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CHEMICAL COMPOSITION AND ORIGIN OF IONIC RATIOS IN THE IWONICZ ANTICLINE MINERALIZED GROUNDWATERS (POLISH OUTER CARPATHIANS)

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Abstract: One of the generally distinguished types of mineralized groundwaters are oil-associated waters, the so-called oil-field brines. The position of mineralized groundwaters of the Iwonicz anticline occurring in the immediate vicinity of oil fields makes it possible to include them among waters of this type. Considerations concerning the waters' chemical composition and ionic ratios using BDP plot and Stiff's diagrams certify to this preliminary conclusion. Because the flysch sediments were deposited in the sea and the composition of seawater is considered to have been constant since the Cambrian, the comparison of seawater chemical composition and of mineralized waters of the Iwonicz anticline has been presented. Analysis of ionic ratios of main and specific components as well as seawater evaporation trajectories (S-E-T) indicates genetic similarities between these two water types. At the same time processes of mixing with fresh water have been noticed. This allows to set forth the hypothesis that the recent chemical composition of the Iwonicz anticline mineralized waters, undoubtedly belonging to "oil-field brines", stays under considerable influence of "old" seawater (connate water) and fresh water of the recent hydrologic cycle.

Key words: brines, groundwater salinity, oil-associated waters, chemical composition, ionic ratios, groundwater origin, evaporation trajectories.

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INTRODUCTION

The anticline of Iwonicz Zdrój, SE Poland, is an object of interest for two reasons: the occurrence of oil fields, and of mineralized groundwaters that are used for balneological treatment since the last century.

Searching for, and discovering oil fields in this area have made valuable contributions to recognizing of geological structure and resulted in a considerable amount of detailed studies by Książkiewicz (1972), Wdowiarz J. (1950), Wdowiarz S. (1985), Wdowiarz S. *et al.* (1988, 1991), Ślączka (1971), Sokołowski (1963) and others. Mineralized groundwaters have been discovered in this area much earlier then the oil fields.

Saline waters in the Iwonicz area were mentioned already in the XVI century and are counted among the earliest discovered and described in Poland. However, till present days there is a lack of studies regarding their origin. Existing published papers and archival documents concern first of all the chemical composition of saline waters and their geological and hydrogeological setting.

The present paper summarizes chemical data on mineralized groundwater in the Iwonicz anticline on the base of latest many-years' archival records of 13 wells and springs in use. The records are the result of monitoring of groundwater quality in spas (Iwonicz Zdrój and Rymanów Zdrój) which was carried out by the "Balneoprojekt" laboratory. The chemical composition and ionic ratios of waters have been interpreted basing on recent trends in hydrogeochemistry in order to present chemical and genetic relations among them. The paper is the first step of research targeting on the "oil-field brines" origin in the main folded structures of the Central Carpathian Synclinorium.

LOCATION OF THE STUDY AREA

Intakes of mineralized groundwater under consideration are located within mine areas of balneological spas at Iwonicz Zdrój and Rymanów Zdrój (10 wells in use and 3 springs). Both areas are placed within the anticline of Iwonicz Zdrój – one of the several geological structures of Central Carpathian Synclinorium, SE Poland. The Synclinorium belongs the Silesian Unit of the Polish Outer Carpathians. The anticline extends on the area of several tenths of kilometers –from Nowy Żmigród in the NW through Luba-

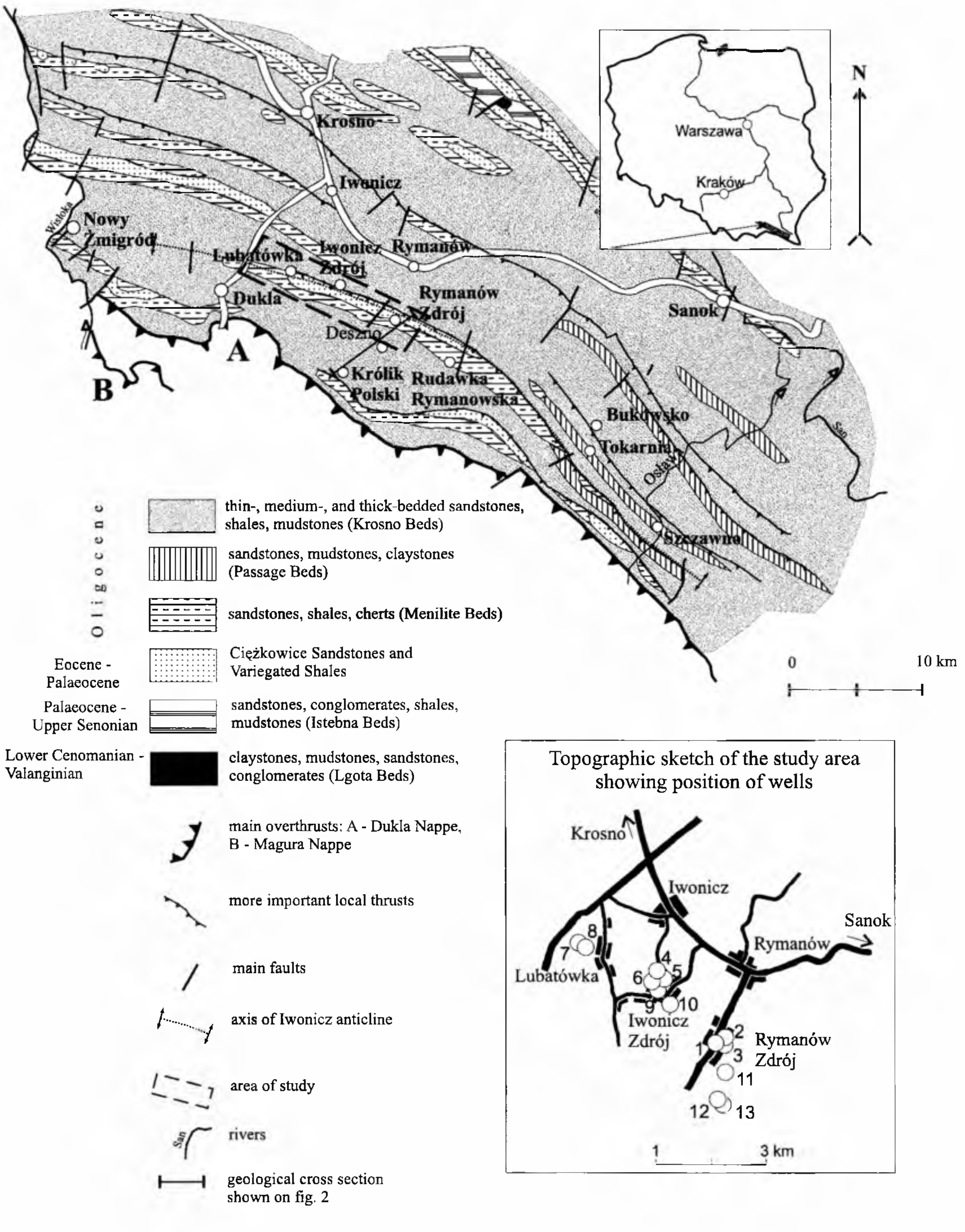

Fig. 1. The Iwonicz anticline and the position of considered mineralized groundwater intakes: 1 – spring Klaudia; 2 – spring Celestyna; 3 – spring Tytus; 4 – Elin 7; 5 – Emma; 6 – Zofia 6; 7 – Lubatówka 14; 8 – Lubatówka 12; 9 – Iwonicz 2; 10 – Klimkówka 27; 11 – Rymanów 2; 12 – Rymanów 5; 13 – Rymanów 6; Geological sketch was modified by the author in relation to source version; source: Poprawa & Nemcok (eds.), 1989

tówka, Iwonicz Zdrój, Rymanów Zdrój to Rudawka Rymanowska and Tokarnia in the SE. The anticline and the position of considered groundwater intakes are shown in Fig. 1.

GEOLOGICAL STRUCTURE OF THE IWONICZ ANTICLINE

Geological features of the anticline – similarly as these of other structures of the Synclinorium – are very complex because of tectonic disturbances. All fault structures within the Synclinorium, usually a few kilometers wide and extended from WNW to ESE, differ among each other in tectonic style and lithostratigraphic profiles (Ślączka, 1977; Wdowiarz S., 1977, 1985; Wdowiarz S. *et al.*, 1977, 1991).

The Upper Cretaceous and Tertiary flysch sediments play a fundamental role in the geological structure of the Iwonicz anticline but there are only Paleogene (Eocene–Oligocene) flysch rocks uncovered at the surface whereas older rocks are recognized in drillings (Fig. 1, Fig. 2)

The Upper Cretaceous is represented by the Godula

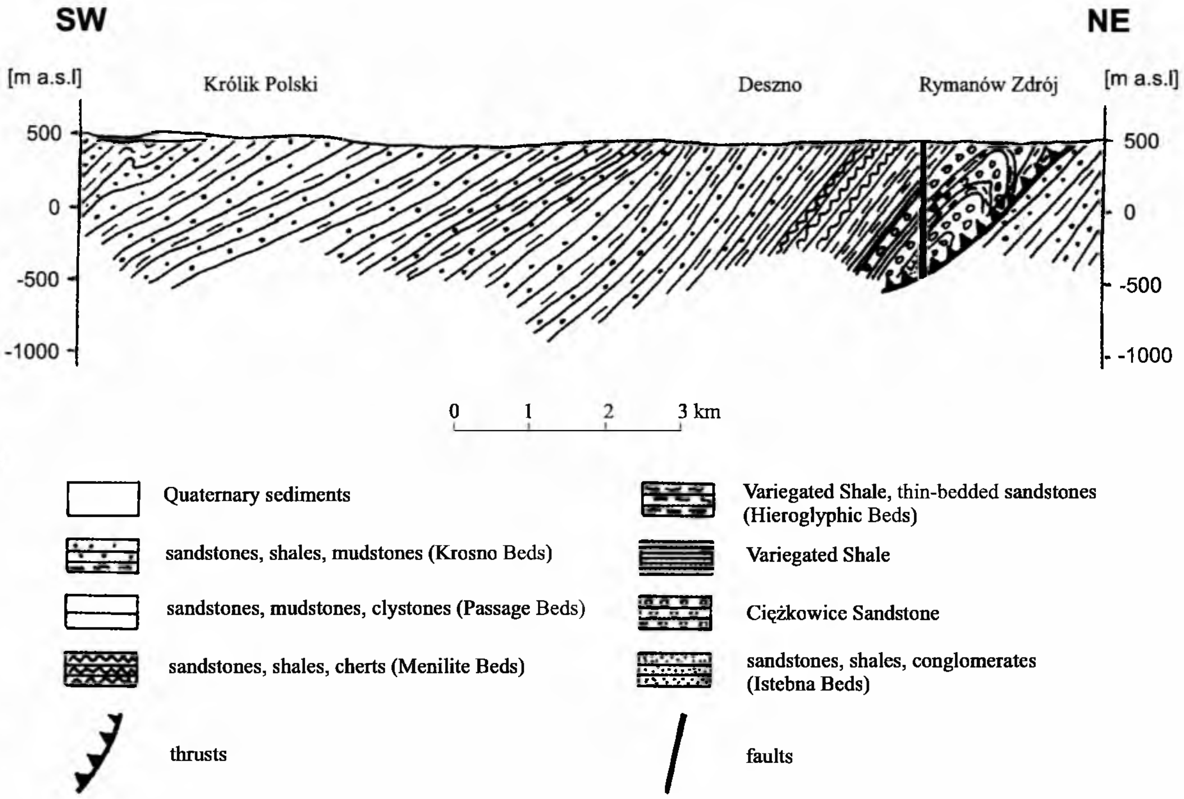

Fig. 2. Schematic geological cross section through the Iwonicz anticline at Rymanów. Modified by the author in relation to source version; source: Wdowiarz *et al.*, 1988

Beds and the Istebna (Czarnorzeki) Sandstone (Lower Istebna Beds). The Godula Beds, represented by fine-grained sandstones and shales, are very difficult to distinguish because of scarcity of characteristic microfauna and big similarities in continuous sedimentation. The drillhole "Tarnawka 26", south-east of Iwonicz and Rymanów, in the depth of 1691–2304 m, pierced through rocks which were recognized as Godula Beds by such authors like H. Kozikowski and A. Tokarski (Wdowiarz S. *et al.*, 1991). Their age was estimated as Upper Turonian–Lower Senonian. The Godula Beds, however, have not been found in the nearest area of Iwonicz Zdrój and Rymanów Zdrój. The Istebna (Czarnorzeki) Sandstone, represented by a mighty complex of sandstones interbedded by shales, overly the Godula Beds. This complex reaches the thickness of about 500 m in the vicinity of Lubatówka, decreasing eastward to about 300 m in the vicinity of Rymanów Zdrój and to about 150 m in the vicinity of Rudawka Rymanowska (Wdowiarz S. *et al.*, 1991). The Istebna (Czarnorzeki) Sandstone (Lower Istebna Beds) pass continuously into the Istebna (Czarnorzeki) Shale (Upper Istebna Beds) of Palaeocene age. The upper part of the Palaeocene and the lower part of the Eocene are represented by alternating series of Variegated Shale and Ciężkowice Sandstone. The anticline of Iwonicz is the zone where the whole complex is very well developed and divided into four series of sandstones interbedded with four series of shales. The thickness of the whole complex in the vicinity of Iwonicz amounts to about 500 m (Wdowiarz J., 1950; Ślączka, 1977; Kulikowska & Pilich, 1978; Wdowiarz S., 1985; Wdowiarz S. *et al.*, 1991). However, in other folded structures of the Central Carpathian Synclinorium, both the number of sandstone-shale series and their thicknesses are variable and sometimes sandstone are absent. Overlying them the Hieroglyphic Beds and Globigerine Shale represent the upper part of the Eocene. Oligocene rocks are formed as Menilite Beds and sandstone-shale Krosno Beds – the best known and the most spread-out at the surface of the Synclinorium (Fig. 1, Fig. 2). They end the sedimentation of flysch rocks in the area.

HYDROGEOLOGICAL CONDITIONS AND OCCURRENCE OF MINERALIZED WATERS

From the hydrogeological point of view the sandstone-shale flysch rocks are counted among those of low permeability. Groundwater flow systems are poorly developed because of numerous shale beds and prevailing argillaceous cement of sandstones and conglomerates. A great number of laboratory tests revealed low intergranular porosity of flysch rocks, especially of the Krosno Beds, the mean porosity of which was estimated at 5–7%, only locally at about 15%. (Krzywina & Sokołowski, 1977; Chowaniec, 1991). Therefore, the freshwater content of flysch sediments depends much more on the quantity and character of faults and fissures than on the porosity. The density and dimensions of fissures depend on the lithology of flysch rocks.

The occurrence of fresh groundwater is connected rather with surface zones of fractured and disintegrated flysch rocks of different age than with typical stratigraphic water-bearing beds. These zones containing water create discontinuous groundwater levels with different storage capacities and permeabilities (Chowaniec, 1991). The depth of freshwater zone in the Krosno Beds was determined at 40 m on the average; only locally, the lower limit of groundwater circulation and exchange zone reaches about 60 m.

The mean value of permeability coefficient for depths between 20 and 40 m was estimated at 2.4 x 10^{-7} m/s (0.17 m/24h) (Chowaniec, 1991). Average values of the permeability coefficient for flysch rocks (calculated on the base of pumping tests) are determined at n x 10^{-5} – n x 10^{-6} m/s, sometimes reaching values of n x 10^{-7} m/s and n x 10^{-8} m/s but seldom n x 10^{-4} m/s (Poprawa, 1970; Chowaniec, 1991). Direct infiltration of precipitations is the main source of fresh water recharge in that area.

The coexistence of fresh and mineralized groundwaters is connected first of all with zones of tectonic dislocations or exposures of more permeable flysch beds like sandstones or conglomerates. It is a common knowledge that one of the most important factors determining the occurrence of oil and mineralized waters are collector features of host rocks, it means – their porosity, which appears to be slightly higher in reservoir beds than the average for flysch rocks. That is why the Ciężkowice Sandstone – thick-bedded, varigrained, sometimes conglomeratic – with mean values of porosity from 7.8% to over 18% become the main reservoir of mineralized groundwaters and oil in the area of Iwonicz anticline. It is noticeable in potentially better exploitation conditions of these waters as compared to the other structures of the Synclinorium or even to surrounding areas (Wdowiarz S., 1974; Krzywina & Sokołowski, 1977). Usually, in the vicinity of Iwonicz Zdrój the discharge of mineralized waters reaches values of several m^3/h while the drawdown is less than 25 m. Also the Istebna (Czarnorzeki) Sandstone are rather good reservoirs with mean values of porosity from 4.5% to 16.8% and of the permeability coefficient from 10^{-3} to 10^{-5} m/s (Poprawa, 1970). To satisfy the demand of balneological spas in Iwonicz Zdrój and Rymanów Zdrój the mineralized groundwaters are exploited from all four series of the Ciężkowice Sandstones and also from the upper part of the Czarnorzeki Sandstone. Figure 1, shows the position of 13 selected wells withdrawing mineralized groundwaters; all of them have many-years' analytical records.

IONIC RATIOS AND THEIR ORIGIN IN THE IWONICZ ANTICLINE MINERALIZED GROUNDWATERS

Chemical composition

The many-years' mean chemical composition record of mineralized groundwaters exploited in the area of Iwonicz and Rymanów has been presented in abbreviated form in Table 1.

The main hydrogeochemical type of mineralized groundwaters are chloride-hydrocarbonate-sodium waters containing bromine and iodine (Cl-HCO_3-Na, Br, I). Some wells like Rymanów 2, Rymanów 5 withdrawing water from jointed horizons of the third and the fourth Ciężkowice Sandstone, and also Klimkówka 27 withdrawing water from the third horizon of the Ciężkowice Sandstone, produce another type of water: hydrocarbonate-chloride-sodium water containing bromine and iodine (HCO_3-Cl-Na, Br, I) (Porowski, 2001).

These two hydrogeochemical types of mineralized groundwater contain variable amounts of free carbon dioxide: from about 0.2 to about 1.0 g/dm^3 on the average. The largest amounts of free CO_2 gas (about 1.0 g/dm^3) occur in springs of Rymanów Zdrój. Thus, mineralized waters of the considered springs, may be qualified as carbonated waters while the other ones – only as waters containing carbon dioxide (Dowgiałło et al., 1969; Dowgiałło *et al.*, 1974; Paczyński & Płochniewski, 1996).

Taking into consideration the values of TDS (total dissolved solids), which are variable from about 3.3 g/dm^3 to about 19.9 g/dm^3, it is not possible to qualify these waters as typical brines (Porowski, 2001). Brines are usually defined as more saline (more concentrated) than seawater (35 g/dm^3 TDS) (Dowgiałło *et al.*, 1969; Drever, 1982; Appelo & Postma, 1996). The two general schemes for the classification of water based on the TDS are clearly presented by Carpenter (1978), as shown in table 2.

Thus, groundwaters under consideration belong to slightly-, moderately- and very saline or, in other words – to brackish and saline waters. Their genesis and the origin of their mineralization are not univocally explained so far.

Starting an introductory analysis of the genetic aspects we must answer the basic question: what natural hydrochemical processes affect the formation of saline waters?

Six main hydrochemical processes may be distinguished (Appelo & Postma, 1996):

- evaporation and concentration / precipitation of dissolved salts
- dissolution of salts
- mixing with recent seawaters
- mixing with connate seawaters
- volcanic exhalations
- ultrafiltration.

The stratigraphic and structural features of Iwonicz anticline eliminate the possibility of such processes like volcanic exhalations or mixture with recent seawaters. The influence of other processes seems to be more or less probable and verifying or excluding whichever requires detailed analyses both, the chemical composition of waters and their rock environment.

Considering the rock environment of mineralized waters occurrence in the Iwonicz anticline three facts appear to be the most important:

1. The waters occur in flysch sediments and they could not be formed during simple processes of evaporation, precipitation and dissolution of salts. Considerable evaporate deposits have not been found in the area of Iwonicz anticline or even in the area of the Central Carpathian Synclinorium. However, in this stage of analysis the phenomenon of an ascent of saline waters from older rocks or even from the other areas can not be definitely excluded. It is very likely that brines produced during evaporation of seawater or dissolution of salts (evaporates) will be moved from their

Table 1

Many-years' mean chemical composition of the Iwonicz anticline mineralized groundwaters

Name of well or spring	Depth of exploitation [m]	Stratigraphy of exploited horizon	Abbreviated form of the chemical composition
Spring Celestyna	–	II Ciężkowice Sandstone	$\mathrm{Br}^{15.6}\mathrm{I}^{4.9}\mathrm{M}^{8.6}\frac{Cl^{79}HCO_3^{20}}{Na^{91}}\mathrm{G}^{0.9}$
Spring Klaudia	–	II Ciężkowice Sandstone	$\mathrm{Br}^{16.2}\mathrm{I}^{3.6}\mathrm{M}^{8.1}\frac{Cl^{80}HCO_3^{20}}{Na^{91}}\mathrm{G}^{1.0}$
Spring Tytus	–	II Ciężkowice Sandstone	$\mathrm{Br}^{14.5}\mathrm{I}^{3.6}\mathrm{M}^{8.4}\frac{Cl^{79}HCO_3^{20}}{Na^{90}}\mathrm{G}^{1.0}$
Elin 7	107.0–230.0	II Ciężkowice Sandstone	$\mathrm{Br}^{9.0}\mathrm{I}^{3.1}\mathrm{M}^{7.1}\frac{Cl^{73}HCO_3^{27}}{Na^{96}}\mathrm{G}^{0.2}$
Emma	113.0–260.5	II Ciężkowice Sandstone	$\mathrm{Br}^{11.2}\mathrm{I}^{3.0}\mathrm{M}^{6.7}\frac{Cl^{72}HCO_3^{28}}{Na^{94}}\mathrm{G}^{0.2}$
Rymanów 6	168.3–238.2	I and II Ciężkowice Sandstones jointed horizons	$\mathrm{Br}^{3.7}\mathrm{I}^{1.4}\mathrm{M}^{3.3}\frac{Cl^{60}HCO_3^{40}}{Na^{89}}\mathrm{G}^{0.2}$
Zofia 6	283.0–325.0	II Ciężkowice Sandstone	$\mathrm{Br}^{23.4}\mathrm{I}^{6.2}\mathrm{M}^{14.9}\frac{Cl^{79}HCO_3^{21}}{Na^{96}}\mathrm{G}^{0.3}$
Iwonicz 2	338.3–394.3	III Ciężkowice Sandstone	$\mathrm{Br}^{10.9}\mathrm{I}^{4.4}\mathrm{M}^{10.2}\frac{Cl^{63}HCO_3^{36}}{Na^{95}}\mathrm{G}^{0.4}$
Klimkówka 27	418.0–476.0	III Ciężkowice Sandstone	$\mathrm{Br}^{11.5}\mathrm{I}^{4.5}\mathrm{M}^{12.9}\frac{HCO_3^{58}Cl^{42}}{Na^{97}}\mathrm{G}^{0.2}$
Rymanów 2	403.0–501.0 478.0–588.0	III and IV Ciężkowice Sandstones jointed horizons	$\mathrm{Br}^{7.1}\mathrm{I}^{2.0}\mathrm{M}^{8.5}\frac{HCO_3^{55}Cl^{45}}{Na^{96}}\mathrm{G}^{0.2}$
Rymanów 5	463.0–554.0	III and IV Ciężkowice Sandstones jointed horizons	$\mathrm{Br}^{3.3}\mathrm{I}^{1.2}\mathrm{M}^{6.5}\frac{HCO_3^{68}Cl^{32}}{Na^{98}}\mathrm{G}^{0.2}$
Lubatówka 14	775.0–782.0 790.0–797.0	II Ciężkowice Sandstone	$\mathrm{Br}^{28.7}\mathrm{I}^{10.1}\mathrm{M}^{18.1}\frac{Cl^{79}HCO_3^{21}}{Na^{96}}\mathrm{G}^{0.3}$
Lubatówka 12	815.0–840.0 891.0–958.0	II and III Ciężkowice Sandstones jointed horizons	$\mathrm{Br}^{32.2}\mathrm{I}^{9.7}\mathrm{M}^{19.1}\frac{Cl^{77}HCO_3^{23}}{Na^{96}}\mathrm{G}^{0.3}$

The abbreviated form of the chemical composition presents specific ions in mg/dm^3, dominant ions in % meq, M (mineralization) in g/dm^3, G (gases – here CO_2) in g/dm^3.

Table 2

Classification of water based on TDS (ppm)
(after Carpenter, 1978)

Krieger (1963)		Davis (1964)	
slightly saline	1000–3000	fresh water	<1000
moderately saline	3000–10000	brackish water	1000–10000
very saline	10000–35000	saline water	10000–100000
brine	35000	brine	>100000

even distant area of origin as a result of sediment compaction, tectonic movements, and other processes (Chave, 1960; Dowgiałło, 1971; Carpenter, 1978; Dowgiałło & Sławiński, 1979).

2. The flysch rocks are marine sediments. Therefore, the seawater is an appropriate reference solution with which the mineralized waters occurring here should be compared. Such a comparison is justified because seawater composition is considered to have been constant since the Cambrian (Holland, 1984).

3. In the area of Iwonicz anticline the Ciężkowice Sandstone and partly the Czarnorzeki Sandstone are the main reservoir of oil (Wdowiarz S., 1985; Wdowiarz S., *et al.*, 1977; Kulikowska & Pilich, 1978). Thus, these waters occurring in the immediate vicinity of oil fields must be counted among oil-associated waters, the so-called oil-field brines.

Origin of ionic ratios

In order to test the origin of ionic ratios and chemical modification of the Iwonicz anticline mineralized waters, their affinity to oil-field brines and seawater was examined.

It should be underlined that the widely used term "oil-field brines" ("oil-field waters") is not a genetic one. In papers written in English this term is used to determine all types of oil-associated waters often having very different chemical compositions and very different values of TDS (Collins, 1975; Hounslow, 1995). Their origin is not univocally defined. It doesnot known what quantity of water, being the component of oil-field brines, originates directly from processes taking place during oil formation, what quantity of water – if any – are connate waters (old seawater trapped within marine sediments), and what is the share of meteoric water flushing the underground rock environment by gravity driven flow. However, an attempt at defining the Iwonicz anticline mineralized groundwaters as oil-field brines appears to be very important. It determines the further basis for analysis of particular geochemical processes affecting the evolution and modification of their salinity and chemical composition not only within the Iwonicz anticline, but also within the other folded structures of the Central Carpathian Synclinorium.

Chemical relations among oil-field brines, seawater and mineralized waters of Iwonicz anticline can be clearly observed using Stiff diagrams presented in Fig. 3. Ratios of six dominant ions for Iwonicz anticline groundwaters show considerable similarity rather to typical oil field-brines distinguished by Hounslow (1995) than to seawater.

In order to diversify main types of brines with respect to the content of four widely determined ions, namely: Na$^+$, Ca^{2+}, Cl$^-$, $SO4^{2-}$, the so-called Brine Differentiation Plot (BDP) can be used (Fig. 4).

Mineralized groundwaters in the Iwonicz anticline are not placed within waters recognized by Hounslow (1995) as typical "oil-field brines" (investigations based on brines from some areas of the USA and Canada). Nevertheless, they are most similar to them among other typical brines shown in the plot and seem to be placed rather far from seawater.

To corroborate or deny the close chemical relations between seawater and mineralized waters under consideration the ratios of the most conservative elements Cl : Br have been examined. During seawater dilution by meteoric water the ratio Cl : Br remains constant; during evaporation of seawater this ratio is constant until halite saturation is reached, at which point Cl is preferentially removed from the solution (Collins, 1975; Connolly *et al.*, 1990; Appelo & Postma, 1996). Presented in Fig. 5, the seawater evaporation trajectory (S-E-T) depicts this relation (Carpenter, 1978; Connolly *et al.*, 1990).

The Iwonicz anticline waters are plotted almost directly on the S-E-T of log Cl vs log Br at concentrations lower than seawater. It indicates approximately the same Cl : Br ratios of considerably diluted solution as compared to seawater. The position of considered mineralized waters on this S-E-T certifies to their seawater origin and the subsequent dilution by meteoric water. Because the mixing with recent seawater has been denied, the mixing with a kind of connate water must have occurred. In this particular case of mineralized waters in the Iwonicz anticline, the processes of dissolution of salts (evaporates) should be excluded. There is no evidence of subaerial evaporation of seawater – in other words, there are no typical brines (TDS > 35 g/dm^3). Also,

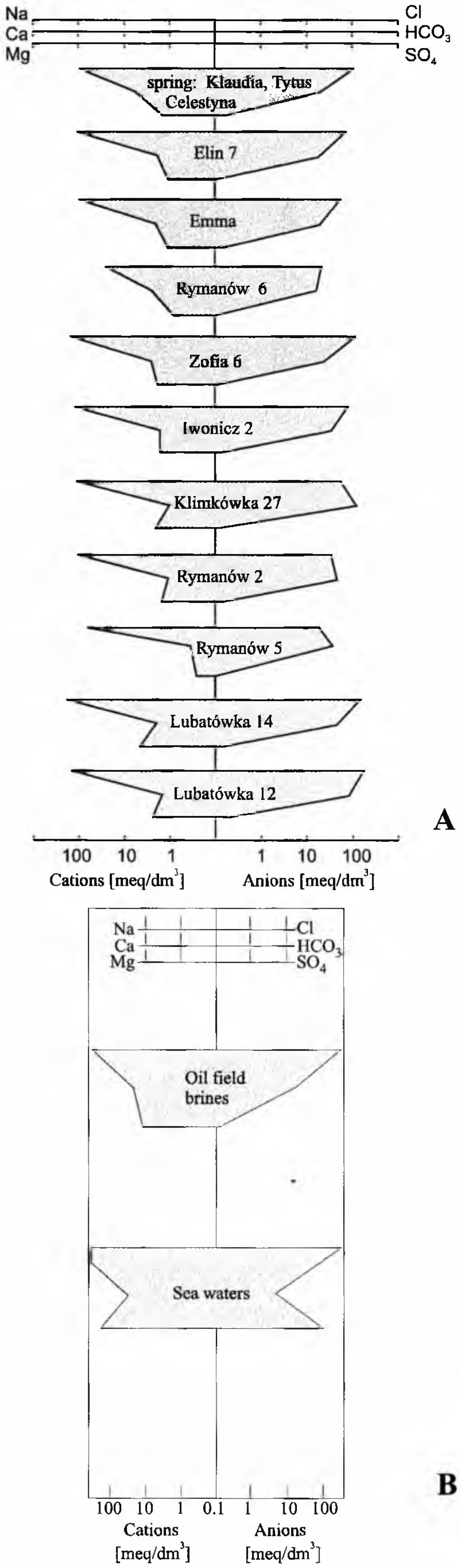

Fig. 3. Stiff diagrams for Iwonicz anticline mineralized groundwaters (**A**), and distinguished by Hounslow (1995) typical seawater and oil-field brines (**B**)

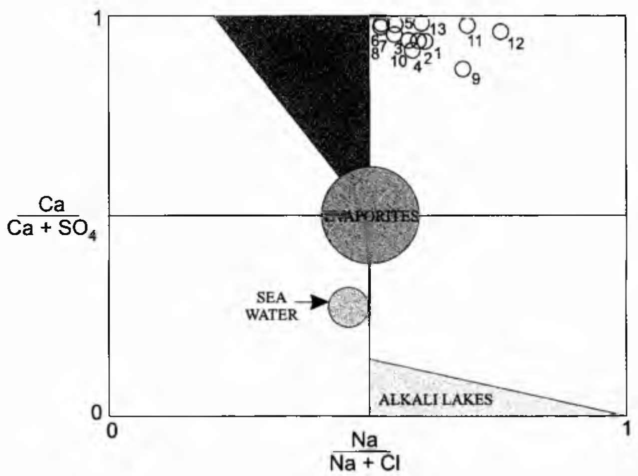

Fig. 4. Brine Differentiation Plot (BDP) (after Hounslow, 1995) and mineralized waters from Iwonicz anticline (open circles). Content of particular ions in mol/dm^3

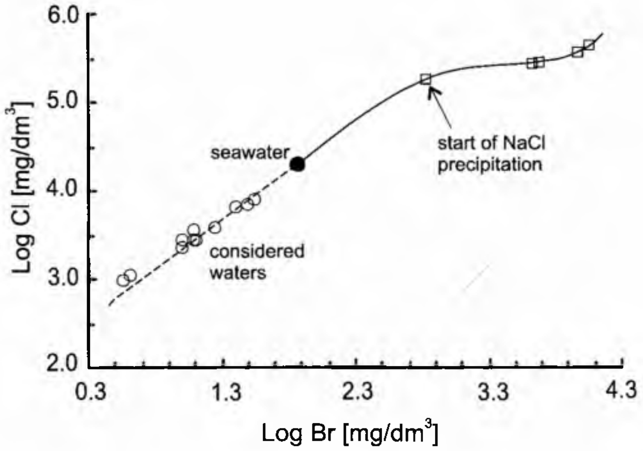

Fig. 5. Log Cl versus log Br for Iwonicz anticline mineralized waters with the seawater evaporation trajectory for reference; open circles – considered waters of Iwonicz anticline; open squares – particular stages of seawater evaporation

there is no large excess of Cl concentration relative to Br which is observed in waters affected by halite dissolution (Connolly *et al.*, 1990). However, in general view on the wide and discussible area of groundwater mixtures, and taking into consideration other types of mineralized waters in the Central Carpathian Synclinorium, such processes as subaerial evaporation of seawater, dissolution of evaporates, interactions of typical brines with fresh water or/and seawater should not be absolutely excluded (Dowgiałło & Sławiński, 1979). It has been clearly explained in Fig. 6 derived by Carpenter (1978).

The plot (Fig. 6) illustrates the mixing effects of fresh and seawater with halite-saturated brines that are not in contact with halite. The mixing of such brine (of composition A) with fresh water causes the Cl and Br concentrations to move along a line with a 1:1 slope toward B. The mixing of halite-saturated brines (A) with seawater trends toward the composition of seawater. The percentages of seawater in brine – seawater mixtures are indicated by nearly horizontal isopleths. The considered hydrogeochemical data from Iwonicz anticline corroborates undoubtedly rather the seawater end-member than the brines of other origin.

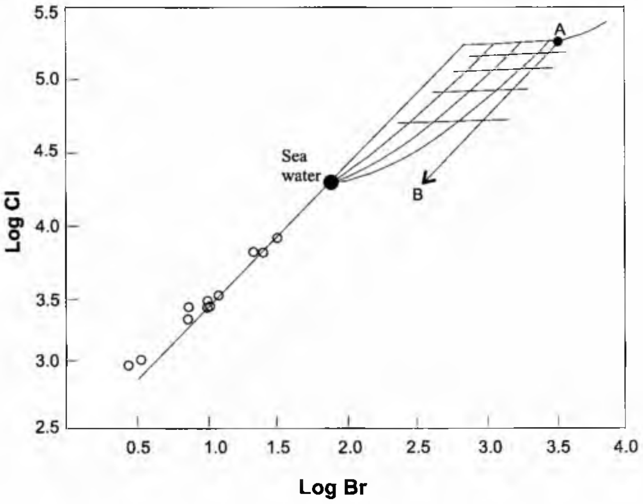

Fig. 6. Mineralized waters of Iwonicz anticline (open circles) and relationship between Cl and Br as a result of mixing NaCl-saturated brines with fresh water and with seawater. (Plot after Carpenter, (1978) modified by the author). For explanation see the text

Geochemical modifications of ionic ratios and chemical composition

Why the similarities to seawater in content of other ions (not only the most conservative ones) are not recognizable on Stiff diagrams or the BDP plot?

There are several reasons for such complex situation. First of all, we are dealing with solutions highly diluted as related to original seawater. This is certified by reduced TDS of waters under consideration: they range from 3.3 g/dm^3 to 19.9 g/dm^3 in relation to about 35 g/dm^3 in seawater. Moreover, concentrations of dominant ions have been modified during diagenetic or post-diagenetic processes, formation and migration of oil and subsequent flushing by very diluted solutions like meteoric waters.

On the Stiff diagrams (Fig. 3) very low (close to zero) concentrations of sulfates ($SO4^{2-}$) are noticeable in all samples of waters under consideration. It is an evidence for a reducing environment and presence of organic matter. The same may be seen in BDP: the ratios $Ca^{2+}/Ca^{2+} + SO4^{2-}$ are close to 1 because of scarcity of sulfates. Another characteristic feature in the chemical composition of mineralized waters in the Iwonicz anticline is an enrichment in iodine (table 3). Generally (and it has been proved experimentally) the main source of iodine content in groundwaters comes from the mineralization of organic matter like algae and other marine organisms from ancient seawater (Dowgiałło *et al.*, 1969; Dowgiałło, 1971; Collins, 1975; Kudelskij, 1976; Krainow & Szwiec, 1980). Although, the concentration of different iodine compounds in the marine and oceanic sediments decreases with depth; it increases with depth in interstitial waters (Shishkina & Pavlova, 1965 after Collins,

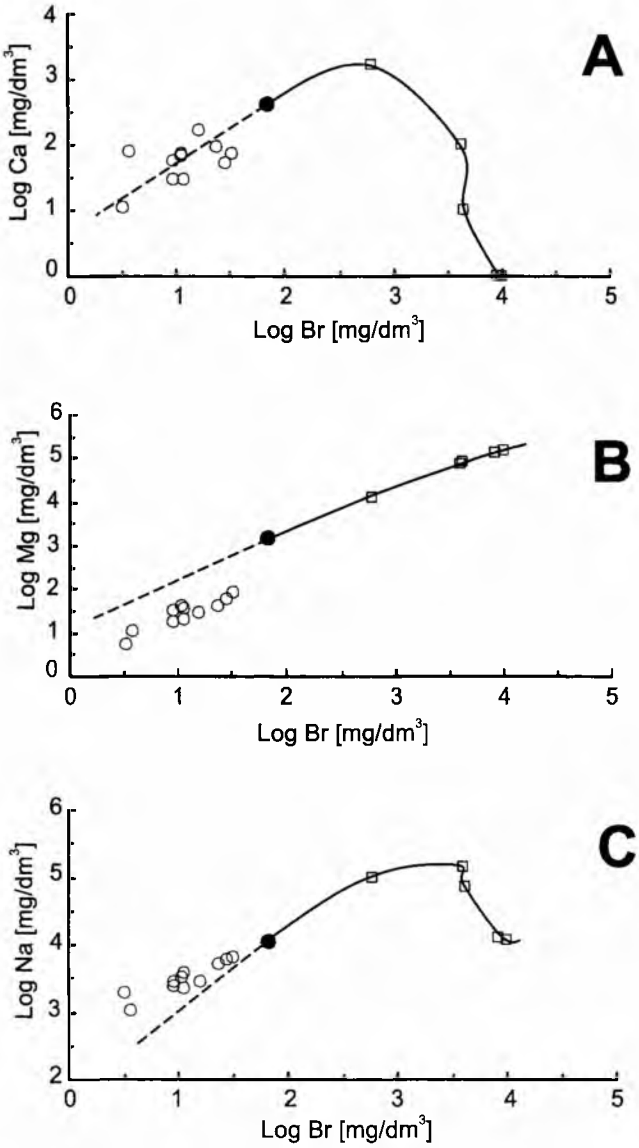

Fig. 7. Plots: **A** – log Ca vs log Br, **B** – log Mg vs log Br, **C** – log Na vs log Br, for Iwonicz anticline mineralized waters (open circles); seawater ewaporation trajectories (open squares) for reference

1975). Thus, some mechanisms such as leaching or solubilization of iodine, iodate, or other iodide compounds, ion filtration, anion exchange, and desorption had to occur to account for this enrichment in the aqueous phase (Collins, 1975).

All these features like reducing environment, scarcity of sulfates and high iodine content allow to qualify mineralized waters of Iwonicz anticline among oil-field brines. On the other hand, because of these factors the seawater end-member for the considered mineralized waters can hardly be distinguished at first glance. In order to see clearly the latter, most important modifications in chemical composition and ionic ratios of considered waters in relation to seawater plots of log Br versus logs of another compound with S-E-T for reference have been constructed, as shown in Fig. 7.

Table 3

Selected ionic ratios for the Iwonicz anticline mineralized groundwaters and seawater

Well or spring	Br/Cl · 10^3	Br/Na · 10^3	Br/Ca	Br/Mg	I/Cl · 10^3
	mg/l				
spring Celestyna	4.49	6.12	0.11	0.60	1.33
spring Klaudia	4.61	6.29	0.10	0.61	1.00
spring Tytus	3.95	5.39	0.09	0.54	1.00
Elin 7	3.26	3.84	0.16	0.53	1.11
Emma	4.16	4.83	0.16	0.56	1.12
Rymanów 6	3.44	3.59	0.05	0.33	1.29
Zofia 6	3.83	4.62	0.26	0.59	0.96
Iwonicz 2	3.25	3.35	0.17	0.28	1.31
Klimkówka 27	4.38	2.94	0.41	0.33	1.70
Rymanów 2	3.21	2.57	0.24	0.23	0.92
Rymanów 5	3.35	1.67	0.31	0.64	1.25
Lubatówka 14	4.35	4.78	0.56	0.52	1.53
Lubatówka 12	4.02	4.93	0.44	0.42	1.21
seawater	**3.53**	**6.38**	**0.16**	**0.05**	**3 · 10^{-3}**

Table 3 shows calculated selected ionic ratios of waters under consideration and of seawater in order to verify relations derived from plots in Fig. 7.

On the plots A and B (Fig. 7) the depletion in concentration of divalent cations: Mg^{2+} and Ca^{2+} may be observed. Only waters from springs and from the shallowest wells like Rymanów 6, Elin 7 are slightly enriched in Ca^{2+}. The chemistry of divalent cations in waters can be monitored by considering the amount of divalent cations charge balanced by Cl (Connolly *et al.*, 1990). This relation, called the Carpenter Function (CF), is defined as:

$$CF = Ca^{2+} + Mg^{2+} + Sr^{2+} - SO_4^{2-} - HCO_3^{-} \quad \text{(in meq/l)}$$
(Carpenter, 1978; Connolly *et al.*, 1990)

Mineralized waters of the Iwonicz anticline are characterized by negative CF values because of extremely high carbonate alkalinity (concentration of HCO_3^-) and high proportions of Na^+ relative to divalent cations. They belong to the Cl–HCO_3–Na and HCO_3–Cl–Na classes and undoubtedly contain a large contribution of meteoric waters. The most negative values of CF are connected with waters of the HCO_3–Cl–Na class withdrawn by such wells as Klimkówka 27, Rymanów 2 and Rymanów 5. Basing on literature a tentative idea explaining such anomalous alkalinity of considered waters could be developed. Usually, a high alkalinity is caused by the carbon dioxide dissolved in water (Connolly *et al.*, 1990). Carbon dioxide is the main byproduct of both the organic matter oxidation and the sulfate reduction (Collins, 1975).

During diagenetic processes anaerobic bacteria attack the sulfate ion which is the second most important ion in the seawater (Collins, 1975). During this process the sulfate is reduced finally to sulfide:

$SO_4^{2-} + 1.33CH_2 + 2H^+ \rightarrow H_2S + 1.33\ CO_2 + 1.33H_2O$ sulfate reduction (Carpenter, 1978)

Meteoric water flowing through the Ciężkowice Sandstone and Variegated Shale or the Czarnorzeki Beds would cause the additional oxidation of organic matter in surrounding shales producing some quantities of CO_2 according to the schematic reaction (Connolly *et al.*, 1990):

$C_2H_m + O_2 \rightarrow nCO_2 + 1/2mH_2O$ bacterial oxidation of organic matter (Collins, 1975)

Depletion in divalent cations and high proportions of Na^+ (Fig. 7C) can be explained by simple cation exchange reactions with clay minerals. Usually Na^+ is removed from solution to clay minerals. However, if the waters characterized by low ionic strength, which depends first of all on concentrations of ions in the solution, than Ca^{2+} is removed from solution and replaced by Na^+ (Connolly *et al.*, 1990; Hounslow, 1995). This process is often called as natural softening and can be schematicly written as follows:

$Na_2\text{-Clay} + Ca^{2+} \rightarrow 2Na^+ + \text{Ca-Clay}$ (Hounslow, 1995)

This enrichment in Na^+ cations seems to be the main cause of shifting mineralized waters of Iwonicz anticline from "oil-field brines" field to the right on BDP plot (Fig. 4).

CONCLUSIONS

Mineralized groundwaters in the Iwonicz anticline belong to two main hydrogeochemical classes: $Cl - HCO_3 - Na$ and $HCO_3 - Cl - Na$. Both of them reveal enrichment in bromine and iodine. TDS of the considered waters varies from about 3.3 g/dm^3 to about 19.9 g/dm^3 which allows counting them among brackish and saline waters.

The area of occurrence, reducing environment, scarcity of sulfates and enrichment in iodine are the main features allowing to count those waters among associated with bitumens, the so-called "oil-field brines". On the other hand, ionic ratios of the most conservative elements like Cl and Br show close connection with seawater –undoubtedly being the kind of connate water. Almost the same Cl : Br ratios but in a much more diluted solution than seawater and their position on S-E-T certify to their seawater origin and their subsequent dilution by meteoric water.

Elemental seawater evaporation trajectories as well as Stiff and BDP diagrams show modifications in concentration of dominant ions: depletion in divalent cations (negative Carpenter Function values), high proportions of Na^+ relative to divalent cations, extremely high carbonate alkalinity, depletion in sulfates. Undoubtedly, such modifications took place during various diagenetic or post-diagenetic processes, the formation and migration of oil and subsequent flushing by very diluted solutions, namely meteoric waters.

All these processes taking place in the complex hydrogeological settings of the Central Carpathian Synclinorium are the reason why the original seawater end-member, not only in considered mineralized waters of the Iwonicz anticline but also in waters of other folded structures, may be hard to distinguish without detailed analysis of chemical modifications.

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Streszczenie

SKŁAD CHEMICZNY I POCHODZENIE STOSUNKÓW JONOWYCH W WODACH ZMINERALIZOWANYCH ANTYKLINY IWONICKIEJ (POLSKIE KARPATY ZEWNĘTRZNE)

Adam Porowski

Antyklina Iwonicza Zdroju jest jedną ze struktur fałdowych centralnego synklinorium karpackiego, znajdującego się w obrębie jednostki śląskiej karpat fliszowych SE Polski. Głównym kolektorem wód zmineralizowanych, jak i towarzyszącej im ropy naftowej, są tutaj piaskowce ciężkowickie i częściowo – czarnorzeckie.

Wody zmineralizowane antykliny Iwonicza Zdroju należą do dwóch klas hydrogeochemicznych: Cl – HCO_3 – Na i HCO_3 – Cl – Na. Obszar występowania tych wód, redukcyjne środowisko, znikome ilości siarczanów, wzbogacenie w jod i brom są głównymi cechami pozwalającymi na zaliczenie ich do wód towarzyszących ropie naftowej, tzw. "oil-field brines". Analiza składu chemicznego tych wód w oparciu o diagramy Stiffa oraz wykres BDP potwierdza taką wstępną klasyfikację. Z jednej strony, sklasyfikowanie tych wód wśród towarzyszących ropie naftowej ma duże znaczenie, gdyż określa podstawy do dalszej analizy szczególnych procesów geochemicznych wpływających na ewolucję ich zasolenia i modyfikację składu chemicznego nie tylko w obrębie antykliny iwonickiej ale również w obrąbie innych struktur centralnego synklinorium karpackiego. Z drugiej zaś – geneza wód towarzyszących ropie naftowej nie jest jednoznacznie wyjaśniona, szczególnie jeżeli chodzi o wody nie będące typowymi solankami jak te w obrębie antykliny iwonickiej, których mineralizacja waha się w granicach od 3,3 do 19,9 g/dm^3. Używany w literaturze angielskiej termin "oil-field brines" nie jest terminem genetycznym. Nie jest wyjaśnione jednoznacznie jakie są w nich proporcje wód powstających podczas formowania się ropy naftowej, wód morskich czy wód atmosferycznych infiltrujących grawitacyjnie w podłoże skalne.

Jest wiele procesów geochemicznych wpływających na powstanie wód o wysokiej mineralizacji. W przypadku wód zmineralizowanych antykliny iwonickiej jednym z najbardziej prawdopodonych jest proces mieszania się wód atmosferycznych z wodami morskimi pogrzebanymi w osadach w przeszłych epokach geologicznych tzw. "connate waters". Z geologicznego punktu widzenia proces taki wydaje się być uzasadniony gdyż osady fliszowe, budujące centralne synklinorium karpackie, osadzały się w środowisku morskim, a skład wody morskiej jest uznawany za niezmienny od kambru. W celu potwierdzenia bliskiego pokrewieństwa wód zmineralizowanych antykliny iwonickiej z wodą morską przeanalizowano stosunki najbardziej konserwatywnych jonów: Cl : Br na tle wykresu ewaporacji wody morskiej. Położenie stosunków Cl : Br niemal dokładnie na przedłużeniu trajektorii ewaporacji wody morskiej potwierdza pochodzenie rozpatrywanych wód od wody morskiej rozcieńczonej wodami atmosferycznymi. Podobieństw do wody morskiej nie widać jednak podczas prostej analizy zawartości głównych jonów na wykresach Stiffa i BDP. Taka skomplikowana sytuacja wynika przede wszystkim z tego, że mamy do czynienia z wodami rozcieńczonymi w stosunku do wody morskiej, a ich skład chemiczny został dodatkowo zmodyfikowany podczas różnych procesów diagenetycznych i postdiagenetyczny jak: mineralizacja materii organicznej, formowanie się i migracja ropy naftowej, redukcja siarczanów, wymiana jonowa z minerałami ilastymi itp.

Z uwagi na to, iż mamy do czynienia z roztworami rozcieńczonymi w stosunku do wody morskiej nie ma możliwości analizy procesów, które świadczyłyby o innej genezie badanych wód, czego nie można definitywnie wykluczyć na tym etapie badań.