Tento závěr podporuje nevýrazná korelace  $\text{Br} / \text{I}$  (zejména u vod skupiny II až IV).

Nízké obsahy a degradace  $\text{SO}_4^{2-}$  a charakterizační parametry ukazují na výrazné procesy působení mikroorganismů v redukční prostředí v období primární a sekundární migrace (Homola, Grmela, 1987). Protože tento stav nenastává měřitelně u současné mořské vody, odchylují se fosilní vody (díky procesům geologických dob, tj. procesům neprobíhajícím v reálném čase) od typu recentních mořských vod. Určitý atenuační proces se projevil v případě iontu  $\text{Mg}^{2+}$  oproti současným SMOW; jeho degradace ve srovnání s  $\text{SO}_4^{2-}$  je zřetelně nižší.

V období primární migrace v podmínkách sedimentace spodního bádenu v jižní části hornoslezské pánve se původní synsedimentární vody pohybovaly v prostředí s převahou karbonátů (dnešní vápnité jíly) a odtud může pocházet jejich nabohacení ionty  $\text{Ca}^{2+}$  oproti stavu odparku vod dnešních moří. Znamenalo by to, že nabohacení  $\text{Ca}^{2+}$  je sekundární a je výrazem geochemické alterace původní mořské vody s horninovým prostředím.

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