

ON THE ORIGIN OF CHLORIDE WATERS IN THE POLISH FLYSCH CARPATHIANS

ANDRZEJ ZUBER¹, JÓZEF CHOWANIEC¹, MACIEJ BOROWIEC¹

Abstract. Chloride waters in the Polish Flysch Carpathians are remnants of marine sedimentation water which was chemically and isotopically changed due to ultrafiltration and the release of dehydration water (diagenetic water) during the burial diagenesis of clay minerals. In the western part of the study area, the diagenetic end-member is characterized by $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values of about +6.5 and –30.0‰, respectively, and Cl^- content in the range of 3.8 and 13.8 g/dm³. In some fault areas, such waters migrate to the surface and mix with local meteoric waters as indicated by mixing lines in $\delta^{18}\text{O}$ – $\delta^2\text{H}$ and $\delta^{18}\text{O}$ – Cl^- graphs. In several wells of the eastern part, waters containing a significant proportion of marine water occur. However, in majority of deep wells, mixtures of diagenetic and meteoric waters of Quaternary and pre-Quaternary climates are present, as deduced from $\delta^{18}\text{O}$ – Cl^- linear relations. In most cases, they do not exhibit linear relations also expected in $\delta^{18}\text{O}$ – $\delta^2\text{H}$ graphs due to the shifts of $\delta^2\text{H}$ to heavier isotopic values supposedly caused by involvement of water in the generation of hydrocarbons.

Key words: chloride waters, ultrafiltration, diagenetic waters, oil-field waters, catagenesis, Flysch Carpathians.

INTRODUCTION

In the Polish Carpathians there are occurrences of highly mineralized waters of different types that are used for medical purposes or production of bottled waters. Their origin is of importance for determining available resources, and for a proper management. Particularly interesting is the origin of numerous occurrences of chloride and chloride CO_2 -rich waters in the flysch formations. On the basis of chemical data, the earliest opinions related their origin to mixing between marine sedimentation and meteoric waters. However, Leśniak (1980), and Dowgiałło and Leśniak (1980) showed their end-members with the highest Cl^- contents to be characterized by $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values of about +6.5 and –25‰, respectively. Such isotopic composition excluded a direct marine origin and suggested the presence of dehydration waters released in the metamorphic processes of clay minerals, similar to those found in California by White *et al.* (1973).

Trying to solve the problem of different Cl^- contents in the end-members having the same isotope composition, Leśniak (1980), and Dowgiałło and Leśniak (1980) proposed a model of mixing between metamorphic, marine and meteoric waters. Zuber and Grabczak (1985) pointed out incon-

sistencies of that model, and suggested the metamorphic dehydration as the only source of water in the end-members, but they were unable to explain reasonably the origin of chlorides. Oszczytko and Zuber (2002) excluded metamorphism as the source of dehydration water and suggested the diagenesis of clay minerals, in which enrichment of water in Na^+ occurs. However, the origin of highly different Cl^- concentrations in waters with similar isotopic composition remained unexplained.

Zuber and Chowaniec (2009) presented a conceptual model in which ultrafiltration and dehydration of clay minerals during burial diagenesis are the main processes in the evolution of chloride waters in flysch formations of the Polish Carpathians. According to these authors, at the early diagenesis, the compaction of clay sediments is accompanied by ultrafiltration process (reverse osmosis) which may lead to a significant enrichment of marine pore water in chlorides, without any significant change in the isotopic composition of water.

In the second stage of the diagenesis, the compaction is accompanied by dehydration of clay minerals initiated at temperatures of about 70°C. The dehydration starts to change

¹ Polish Geological Institute – National Research Institute, Carpathian Branch, Skrzatów 1, 31-560 Kraków, Poland; e-mail: andrzej.zuber@pgi.gov.pl, jozef.chowaniec@pgi.gov.pl, maciej.borowiec@pgi.gov.pl

the isotopic composition of pore water and leads to the dilution of chlorides, whereas the ultrafiltration still leads to the chemical enrichment. In the final stage of diagenesis, when the temperature of about 170–190°C is reached, the isotopic composition of pore water is in equilibrium with the remaining bound water and characterized in the Polish Flysch Carpathians by $\delta^{18}\text{O}$ and $\delta^2\text{H}$ end values in the ranges of about from +6 to +7‰ and from –30 to –20‰, respectively. Depending on the mineralogy of clay minerals undergoing diagenesis, significantly wider ranges can be expected in other world regions (Longstaffe, 1987).

Further compaction and release of dehydration water does not change the isotopic composition of pore water, however still contributing to its freshening. The final chloride content depends on that whether ultrafiltration or dilution dominates during the whole process of burial diagenesis. In the Polish Carpathians, the final Cl^- content in purely dehydration waters ranges between 3.8 and 13.8 g/dm³, whereas in waters with a significant contribution of the remnant of marine water, the largest observed concentration is close to 26 g/dm³. For “metamorphic” waters in California, White *et al.* (1973) reported Cl^- contents from 0.75 g/dm³ (Sulphur Bank, Ink Spring) to about 15 g/dm³ (Cymric field, well 22-256).

Mineralogy of flysch shales in the Magura Unit shows that they were formed in the process of burial diagenesis in temperatures below 200°C (Świerczewska, 2005; Środoń, 2007). In addition to ultrafiltration and dehydration, other processes also take place, among them the release of Na^+ during the diagenetic changes of clay minerals (Hower *et al.*, 1976; Środoń *et al.*, 1992), and cation exchange between Ca^{2+} in pore water and Na^+ in minerals. These two processes lead to the relative enrichment of pore water in Na^+ at the cost of other cations, which results in the mNa^+ to mCl^- ratio usually significantly larger than 1 (Zuber, Chowaniec, 2009).

Chloride waters in the western part of the Polish Flysch Carpathians are commonly related by geologists to the sediments of the Magura Unit. However, they may originate in other units as it was shown by Rajchel *et al.* (2004) for diagenetic waters in Sól, which undoubtedly originate in the Sub-Magura Unit and ascend to the surface through the formations of the Magura Unit.

In the eastern part of the Polish Flysch Carpathians, where oil and gas fields exist, relations between the isotope composition and Cl^- contents are not so simple as in the western part, suggesting a possible existence of several different end-components of mixing processes (Porowski, 2006). The aim of the present paper is to describe a possible explanation for these distinct differences in the isotopic compositions of chloride waters between two parts of the Carpathians. No new data are presented, but only the most important findings of Zuber and Chowaniec (2009) are recalled, and the isotope and Cl^- data of Porowski (2006) are given in graphical forms in order to illustrate the hypotheses on the evolution of the isotopic composition of chloride waters in the study area according to the new hypotheses. It will be shown that in addition to ultrafiltration and diagenesis of clay minerals, the isotopic composition of oil field waters may be changed by generation of hydrocarbons (catagenesis). Marine and non-marine organisms are characterized by $\delta^2\text{H}$ values in the ranges of from –166 to –13‰ and from –237 to +66‰, respectively, whereas for crude oil and naturally occurring methane, $\delta^2\text{H}$ values range from –163 to –80‰ and from –531 to –133‰, respectively (Coplen *et al.*, 2002). Therefore, if pore water is involved in the generation of hydrocarbons it may become enriched in deuterium at the cost of hydrocarbons which become depleted.

STUDY AREA

A simplified geological map of the Polish Carpathians is shown in Figure 1. Within the Inner Carpathians (Tatra Mts., Podhale Basin and Pieniny Klippen Belt), there are no occurrences of highly mineralized waters, whereas within the Outer Carpathians and their floor formations, highly mineralized waters are common (Zuber, Chowaniec, 2009). The Outer Carpathians are mainly built of Cretaceous and Paleogene flysch formations (mainly shales and sandstones of different thickness). In the western part, the oldest flysch sediments are of Jurassic age, whereas in the eastern part, the youngest flysch sediments are of Miocene age. Flysch formations were overthrust and folded in a number of orogenic cycles in the Paleogene and Neogene up to the late Miocene. There are several orogenic units (nappes) which were overthrust from the south to the north-west and north-east. Their tectonic and lithostratigraphy differ as a result of differences which existed in sedimentary basins and overthrust distances. In some re-

gions, the flysch formations cover Miocene sediments, or lie below them.

Significant differences in the styles of folding and lithologies between the western and eastern parts can be seen from the cross-sections shown in Figures 2 and 3. In the western part, the dominating Magura sandstones have poor reservoir characteristics, whereas in the eastern part, the Krosno sandstones dominate, which have much better characteristics as collectors of fluids.

Sampling areas of chloride waters related to flysch formations in the western part (W), for which isotope data are available, are shown in Figure 1 with numbers as in Zuber and Chowaniec (2009). In areas of Nos. 1, 3, 11 and 16, chloride waters occur only in deep wells (500–1830 m) whereas in other areas they occur in springs with ‘purely’ diagenetic component also observed at the surface (one site in Szczawnica, No. 9 and one in Sól, 19) or in shallow wells (about 100 m)

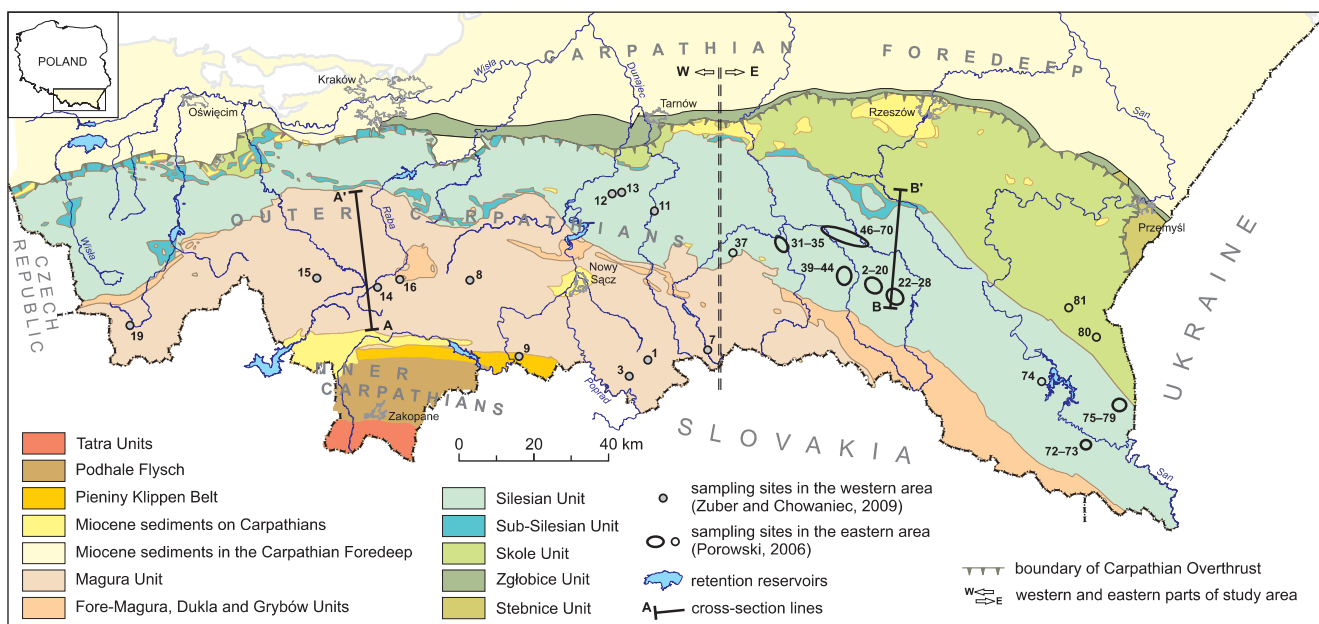


Fig. 1. Simplified geological map of the Polish Carpathians with indicated sampling sites and cross-section lines (samling site numbers as in references)

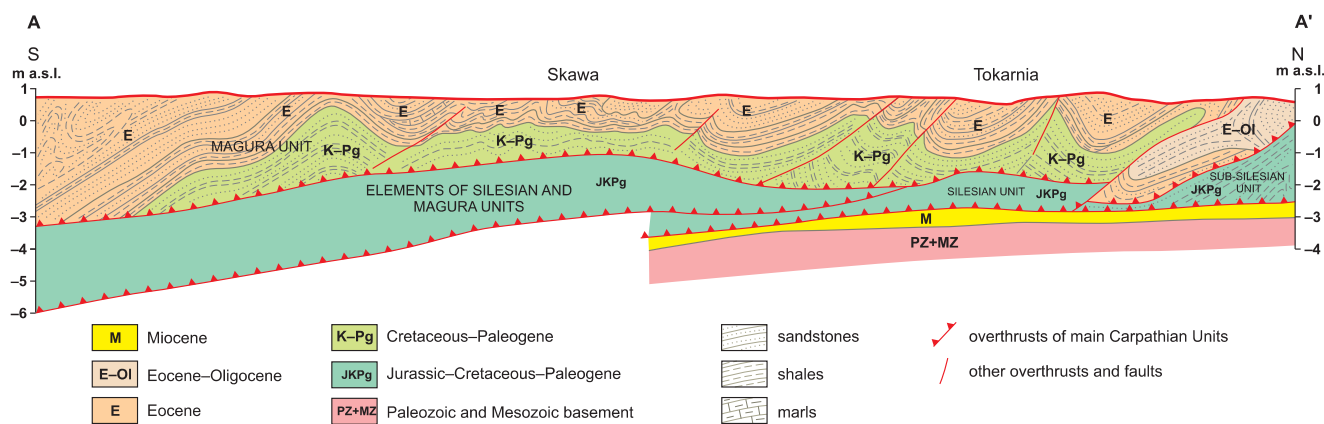


Fig. 2. Simplified geological cross-section through a part of the western area of the Polish Carpathians (adapted from Golonka *et al.*, 1979)

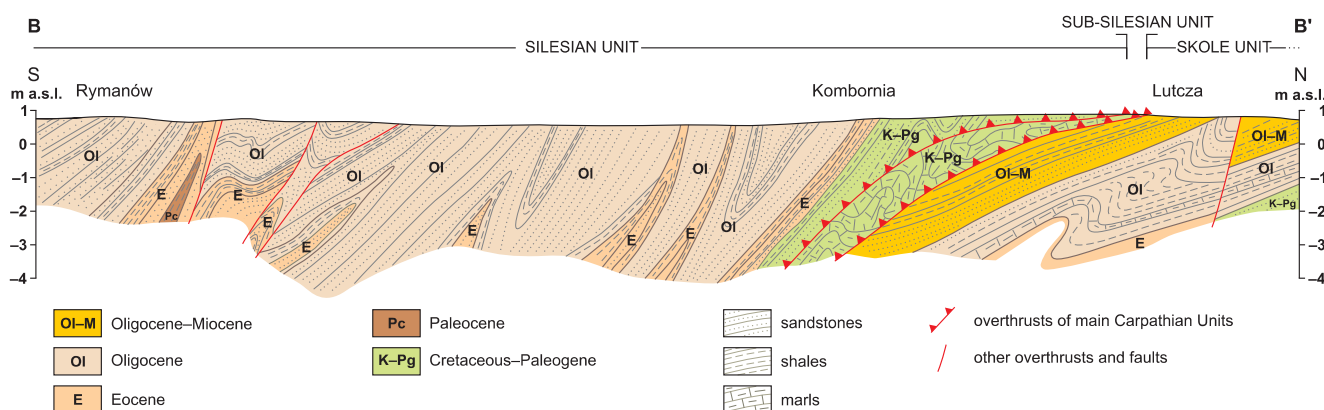


Fig. 3. Simplified geological cross-section through a part of the eastern area of the Polish Carpathians (adapted from Nieścieruk *et al.*, 1995)

in Wysowa (7), Szczawa (8) and Rabka (14). Some of these waters are exploited for therapeutical purposes.

In the eastern part (E), for the sake of the reader, sampling areas are shown in Figure 1 with the same sample numbers as those used by Porowski (2006). Chloride waters in that part of the Carpathians are related to oil and gas deposits, being used for therapeutical purposes in the Iwonicz Spa (samples 2–20)

ISOTOPE AND CHLORIDE DATA

All the data discussed within this work are shown in Figures 4a and b. Possible evolution paths of marine water during diagenesis in the Polish Flysch Carpathians are shown after Zuber and Chowaniec (2009). The lower diagenetic lines describe the typical evolution of oceanic sedimentation pore water caused by admixture of dehydration water released from clay minerals during burial diagenesis. The upper lines represent an example of the evolution of marine pore water, which was first significantly enriched in chlorides due to ultrafiltration. In some fault areas of the western part of the Flysch Carpathians, diagenetic waters ascend to the surface and mix with local modern meteoric waters along typical mixing lines which are also shown in Figures 4a and b. Chloride waters in flysch formations of the eastern part are represented by points, which, with several exceptions, evidently do not fit to the mixing lines observed in the west.

All waters in the east are chemically similar to those in the west, being of Na–Cl, Na–Cl–HCO₃ and Na–HCO₃–Cl types, with TDS contents from several to more than 50 g/dm³ and mNa⁺/mCl⁻ ratio distinctly above 1. As shown by Zuber and Chowaniec (2009), such molar ratio of Na⁺ to Cl⁻ in highly mineralized waters is characteristic for waters of diagenetic origin. Therefore, differences in the isotopic com-

position of waters between the west and east are most probably caused by other reasons than the chemistry of water. In order to find the explanation for the differences in the isotopic composition of waters in the west and east, the data from Figure 4 are separated in the next figures according to the areas of their occurrences.

In Figures 5a and b, the data from the Osobnica–Bóbrka–Rogi fold area are given. Their isotopic composition seen in part (a) suggest a significant contribution of marine sedimentation water and/or evaporated water of warm climates. However, the $\delta^{18}\text{O}$ –Cl⁻ relation seen in (b) indicates mixing between purely diagenetic water (with $\delta^{18}\text{O}$ of about 6–7‰ and Cl⁻ content of about 3.5 g/dm³) and the meteoric water with isotopic composition close to that of modern precipitation, i.e., presumably water of the Quaternary climates. The mixing line from (b) may yield a number of mixing lines in (a), depending on the $\delta^2\text{H}$ values of the diagenetic end-component. The mixing line shown in (a) represents the lowest possible mixing scenario, though, whichever mixing scenario is assumed, the $\delta^2\text{H}$ values are evidently shifted from the mixing line to less negative values (enriched in deuterium). Such shifts can be caused by generation of hydrocarbons (catagenesis), if pore water took part in that process.

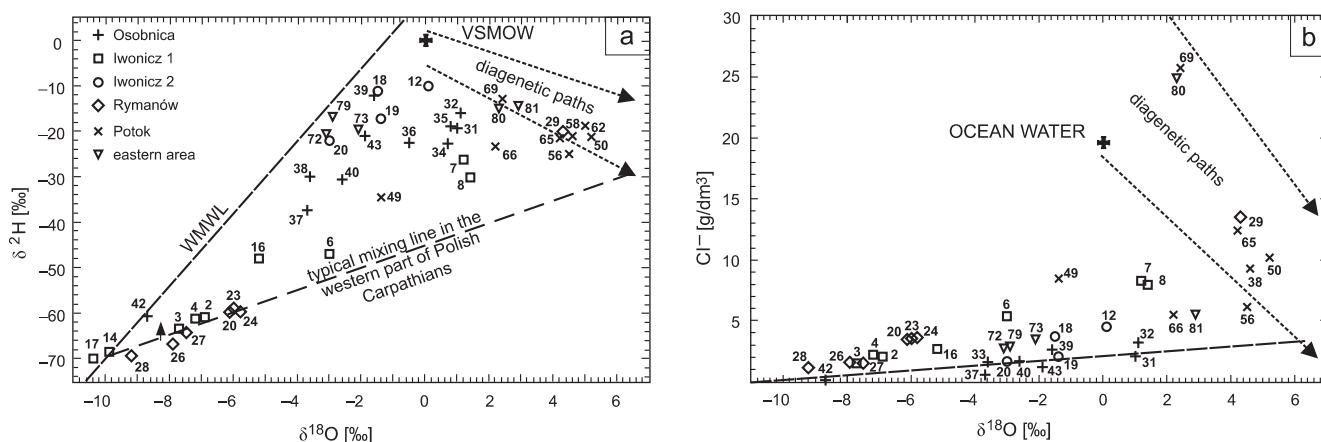


Fig. 4. $\delta^{18}\text{O}$ – $\delta^2\text{H}$ (a) and $\delta^{18}\text{O}$ –Cl⁻ (b) data of Central Carpathian Synclinorium (adapted from Porowski, 2006)

Lines showing the isotopic evolution of water during burial diagenesis and mixing with meteoric waters after uplifting are shown after Zuber and Chowaniec (2009). Sample numbers like in Porowski; isotope data of sample No. 69 after Zuber and Chowaniec (*op. cit.*).

In Figures 6a and b, the data from the Iwonicz Spa–Rudawka Rymanowska fold are given, which can be divided into two groups. For the group 1, the $\delta^{18}\text{O}\text{--Cl}^-$ relation suggests mixing between purely diagenetic water with Cl^- content of about 11 g/dm^3 , and the Quaternary meteoric water. Some samples of that group confirm that hypothesis in (a) whereas four samples are shifted, most probably due the enrichment in deuterium. Sample No. 29 is an exception because most probably it does not contain a meteoric component but about 70% of diagenetic water and 30% of marine water.

A high uncertainty is related to group 2 which is represented only by four samples. Under an assumption that these four samples are representative, the isotopic data of that group seen in Figure 6a suggest mixing between marine water with some contribution of diagenetic water and meteoric water of a very warm pre-Quaternary climate. However, low Cl^- contents rather exclude such a hypothesis, and the mixing line of that group seen in Figure 6b suggests that end-components of the mixing process are represented by pure diagenetic water and meteoric water with $\delta^{18}\text{O}$ values of

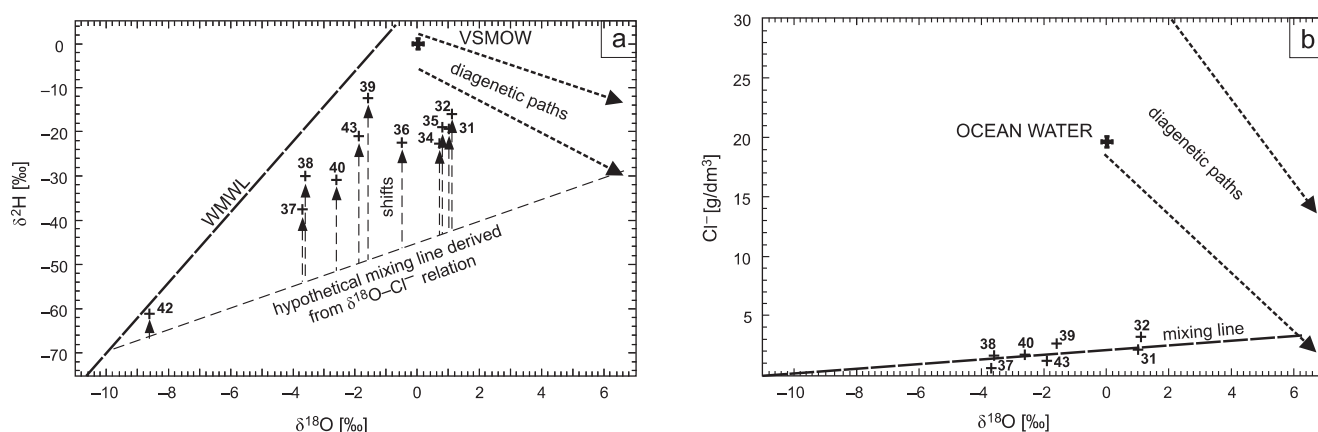


Fig. 5. $\delta^{18}\text{O}\text{--}\delta^2\text{H}$ (a) $\delta^{18}\text{O}\text{--Cl}^-$ (b) data of the Osobnica–Bóbrka–Rogi fold area

Symbols and numbering like in Fig. 4; extrapolated $\delta^{18}\text{O}\text{--Cl}^-$ relationship suggests the heavy end-member to correspond to the final stage of diagenesis whereas the $\delta^2\text{H}$ values in (a) do not correspond to the expected mixing line due to shifts to heavier values (indicated by vertical arrows), which are supposedly caused by catagenesis.

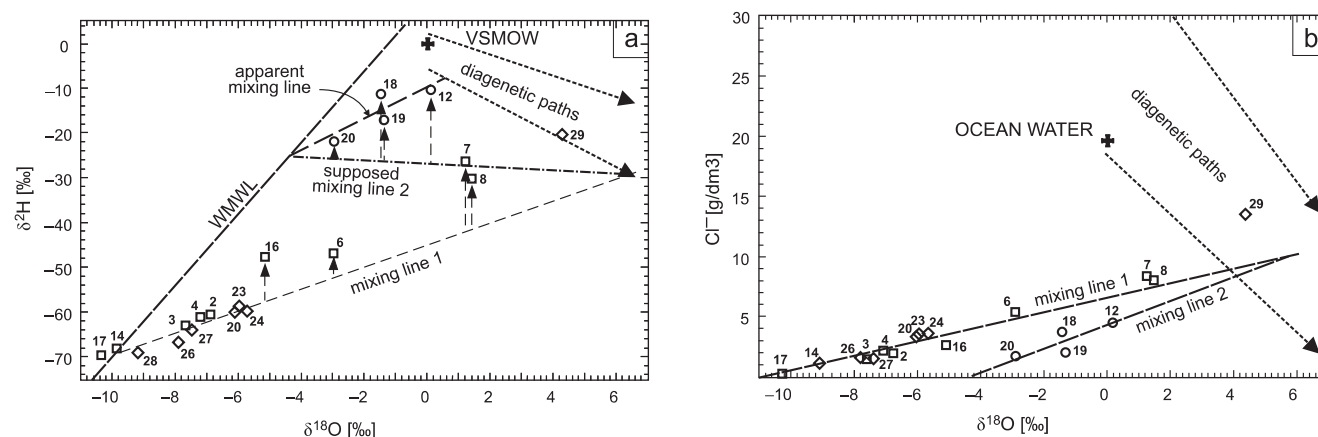


Fig. 6. $\delta^{18}\text{O}\text{--}\delta^2\text{H}$ (a) and $\delta^{18}\text{O}\text{--Cl}^-$ (b) data of the Iwonicz Spa–Rudawka Rymanowska fold area where two groups of samples can be distinguished

Symbols and numbering like in Fig. 4; the $\delta^{18}\text{O}\text{--Cl}^-$ relations suggest a similar isotopic heavy end-member as in Fig. 5 but with a higher Cl^- concentration; the mixing lines shown in (a) are deduced from the $\delta^{18}\text{O}$ values indicated in (b) in disagreement with the $\delta^2\text{H}$ values supposedly shifted by catagenesis; the hypothetical meteoric end-member for group 1 corresponds to recharge in a very warm pre-Quaternary climate.

about -4.5% . The mixing line corresponding to that hypothesis seen in Figure 6a suggest in turn all four $\delta^2\text{H}$ values of that group to be shifted to heavier values.

In Figures 7a and b, the data from the Potok fold area are given. Due to a large scatter of data, it is difficult to draw representative mixing lines. However, large values of the $\text{mNa}^+/\text{mCl}^-$ ratio (1.08–1.52) of points with Cl^- content below 13 g/dm^3 suggest that final stages of diagenesis were probably reached. Mixing lines shown in Figures 7a and b present possible scenarios with a high uncertainty.

According to Zuber and Chowaniec (2009), sample No. 69 with Cl^- content of 25.7 g/dm^3 is a mixture of marine water (60%) enriched in chlorides by ultrafiltration with diagenetic

water (40%). For that sample, a relatively low $\text{mNa}^+/\text{mCl}^-$ ratio of 0.97 corroborates that hypothesis. The presence of such water indicates that diagenesis process has not reached the final stage at some depths of that area, and the molecules of marine water has not been completely removed by dehydration water.

In Figures 8a and 8b, the data from the scattered areas in the most eastern part of the Polish Carpathians are given. In (a), the data slightly scatter along a straight line which suggests mixing between meteoric water of a very warm climate and a mixture of marine and diagenetic waters. However, such a hypothesis is in disagreement with the mixing line and low Cl^- contents seen in (b). Therefore, these waters supposedly result from mixing between purely diagenetic

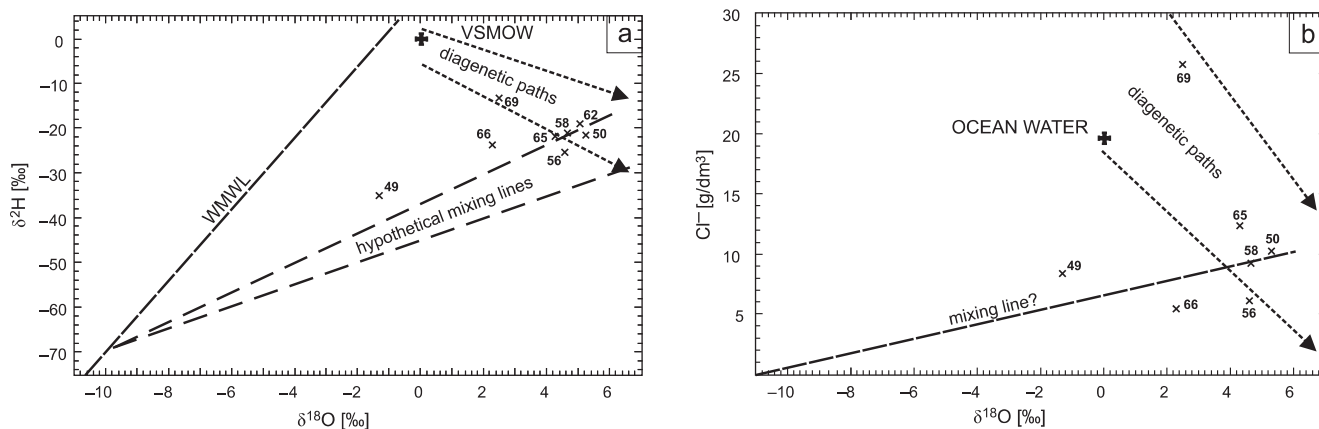


Fig. 7. $\delta^{18}\text{O}$ – $\delta^2\text{H}$ (a) and $\delta^{18}\text{O}$ – Cl^- (b) data of the Potok fold area

Symbols and numbering like in Fig. 4. The $\delta^{18}\text{O}$ – Cl^- data are highly scattered which makes difficult to draw a mixing line; however, if mixing is assumed to be like that given by line 1 in the previous example, several mixing scenarios can be assumed for $\delta^{18}\text{O}$ – $\delta^2\text{H}$ relations in (a), which either suggest large or negligible shifts of $\delta^2\text{H}$ values.

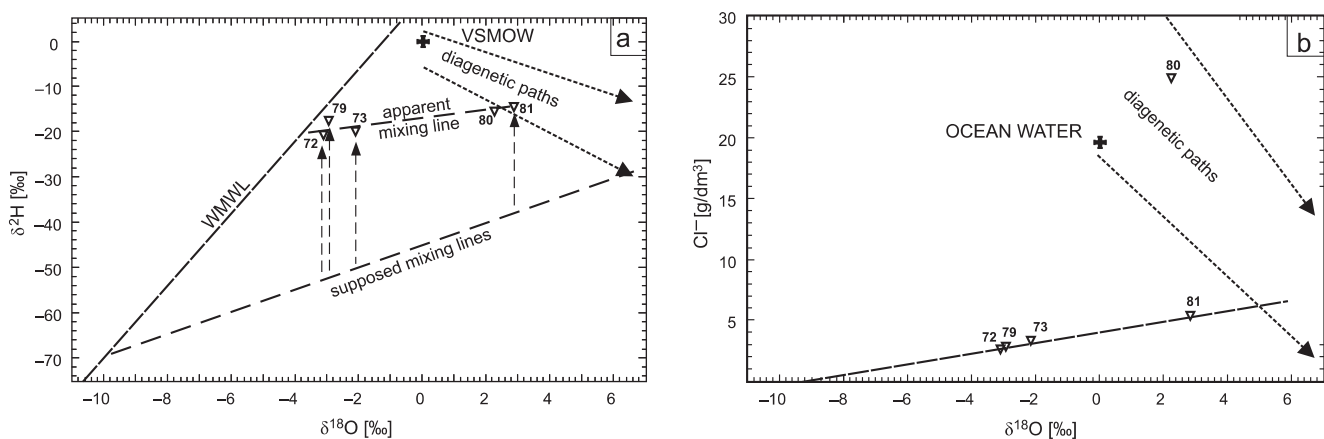


Fig. 8. $\delta^{18}\text{O}$ – $\delta^2\text{H}$ (a) and $\delta^{18}\text{O}$ – Cl^- (b) data of the eastern part of the study area

Symbols and numbering like in Fig. 4.

and meteoric water of a Quaternary climate with a significant enrichment in ^2H due to the generation of hydrocarbons. Samples 80 and 81 have practically the same isotope composition but their origin significantly differs. Sample 80 is an exception similar to sample 69 in the Potok fold area, i.e. it still contains a large amount of preserved sedimentation water of marine origin mixed with diagenetic water, whereas

sample 81 represents pure diagenetic water partly diluted by meteoric water.

Judging from the position of data in Figures 5–8, the generation of hydrocarbons took place mainly after the mixing event, otherwise the hypothetical diagenetic end-components should be represented by heavier $\delta^2\text{H}$ values, which cannot be excluded in some cases, e.g. in the Potok fold (Fig. 7).

DISCUSSION AND CONCLUSIONS

Chlorides in waters in the western part of the Polish Flysch Carpathians are of marine origin, but the isotopic composition of these waters is in most cases completely changed by contribution of dehydration water released during the burial diagenesis of clay minerals. As a consequence of diagenetic processes, the final preserved pore waters can be regarded as being of diagenetic origin. In several fault areas of the western part of the Polish Carpathians, these diagenetic waters travel to the surface and mix with local meteoric waters. Mixing process is well documented by typical mixing lines in $\delta^{18}\text{O}$ – $\delta^2\text{H}$ and $\delta^{18}\text{O}$ – Cl^- or $\delta^2\text{H}$ – Cl^- graphs (Zuber, Chowaniec, 2009).

The isotope and chemical data of chloride waters from the eastern part of the Polish flysch Carpathians were presented by Porowski (2006). Neither the isotope data nor the chloride data of these waters exhibit a simple mixing process like that observed in the western part. However, as shown within the present work, when the data from different fold areas are considered separately, most samples show linear rela-

tions in $\delta^{18}\text{O}$ – Cl^- graphs, which are typical for a two-component mixing between typical diagenetic water and meteoric water of either Quaternary or pre-Quaternary climate. In $\delta^{18}\text{O}$ – $\delta^2\text{H}$ graphs, the linear relations are in most cases distorted by shifts of $\delta^2\text{H}$ to heavier values supposedly caused by the involvement of pore water in the generation of hydrocarbons. Occasionally occur waters with isotopic composition and chloride contents indicating only a partial removal of sea water molecules by molecules released during the diagenesis, which additionally complicates the picture in the eastern part.

Undoubtedly isotopic composition of waters in the eastern part of the study area differs from that in the western part, indicating to differences in the diagenesis stages and in mixing processes with meteoric waters. All these differences can result from differences in tectonic structures and orogenic history, lithology and depths of flysch formations, and perhaps also the lithology of bedrocks. Further studies are needed to clarify which factors played the main role in the formation of waters in the both parts of the study area.

REFERENCES

- COPLIN T.B., HOPPLE J.A., BÖHLKE J.K., PEISER H.S., RIEDER S.E., KROUSE H.R., ROSMAN K.J.R., DING T., VOCKE R.D., RÉVÉSZ K.M., LAMBERTY A., TAYLOR P., De BIÈVRE P., 2002 — Compilation of minimum and maximum isotope ratios of selected elements in naturally occurring terrestrial materials and reagents. Water-Resources Investigations Report 01-4222. USGS, Reston.
- DOWGIAŁŁO J., 1980 — Polygenetic model of the Carpathian chloride waters and its some consequences. *In: Współczesne problemy hydrogeologii*: 275–290. UW, Warszawa [in Polish].
- DOWGIAŁŁO J., LEŚNIAK P.M., 1980 — The origin of chloride waters in the Polish Flysch Carpathians. *In: Proc. 3rd Int. Symp. Water-Rock Interaction*: 20–24. Edmonton.
- GOLONKA J., BORYSŁAWSKI A., PAUL Z., RYŁKO W., 1979 — Mapa geologiczna Polski 1:200 000, ark. Bielsko-Biała. Inst. Geol., Warszawa.
- HOWER J., ESLINGER E., HOWER M., PERRY E., 1976 — Mechanism of burial metamorphism of argillaceous sediment: 1. Mineralogical and chemical evidence. *Geol. Soc. Am. Bull.*, **87**: 725–737.
- LEŚNIAK P.M., 1980 — The origin of the chloride waters at Wysowa, West Carpathians – chemical and isotopic approach. *Acta Geol. Pol.*, **30**: 519–550.
- LONGSTAFFE F.J., 1987 — Stable isotope studies of diagenetic processes. *In: Short Course in Stable Isotope Geochemistry of Low Temperature Fluids* (ed. T.K. Kyser): 187–257. Mineralogical Association of Canada, Saskatoon.
- NIEŚCIERUK P., PAUL Z., RYŁKO W., SZYMAKOWSKA F., WÓJCIK A., ŻYTKO K., 1995 — Mapa geologiczna Polski 1:200 000, ark. Jasło. Państw. Inst. Geol., Warszawa.
- OSZCZYPKON., ZUBER A., 2002 — Geological and isotopic evidence of diagenetic waters in the Polish Flysch Carpathians. *Geol. Carpath.*, **53**, 4: 1–13.
- POROWSKA A., 2006 — Origin of mineralized waters in the Central Carpathian Synclinorium, SE Poland. *Stud. Geol. Pol.*, **125**: 5–67.
- RAJCHEL L., ZUBER A., DULINSKI M., RAJCHEL J., 2004 — Occurrences and genesis of chloride waters in Sól (S Poland). *Prz. Geol.*, **52**, 12: 1179–1186 [in Polish].

- ŚRODOŃ J., 2007 — Illitization of smectite and history of sedimentary basins. *In: Invited Lectures of the 11th EUROCLAY Conference: 74–82. Aveiro, Portugal.*
- ŚRODOŃ J., ELSASS F., McHARDY W.J., MORGAN D.J., 1992 — Chemistry of illite-smectite inferred from TEM measurements of fundamental particles. *Clay Minerals*, **27**: 137–158.
- ŚWIERCZEWSKA A., 2005 — The interplay of the thermal and structural histories of the Magura Nappe (Outer Carpathians) in Poland and Slovakia. *Miner. Pol.*, **36**: 91–144.
- WHITE, D.E., BARNES, I., O'NEIL, J.R., 1973 — Thermal and mineral waters of nonmeteoric origin, California Coast Ranges. *Geol. Soc. Am. Bull.*, **84**: 547–560.
- ZUBER A., CHOWANIEC J., 2009 — Diagenetic and other highly mineralized waters in the Polish Carpathians. *Appl. Geochem.*, **24**: 1889–1900.
- ZUBER A., GRABCZAK J., 1985 — Origin of some mineral waters in southern Poland as deduced from isotope investigations. *In: Aktualne problemy hydrogeologii: 135–148. Wyd. AGH, Kraków [in Polish].*