

Origin of groundwater mineralization in coarse-grained lower Badenian aquifer in the Czech part of the Upper Silesian Coal Basin

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The coarse-grained aquifer of lower Badenian forms the most important hydrostructure in the Czech part of the Upper Silesian Coal Basin (USCB). In order to determine the sources of its groundwater mineralization the hydrochemical relationships between ion concentrations and other specific parameters were examined. Most of the water was probably derived from the seawater, evaporated to a various extent, but not reaching halite crystallization point. Water with higher TDS may represent mixture between evaporated seawater and the residual brine (after halite crystallization). In less mineralized waters of HCO₃-Na type, elevated concentrations of Br and I could be attributed to the decay of organic matter. For the most samples of waters representing Cl-Na type, the differentiation in Br and I concentrations was controlled independently.

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Key words: the Upper Silesian Coal Basin, lower Badenian, groundwater, hydrochemistry, seawater evaporation.

INTRODUCTION

Because of hydrogeological problems affecting coal mining the coarse-grained lower Badenian aquifer is the most important hydrostructure in the Czech part of the Upper Silesian Coal Basin (USCB). Groundwaters of this structure are hazardous to mine workings situated underneath, in the Carboniferous coal-bearing strata. On the other hand, they contain considerable amounts of Br and I, enabling their possible utilization in balneology. The purpose of this study was to reconstruct the sources of mineralization of these groundwaters assuming that their description might be useful in controlling the inflows into coal mine workings, and also in their future exploitation as therapeutic waters.

HYDROGEOLOGIC SETTING

The coarse-grained sediments of lower Badenian (so-called “detrit”) fill deep depressions in the roof of Carboniferous sediments (Figs. 1 and 2). Their equivalent in Poland is the

Dębowiec Formation (informal name). The main feature of this formation is fining upwards sequence of detrital sediments.

Lower Badenian sediments represent three types:

- sands with gravels (polymictic, poorly sorted with admixture of calcareous-clayey material);
- coarse clastic rocks with clasts from centimetre to over 1 m in diameter. Smaller clasts were derived from Culm and Upper Carboniferous sediments, the bigger ones consists mainly of conglomerates made of clasts of fine-grained sandstone;
- scree breccia comprising fragments of Carboniferous rocks, cemented by sandy and clayey matrix.

These sediments occur in two main depressions: the Detmarovice Depression — in the northern part of the examined area, and the Bludovice Depression — in the southern part (Fig. 3). The deepest part of the Detmarovice Depression reaches 700 m below the sea level, while the deepest part of the Bludovice Depression is at 1100 m b.s.l. The maximum thickness of the sediments (268 m) was measured in the axial parts of these depressions (Hufova, 1971). The main depressions are connected to smaller, meridionally oriented second-order depressions, which are incised into elevations of the Carboniferous sediments. Some of the second-order de-

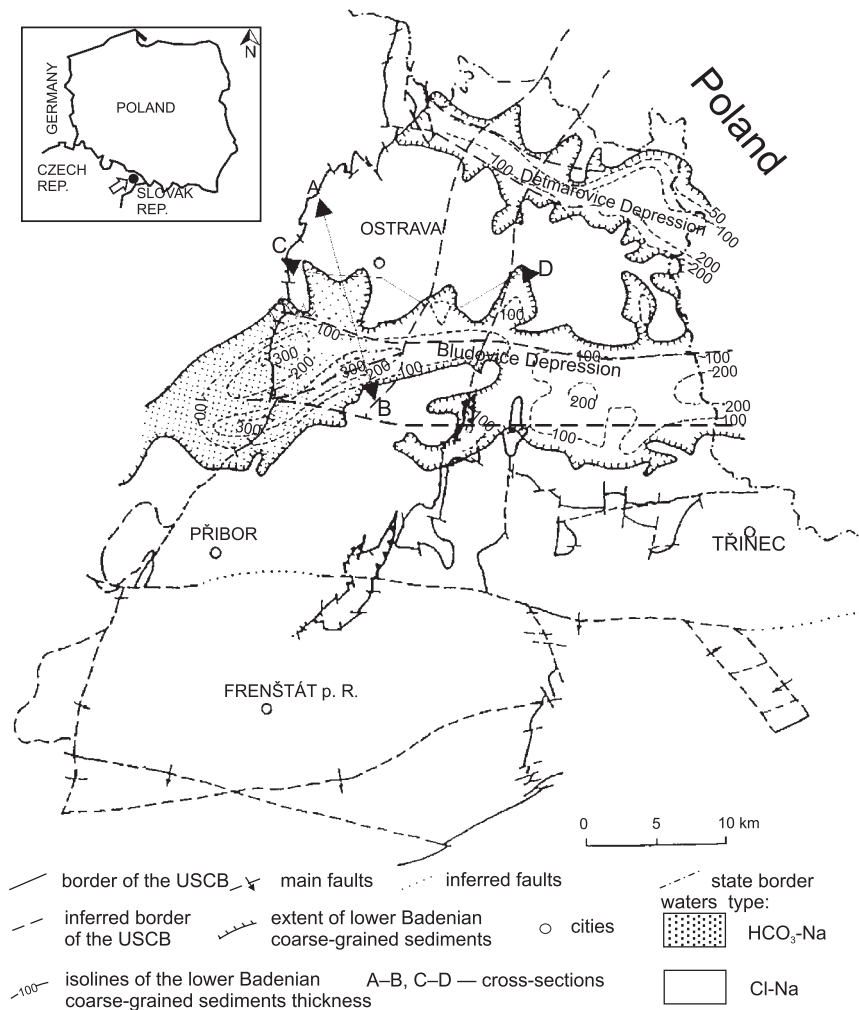


Fig. 1. The lower Badenian coarse-grained sediments in the Czech part of the USCBB (after Grmela, 1997, modified)

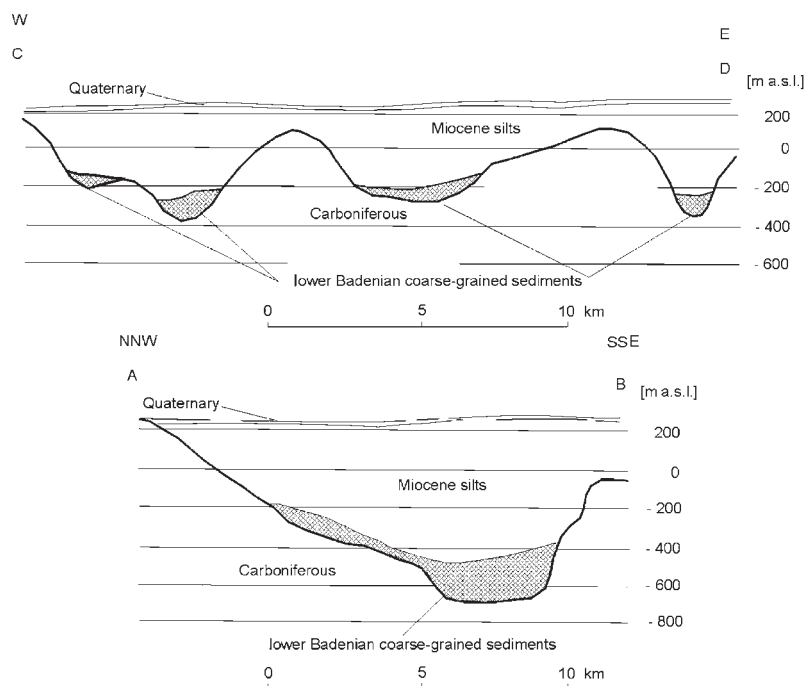


Fig. 2. Schematic cross-sections A–B and C–D (after Pišta, 1961, modified)

pressions (e.g. Svinov Depression) have hydraulic connections with the main ones, while the others (e.g. Vrbice Depression — completely dewatered presently) are isolated (Pišta, 1961; Hufova, 1971). Lower Badenian sediments form one hydrogeological system underlied by weathered and fractured rocks of the uppermost part of the Carboniferous. The confined aquifer of this system is strongly influenced by coal mining, resulting in the decrease of original water pressure from 8 to about 4.5 MPa, and in disturbances in vertical zonation of groundwater chemistry (Grmela, 1997).

Lower Badenian impermeable calcareous silts (so-called Tertiary pelitic facies, up to over 800 m thick) form a confining bed above the other lower Badenian sediments. Recent groundwater recharge is possible in the area of the Moravian Gate and in the upper parts of the Ostrava–Karvina Ridge (mainly on its northern slope). Local recharge from fissured aquifers of Devonian and Culm is also probable (Hufova, 1971; Grmela, 1997). Rózkowski (1971a) considered a possibility of lateral recharge of the Dębowice Formation from the Carboniferous aquifers.

GROUNDWATER HYDROCHEMISTRY

The presented research is based on interpretation of data from the hydrogeological database developed by the Czech coal mines. Groundwater analyses were performed in 1959–2002 by a range of laboratories (mainly OKD, DPB Paskov and Technical University of Ostrava in the Czech Republic). Supplementary samples, collected in 2002–2003, were analysed in the laboratory of the Institute of Wastewater and Water Engineering of the Silesian University of Technology. Analyses were accepted if their charge balance error was less than 5% (TDS up to 2 g/l) or 2% (TDS over 2 g/l).

Statistical (cluster) analysis of groundwater analyses (inflows into mine workings, and samples taken from exploratory boreholes) allowed

to distinguish hydrochemical groups of waters (Labus and Grmela, 2004) marked I–IV (Table 1), specific for particular areas in the territory examined.

Group I covers western part of the Bludovice Depression, NE slope of the Ostrava–Karvina Ridge (Fig. 4) and the Rychvald Depression.

Waters of the $\text{HCO}_3\text{-(SO}_4\text{-Cl)-Na(Ca-Mg)}$ type occur in the western part of the Bludovice Depression, while waters of Cl-Na type are observed in its remaining part. The most remarkable change in water type is observed in the narrow, central zone of the Bludovice Depression. Groups II to IV are represented exclusively by stagnant waters of the Cl-Na type. For groundwaters in depressions of the second order (connected to the main depressions of Bludovice and Detmarovice) two variability models of ion concentrations were formulated. The first is featured by the ion concentration increase towards the connection with the main depression, e.g. the Stonava Depression. The second model is defined by maximum ion concentrations in the center of the second-order depression, e.g. the Petřvald Depression. The highest I concentrations are typical of waters in the second-order Darkov Depression, and of the region of Darkov. Waters of the Lutyňe and Zavada depressions are particularly rich in Br.

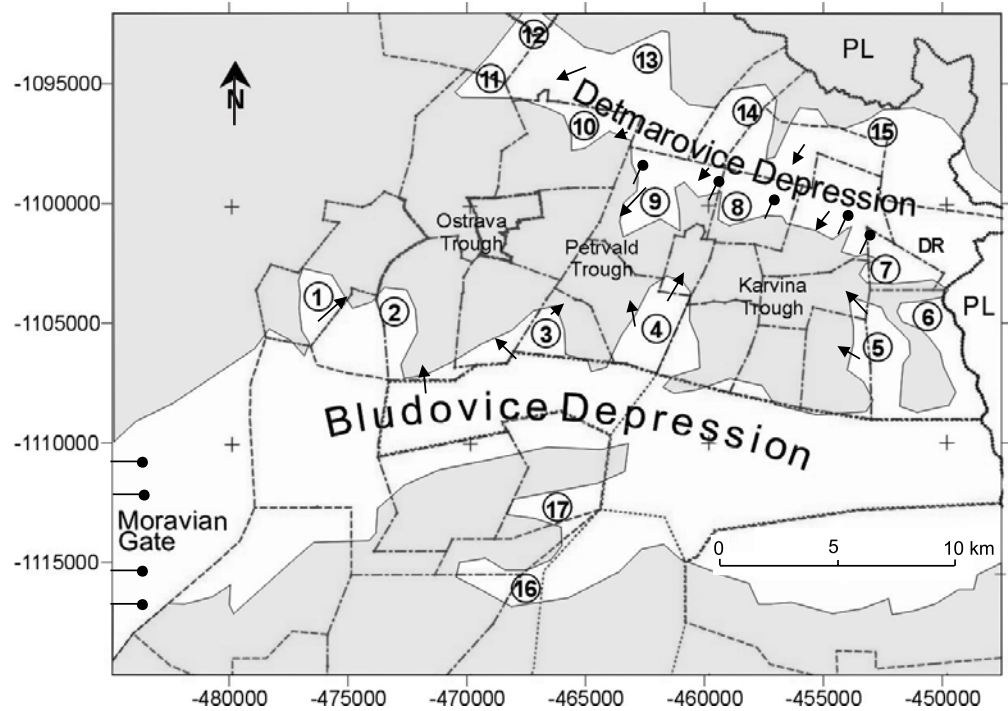


Fig. 3. Sketch of the examined area on the background of the mining areas in the Czech part of the USC B

White colour — area of lower Badenian sediments occurrence; depressions: 1 — Svinov, 2 — Bedřiš, 3 — Radvanice, 4 — Petřvald, 5 — Stonava, 6 — Darkov, 7 — Karvina, 8 — Orlova, 9 — Rychvald, 10 — Vrbice, 11 — Ludgeřovice, 12 — Hat, 13 — Skřečůň, 14 — Lutyňe, 15 — Zavada, 16 — Oprechtice, 17 — Vratimov; DR — the Darkov Region; arrows indicate groundwater flow direction; possible recharge zones marked with lines with circle ending; numbers outside the picture frame are the metric coordinates of the JTSK topographic system

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Table 1

Mean values and standard deviations of parameters for groups I–IV of waters from the coarse-grained lower Badenian aquifer, identified using cluster analysis

	Group I <i>n</i> = 55		Group II <i>n</i> = 40		Group III <i>n</i> = 67		Group IV <i>n</i> = 29	
	ar. mean	std. dev.	ar. mean	std. dev.	ar. mean	std. dev.	ar. mean	std. dev.
Ca	145.40	108.47	552.37	228.50	1447.13	314.57	2463.70	771.77
Mg	132.08	123.19	242.91	126.47	551.72	214.24	793.64	225.79
Na+K	3310.80	1780.68	8251.18	1782.55	13243.88	1148.19	17236.56	1341.95
Cl	4276.85	3076.12	13999.03	3105.13	24115.47	2526.54	33247.37	3308.36
I	6.02	9.60	10.98	6.62	22.12	12.86	23.22	8.33
SO ₄	69.28	89.11	39.97	51.04	36.52	39.23	41.67	22.10
HCO ₃	2184.93	2150.30	240.26	205.31	129.39	80.24	82.51	35.31
pH	7.79	1.10	6.69	1.17	7.09	0.95	7.02	1.06
Br	30.05	12.85	88.04	22.02	113.34	47.60	202.74	114.26

Units for dissolved constituents are in mg/l; *n* — number of samples; ar. mean — arithmetic mean

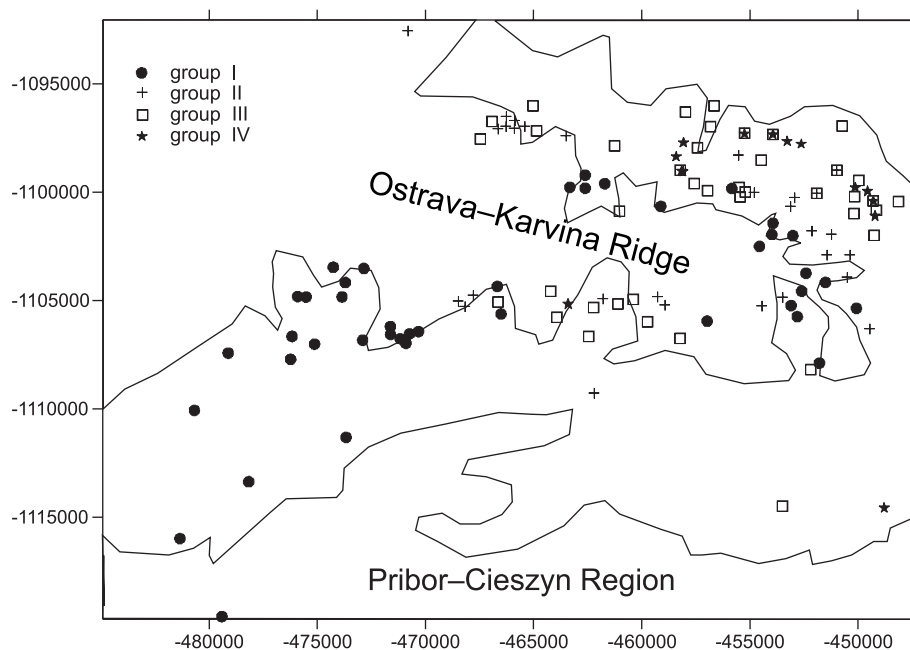


Fig. 4. Location of samples representing hydrochemical groups I-IV

Other explanations as on Figure 3

INTERPRETATION OF MINERALIZATION SOURCES

Data on the isotopic composition of lower Badenian waters from the Czech part of the USCB are scarce. As a result only hydrochemical relationships between ion concentrations and pH were studied to determine the sources of mineralization. On the other hand, the Dębowiec Formation waters (Poland), on the basis of their isotopic composition, were interpreted as originated from infiltration that occurred before the last Tertiary transgression (Pluta and Zuber, 1995).

In this study methods used for interpretation of oil-field brines and fluid inclusions in minerals were applied. They included analysis of relationships between calcium excess and sodium deficit in waters, and examination of graphs showing relationships between major ion concentrations and salinity (expressed by chloride concentration), against the background of the seawater evaporation/dilution trajectory (SET).

Most of points representing the waters examined are situated above the SET, which indicates a relative enrichment in Ca compare with the seawater (Fig. 5). Balance between Cl and Ca is apparent only for the groups II-IV. Steep regression line for these samples proves that Ca concentrations increase more intensively than in the case of evaporation of seawater. Such a model suggests that the enrichment in Ca is associated with calcite dissolution during the primary migration of waters in calcareous pelitic lower Badenian sediments.

Two sub-populations of samples are observed in Figure 6. The first groups I and II — is featured by high correlation between Br and Cl; samples are situated above SET, which means that bromine is slightly enriched in relation to the seawater evaporation curve. The second sub-population groups III and IV — is represented by points situated along the line of Cl concentrations

around the point of ca. 30 g/l Cl. It is also characterized by a broad range of Br concentrations (from 20 to 550 mg/l). Extreme values are typical of the central (and rarely of the eastern) part of the Detmarovice Depression.

Typical Br/Cl ratios, resulting from halite dissolution, are much lower than those in brines at the onset of halite precipitation (Richter and Kreitler, 1986; Fontes and Matray, 1993a). This is why halite dissolution should produce a low Br/Cl ratio compare with evaporated seawater. Halite excludes most Br during precipitation, but still contains about 30 to 260 ppm Br, depending on the salinity of evaporating water (Rittenhouse, 1967; McCaffrey *et al.*, 1987; Fontes and Matray, 1993b). Seawater evaporation, beyond the point of halite crystallization, results in forming of a residual brine with elevated Br/Cl ratio (Carpenter, 1978; McCaffrey *et al.*, 1987). Therefore high Br concentrations and Br/Cl values may indicate the evaporative origin of waters, similarly to other formation waters (e.g. Egeberg and Aagaard, 1989; Connolly *et al.*, 1990; Fontes and Matray, 1993b; Nativ, 1996).

Br enrichment, however, may be attributed to slow recrystallization of halite from brines thought to have originated from dissolution of this salt (Land and Prezbindowski, 1981; Moldovanyi and Walter, 1992). Fontes and Matray (1993a) question the effectiveness of this phenomenon. Points

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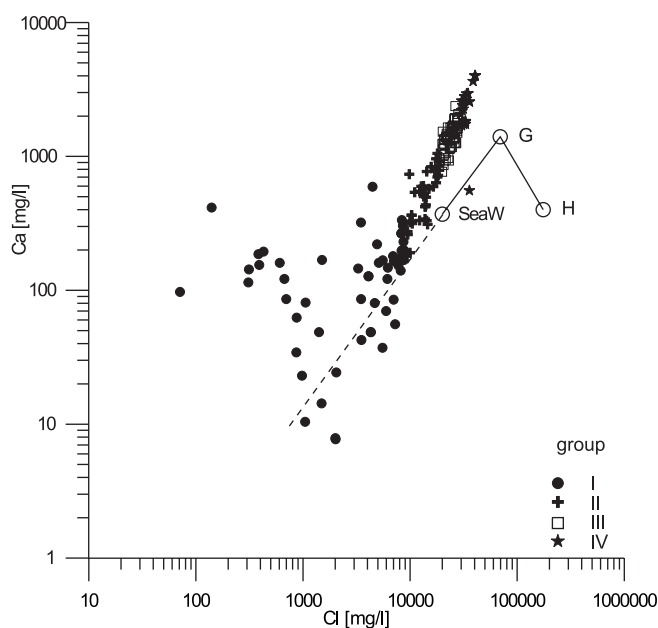


Fig. 5. Relationships between Ca and Cl against the background of the seawater evaporation trajectory (SET)

SeaW — seawater; points of evaporates crystallization: G — gypsum, H — halite, E — epsomite, S — sylvinite, C — carnallite, B — bischofite

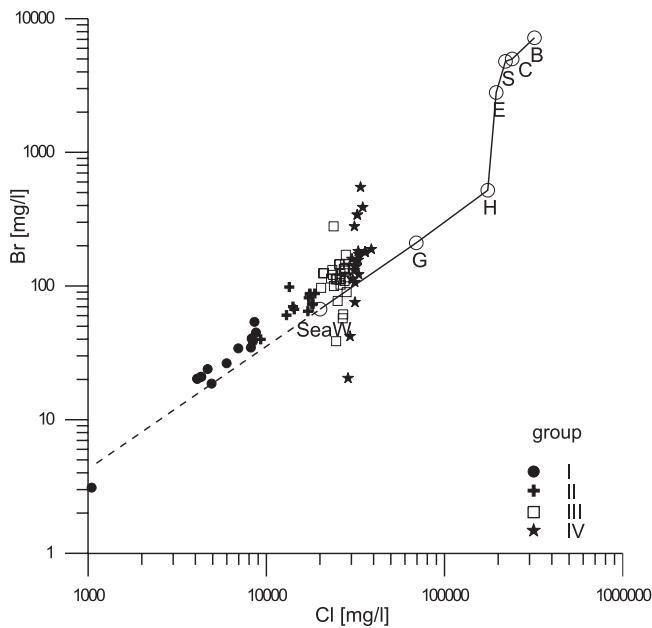


Fig. 6. Relationships between Br and Cl against the background of the seawater evaporation trajectory

Explanations as on Figure 5

situated below the SET may then represent fluids formed in the halite dissolution (Br depletion), diluted by fresh- or seawater. Points located on the line parallel to seawater during halite crystallization above the evaporation curve, may represent waters formed from the residual (after halite crystallization) brine dilution by waters with low TDS. Halite crystallization occurs when salinity reaches 26 wt% (NaCl eqv.). Therefore, if salinity of the waters examined is lower, their past dilution needs to be taken into consideration.

The Br/Cl ratios are affected by presence of residual brine in pores and fluid inclusions. Evaporites may have porosities reaching 40–50% (Sonnenfeld, 1984), and contain considerable amounts of residual fluids. Dissolution of such rocks should increase the Br/Cl ratio compared with that, expected from dissolution of pure halite.

Poor correlation between SO_4 and Cl (Fig. 7) indicates the origin of sulfates other than seawater. Waters of groups II–IV are depleted in sulfates in relation to seawater. Brines which are formed during the seawater evaporation are initially enriched in SO_4 . If the aquifer contains organic matter, however, they may be reduced to sulfides: $\text{SO}_4^{2-} + 2\text{CH}_2\text{O} \rightarrow \text{H}_2\text{S} + 2\text{HCO}_3^-$ (Appelo and Postma, 1993). Most of the analysed waters show also a deficit of sulfates and an enrichment in Ca ions in comparison to seawater. A similar phenomenon was also observed in the Polish part of the USCBA (Rózkowski, 1971b). The lack of correlation between Ca and SO_4 corroborates the hypothesis concerning the reduction of sulfates initially present in the waters.

Mg is well correlated with Cl in waters of II–IV groups. These waters are depleted in Mg with respect to SET. This could be explained by dolomitization (Carpenter, 1978; Stoessel and Moore, 1983).

The regression line for the $r(\text{Na} + \text{K})$ and Cl relationship of waters of groups III and IV (Na and K well balanced by Cl), intersects with the evaporation curve at the seawater point (Fig. 8).

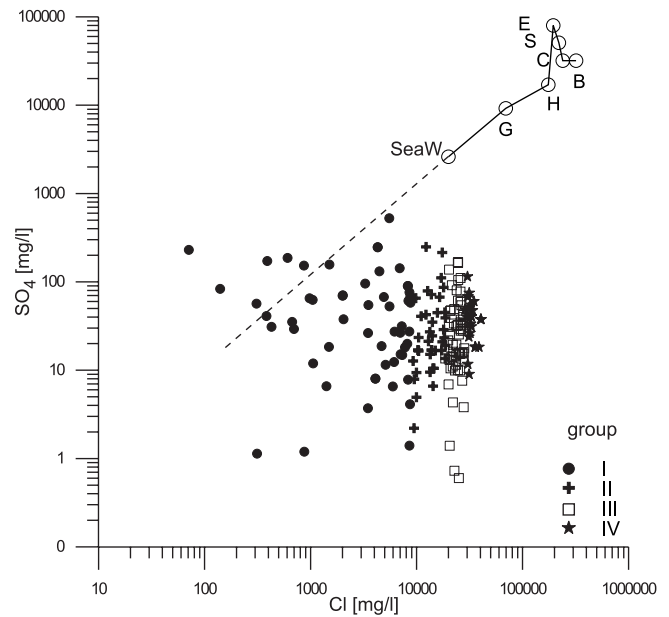


Fig. 7. Relationships between SO_4 and Cl against the background of the seawater evaporation trajectory

Explanations as on Figure 5

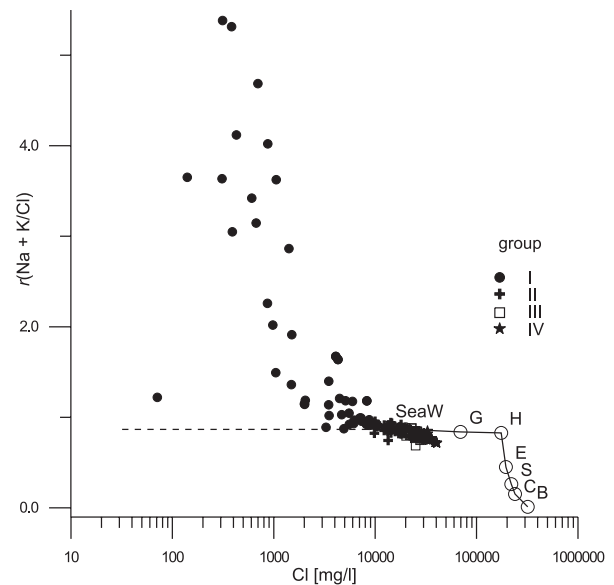


Fig. 8. Relationships between $r(\text{Na} + \text{K})$ and Cl against the background of the seawater evaporation trajectory

Explanations as on Figure 5

Halite crystallization decreases the $r\text{Na}/\text{Cl}$ value in the residual brines (Nativ, 1996). Low values of this ratio could indicate the evaporative nature of the brines. In this study, the observed values of $r\text{Na}/\text{Cl}$ are lower than those of seawater, and are lower than the typical values for halite dissolution, where $r\text{Na}/\text{Cl} = 1$. This indicates a modification of initial water composition by rock-water interactions e.g. ion exchange in waters mineralized stronger than seawater.

Values of $r\text{Na}/\text{Cl} > 1.5$ are typical of the group I, representing the western part of the Bludovice Depression, where the $\text{HCO}_3\text{-Na}$ water type dominates.

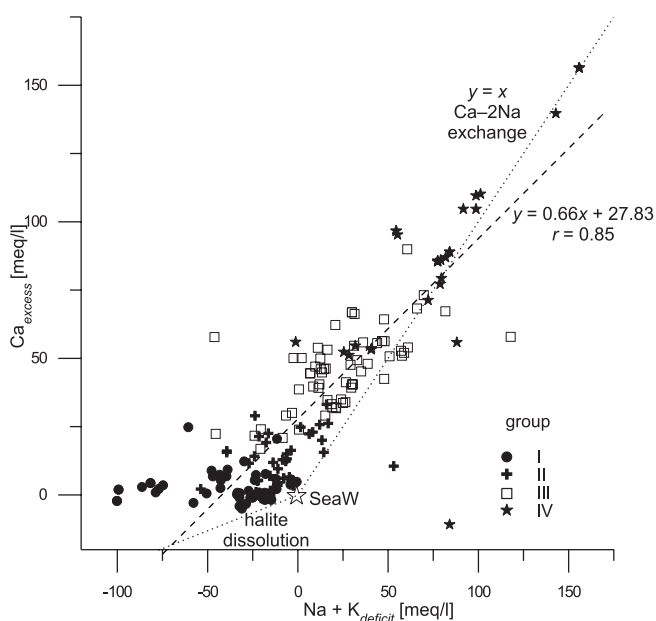


Fig. 9. $Ca_{excess} - Na_{deficit}$ diagram for the examined waters

Explanations as on Figure 5

The relationship between the $Na_{deficit}$ and Ca_{excess} in basinal fluids was presented by Davisson *et al.* (1994) and Davisson and Criss (1996) by means of two parameters:

$$Ca_{excess} = 2[Ca_{meas} - (Ca/Cl)_{SW}Cl_{meas}]/40.08 \quad [1]$$

$$Na_{deficit} + [(Na/Cl)_{SW}Cl_{meas} - Na_{meas}]/22.99 \quad [2]$$

Measured (*meas*) ion concentrations (mg/l) are compared to those of seawater (*SW*), and converted to meq/l using numerical constants. The formulae allow to obtain a linear relationship (expressed as Basinal Fluid Line — BFL) between Na, Ca and Cl concentrations for numerous basinal brines. The correlations are the effect of possible net cation exchange ratio of [2] Na for [1] Ca — typical for modification of original Na-rich waters through albitization of plagioclase (present in the aquifer material).

The *y*-intercept of BFL (intercept with the Ca_{excess} axis) increases with the chlorinity of the water. The seawater evaporation, after an initial vertical decent, may be plotted as a line parallel to the $Na_{deficit}$ axis. Both parameters are not significantly correlated with other major ions and the temperature of water. Hydrothermal fluids and fresh waters have low concentrations of Ca and Na, and are plotted mainly in the negative quadrants (Davisson and Criss, 1996). Origin of such waters — represented in this study by group I — is distinct from those of the basinal fluids (Fig. 9).

Halite dissolution in fresh- or seawater shows a trend of positive slope of about 0.25, extending from the origin (0;0) point towards the negative quadrant of the plot. If Ca-Na exchange is following the dissolution of halite, then positive linear trajectory starts at the dissolution line. The magnitude of the *y*-intercept increases with the amount of dissolved halite. Dissolution of calcite, gypsum and dolomitization of calcite in-

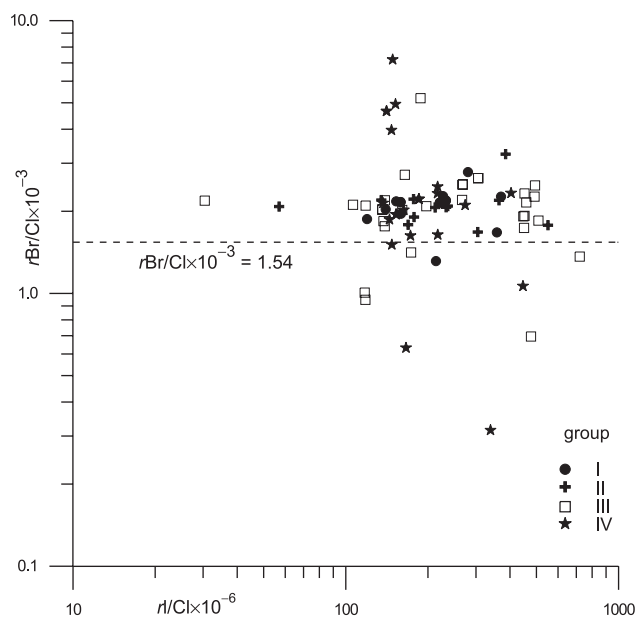


Fig. 10. Relationships between rBr/Cl and rI/Cl of waters considered

Explanations as on Figure 5

creases the Ca_{excess} without changing the $Na_{deficit}$. On the other hand, the excess of Ca is reduced by calcite precipitation.

The regression line for groups II to IV has a slope less steep than the BFL. Position of groups III and IV suggests their origin from mixing of evaporated seawater with waters into which halite was dissolved. These waters should also undergo cation exchange processes. Both water types may coexist in sedimentary basins. Sediments compaction and tectonic activity may initiate their migration and mixing (Chi and Savard, 1997). Interpretation of the relationship rCl/Br vs. Na/Br confirms such a hypothesis (Fig. 11). Contrary to group I, Ca_{excess} and $Na + K_{deficit}$ are well correlated in groups II, III and IV ($R^2 = 0.725$).

Points situated well above the seawater line — $rBr/Cl = 1.54 \cdot 10^{-3}$ suggest the origin of waters associated with residual brines, remaining after halite crystallization (Fig. 10).

Values of rI/Cl (from about $30 \cdot 10^{-6}$ to $800 \cdot 10^{-6}$) are higher than the relevant values for the seawater (Zherebtsova and Volkova, 1966). Presence of iodine in the examined waters is probably controlled by its supply by organic matter. The rI/Cl values are similar to these of oil-field brines (Worden, 1996). Lack of positive correlation between rBr/Cl and rI/Cl suggests that the organic matter is not a significant source of Br (Kendrick and Burgess, 2002). Taking into account the above observations, the examined waters are interpreted as associated with seawater evaporation (including some of them above the halite saturation point), and consequent dilution with fresher waters (the analysed waters have lower salinity than the seawater saturated with halite). The enrichment in I, in waters of the lower Badenian, could be attributed to their interaction with the organic matter contained in the aquifer. Points situated between the values of $rBr/Cl = 0.18 \cdot 10^{-3}$ and $1.54 \cdot 10^{-3}$ represent the residual brines after halite crystallization, mixed together with waters which were formed later, in the process of halite dissolution.

The $Na/Br-Cl/Br$ diagram (Fig. 11) was proposed by Walter *et al.* (1990, *vide* Chi and Savard, 1997). According to the diagram,

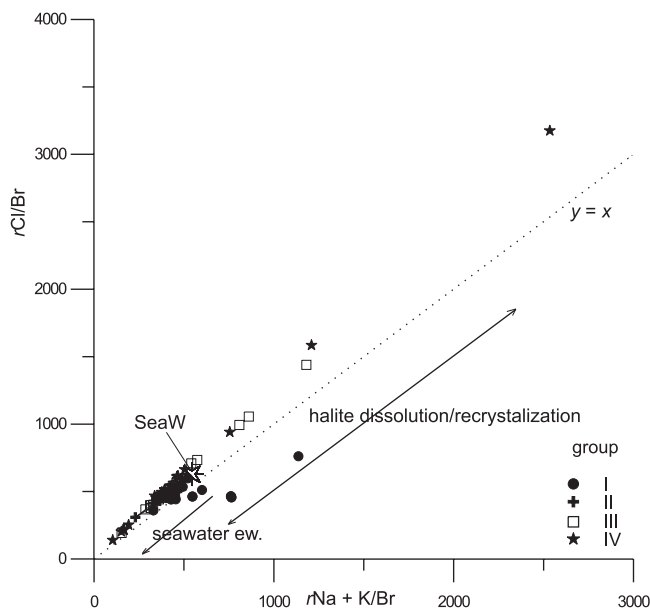


Fig. 11. Relationships between rCl/Br and $rNa + K/Br$ of waters considered

Explanations as on Figure 5

brines derived from evaporation of seawater, after saturation with halite, are reaching values of rNa/Br and rCl/Br lower than in seawater, contrary to brines derived from halite dissolution.

Chi and Savard (1997) proved that lower than in seawater proportions of rNa/Br and rCl/Br should not only be attributed to the evaporation of seawater but alternatively be explained by mixing of an evaporated seawater with water originated from halite dissolution. On the other hand, the brines featured by rNa/Br and rCl/Br values higher than in the seawater may contain evaporated seawater. On this basis, the analysed waters can be considered as a result of mixing between waters containing dissolved halite together with residual fluids after halite crystallization. Such a possibility is also supported by the interpretation of $Ca_{excess} - Na_{deficit}$ diagram.

Waters of group I are characterized by rCl/Br values similar to these of seawater (they are situated along the virtual line 1:1 [$x = y$] — dissolution-evaporation), but their Cl content is lower than in the case of seawater. It is probable that they originate from seawater (possibly partly evaporated), diluted by meteoric waters. Most of the examined waters (the entire group II) has rCl/Br values lower than seawater. They are scattered close and above the SET, reflecting a slight decrease in Na and K content in favour of other cations (e.g. Ca).

Waters of the lower Badenian (most of the samples from groups I and II) originate probably from seawater, evaporated to a various extent, but not reaching the halite crystallization point. Samples of group III and IV (shifted left from the SET) represent mixing between evaporated seawater and the residual brine (after halite crystallization).

The initially precipitating halite contains 65 to 75 ppm Br (Holser, 1979; Herrmann, 1980 *vide* Banks *et al.*, 2002), and, if dissolved, would generate rCl/Br molar ratio of approx. 20 000. The rCl/Br molar ratio decreases to approx. 7000 at the end of halite precipitation. Waters originating from halite dissolution are represented by points scattered along the 1:1 line

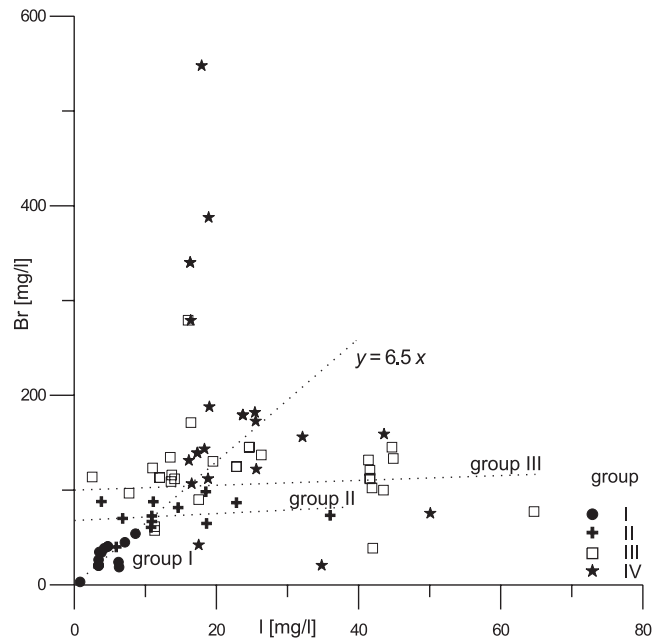


Fig. 12. Relationships between Br and I of waters considered

Explanations as on Figure 5

and are characterized by high rCl/Br and rNa/Br values. The samples with higher rCl/Br and rNa/Br values in groups III and IV represent waters of such an origin (Fig. 11).

Br and Cl behave conservatively during the evaporation of seawater. Waters with elevated I concentrations are thought to be enriched with biogenic Br (Fisher and Boles, 1990). On the other hand, Worden (1996) states that Br is correlated mainly with Cl. In case of groups II, III and IV there is no evident correlation between Br and I (Fig. 12). This may suggest that such waters contain Br of abiogenic origin (Cai *et al.*, 1997).

Samples of group I and partly of groups II to IV are scattered along a regression line that starts at the origin of the diagram (Fig. 12). Such a situation is typical of samples derived from dilution of waters with constant I to Br ratio. These samples, mainly of group I, are interpreted as a result of mixing between a certain initial water and meteoric waters. It can be argued that the intercept of the regression line (mixing line) at zero I ($I = 0$ mg/l) reflects the non-organic Br content of water (Buzek and Michaliček, 1996). Basing on this assumption it is proposed that the Br contents in waters of group I is associated with iodine and derived from organic matter. It also appears that for the majority of samples representing groups II–IV varying Br concentrations are independent of the processes that controlled iodine contents in these waters. Rózkowski (1971a) argued that the enrichment in iodine of groundwater in the lower Badenian sediments results from the decay of marine organisms.

CONCLUSIONS

Most of the samples from hydrochemical groups I and II originate from seawater, evaporated to a various extent, but not reaching the halite crystallization point. Samples of group III

and IV represent mixing of evaporated seawater with the residual brine (after halite crystallization).

Deficit of sulfates and enrichment in Ca ions in most of the analysed samples compared with the seawater, suggests calcite dissolution during the primary migration of waters in calcareous pelitic lower Badenian sediments. Poor correlation of SO₄ with Cl suggests the initial reduction of sulfates in the waters.

Mg is well correlated with Cl in waters of II–IV groups. These waters are depleted in Mg with respect to the SET. This fact might be explained by dolomitization.

Lower than seawater values of $r(\text{Na} + \text{K}/\text{Cl})$ in groups III and IV indicate modification of their composition by rock-wa-

ter interactions. Values of $r\text{Na}/\text{Cl} > 1.5$ are typical of group I, representing the western part of the Bludovice Depression, where the HCO₃-Na water type dominates.

The Br contents in waters of group I is associated with organic matter. For most samples of groups II–IV variations in Br concentration are independent of the processes that controlled iodine contents in these waters.

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