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GEOLOGICAL AND ISOTOPIC EVIDENCE OF DIAGENETIC WATERS IN THE POLISH FLYSCH CARPATHIANS

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Abstract: The origin of CO_2-rich chloride waters in the Polish Flysch Carpathians is the subject of controversies. They often contain a non-meteoric component, with isotopic composition characteristic for dehydration waters released in metamorphic processes, that is $\delta^{18}O \cong +6.5$ ‰ and $\delta^2H \cong -25$ ‰. However, comparison with other known occurrences of waters of a similar isotopic composition suggests that they mainly result from the transformation of smectites to illities during the burial diagenesis of flysch sediments. These waters are characterized by high chloride contents (up to about 14 g/l), which differ in different regions, and remain difficult to explain as the $\delta^{18}O$ and δ^2H values are slightly scattered and do not show any distinct contribution of marine water. It is shown that such waters are also characterized by high ratios of Na^+/Cl^- and B/Cl^-, which can be useful in their identification. Particularly interesting waters occur in the four deepest wells of the Krynica Spa, which undoubtedly contain a non-meteoric chloride component. Their positions on $\delta^{18}O$-δ^2H diagrams are scattered to the left from a typical mixing line of meteoric waters with dehydration waters, which makes it difficult to determine their origin. However, they can be regarded as containing different percentages of a dehydration component because their Cl^--δ^2H relation is linear and similar to typical mixing lines of dehydration waters with meteoric waters. The untypical positions of these waters on the $\delta^{18}O$-δ^2H diagram can be explained by isotopic shifts of $\delta^{18}O$ from a typical mixing line to more negative values, supposedly caused by isotopic exchange of oxygen between CO_2 and water. In that process, small volumes of water are involved, as deduced from very slow flow rates in rocks of a low porosity, and a large amount of CO_2, as deduced from very high pressures measured at well heads, and an eruption of CO_2, which occurred during drilling one of the wells.

Key words: Western Carpathians, flysch, burial diagenesis, metamorphic water, diagenetic water, carbon dioxide, chloride water, hydrogen isotopes, oxygen isotopes.

Introduction

The presence of increased chloride contents in mineral waters of the Polish Outer Carpatians (POC) was generally thought to be the remnant of marine sedimentation water (e.g. Dowgiałło 1976). First isotope determinations of CO_2 rich chloride waters from Wysowa and several other sites indicated the presence of water resulting probably from the dehydration of clay minerals in metamorphic processes (Dowgiałło 1980; Leśniak 1980; Dowgiałło & Leśniak 1980). That hypothesis was based on the works of White et al. (1973) and Taylor (1974). However, contrary to White et al. (1973), Leśniak (1980) and Dowgiałło (1980) assumed the dehydration waters to be by definition fresh, and the salt component(s) to result from an admixture of connate water. In some cases, the chloride component was related to sedimentation water migrating from Miocene formations covered by the Carpathian overthrust. That two-component primary mixing was supposed to take place in the past on a regional scale, whereas the secondary mixing with local meteoric water was shown to be a modern process (Leśniak 1980). A contribution of paleoinfiltration water with an isotopic composition different than that of the modern precipitation was also suggested (Dowgiałło 1980; Leśniak 1980). Zuber & Grabczak (1985a, 1986, 1987) were critical about the hypothesis on the regional mixing of dehydration and marine waters, because there are no physical mechanisms of regional mixing which would yield the same $\delta^{18}O$–δ^2H values at different sites with large differences in chloride content. The similarity of the isotopic composition of dehydration waters in the POC to dehydration waters known in other world regions is also difficult to explain by the mixing hypothesis. It is highly improbable that waters in different regions of the world mix in such a way that the same isotopic composition is produced. In addition, for the hypothesis of regional mixing with marine water, it was necessary to assume the initial $\delta^{18}O$ value of the dehydration water to be equal to +25 ‰ (Leśniak 1980; Dowgiałło & Leśniak 1980). Such a high $\delta^{18}O$ value would require a high-grade metamorphism, as can be deduced from the isotopic composition of bound water in clay minerals (Taylor 1974) and from fractionation factors given by Friedman & O'Neil (1977). No evidence for either such metamorphism or such high $\delta^{18}O$ values exists in the POC.

In the Krynica Spa, four deep wells (670–919 m) withdraw CO_2-rich waters of HCO_3–Na type, with increased Cl^- and Mg^{2+} contents. They are called the Zuber waters after the name of their discoverer, Prof. Rudolf Zuber, or chloride CO_2-rich waters to distinguish them locally from other CO_2-rich waters with low Cl^- contents. The Zuber waters were generally thought to be of connate origin mainly due to the presence of elevated contents of chlorides, the large depths of their occurrences, and very low outflow rates (Świdziński 1972; Pazdro 1983). However, preliminary stable isotope determinations yielded values close to the world meteoric line and far from the value of SMOW, suggesting a meteoric origin with a possible replenishment (Dowgiałło 1973). Later Dowgiałło (1980) regarded the Zuber waters as the result of three-component mixing between connate water of the flysch sediments with the dehydration water of metamorphic origin, later diluted by very old meteoric water of a distant recharge area. According to that hypothesis, their replenishment ability was rather questioned. Zuber & Grabczak (1985a, 1986) were in favour of a dominant role of an old meteoric component, without explaining the origin of the elevated chloride contents. Zuber (1987) was in favour of two-component mixing between dehydration and old meteoric waters, with diagenesis as a possible source of the chloride water component.

Within the present work it will be shown that none of the above mentioned hypotheses related to the origin of dehydration waters in the Polish Outer Carpathians (POC) in general, and to the Zuber waters in particular, was quite correct. The isotope and hydrochemical data of typical chloride waters in Poland will be recalled, and against that background the characteristic features of dehydration waters in the POC indicated. For a more complete comparison, selected examples of well-known world occurrences of dehydration waters will also be given. It will be shown that the dehydration of clay minerals in diagenetic transformations is possible considering the maximal depths of sediments obtained by the reconstruction of the burial history of the flysh basin in the Krynica area.

Geological setting

The Polish part of the Outer Carpathians (POC) are mainly composed of the flysch sediments deposited through the Late Jurassic to the Early Miocene. They were deposited by gravitational flows in a deep-sea environment. The flysch sequences consist of sandy-clayey deposits, which derive from marginal and intra-basinal tectonic lands intermittently uplifted and eroded. The flysch sedimentation took place in several sub-basins, which were transferred during the Late Eocene through to Early Miocene tectonic movements into separate tectono-stratigraphic units. The POC were built up from a stack of nappes and thrust-sheets, completely uprooted from their basement. From the south to the north there are: the Magura Nappe, the Fore-Magura-Dukla group of units, the Silesian Nappe, the Sub-Silesian Unit, and the Skole Nappe (Fig. 1).

The POC are flatly overthrust onto the Middle Miocene deposits of the Carpathian Foredeep. As a consequence, a narrow zone of folded Miocene deposits developed along the frontal Carpathian thrust (Fig. 1). The thickness of the Carpathian accretionary wedge is documented by boreholes and varies from a few hundred metres at the front of the orogeny to more than 7 km in the Kuźmina-1 borehole (S of Przemyśl). The extent of the Carpathian overthrust varies from about 60 km at the Kraków meridian (Figs. 2 and 3) to about 100 km at the Krosno meridian (Oszczypko 1998). In areas where mineral waters with a non-meteoric component occur the thickness of the Carpathian nappes is as follows: 2.5–3 km in Słona and Bieśnik; 4–4.5 km in Ciężkowice and Sól; 5–6 km in Sidzina, Rabka, Poręba Wielka and Szczawa; and 8–10 km in Krościenko, Szczawnica, Złockie, Krynica, Wysowa, Lubatówka, Iwonicz and Rymanów (Figs. 1 and 2). In Ciężkowice, Poręba Wielka, Złockie, Krynica, Lubatówka and Iwonicz such waters were found only in deep wells (up to about 1000 m), whereas in other locations, they occur in both springs and shallow wells. Chloride waters rich in CO_2 also outflow at the areas where

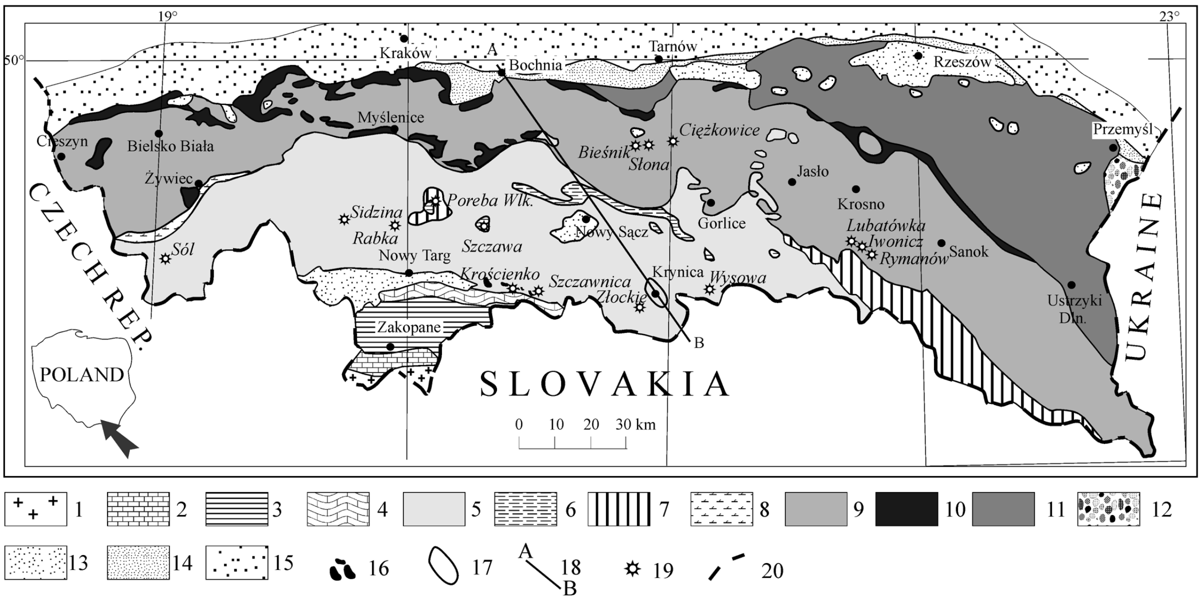

Fig. 1. Geology of the Polish Carpathians (after Oszczypko et al. 1999, supplemented). **1** — crystalline core of the Tatra Mts, **2** — High Tatra and sub-Tatra units, **3** — Podhale flysch, **4** — Pieniny Klippen Belt, **5** — Magura Nappe, **6** — Grybów Unit, **7** — Dukla Unit, **8** — Fore-Magura Unit, **9** — Silesian Nappe, **10** — Sub-Silesian Unit, **11** — Skole Nappe, **12** — Sambor-Rożniatov Unit, **13** — Miocene deposits upon the Carpathians, **14** — Zgłobice Unit, **15** — Miocene deposits of the Carpathian Foredeep, **16** — andesites, **17** — area of Krynica Spa, **18** — cross-section, **19** — occurrences of discussed waters, **20** — state border.

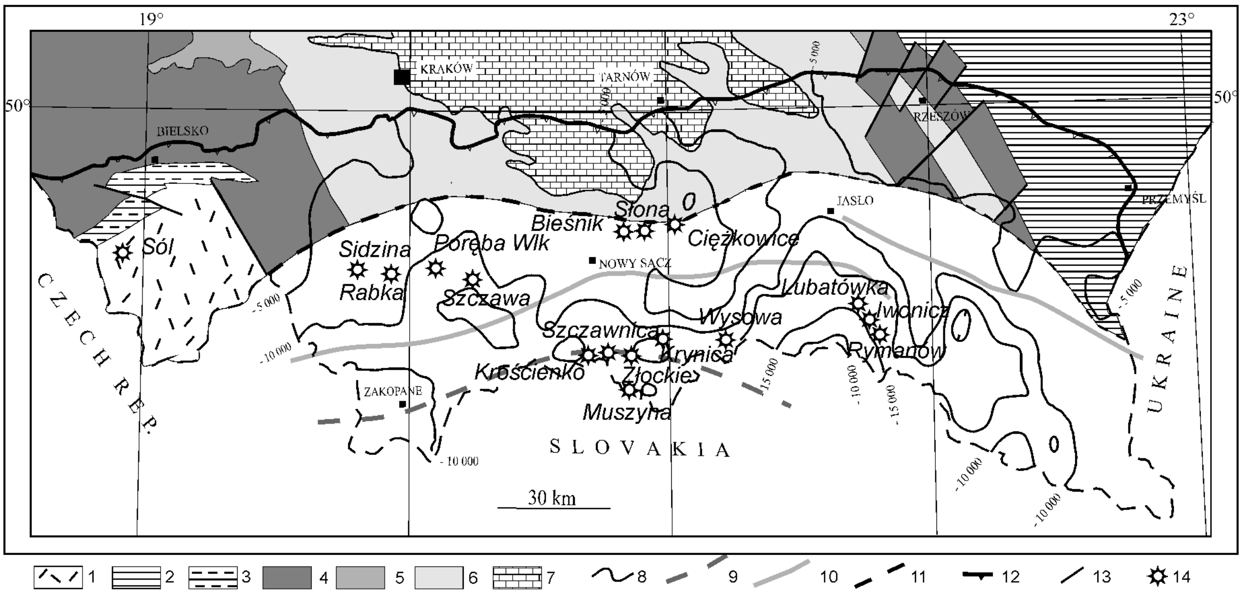

Fig. 2. Sketched map of the platform basement of the Polish Outer Carpathians (after Oszczypko 1998, supplemented). **1** — Proterozoic igneous rocks, **2** — Lower Cambrian and Vendian slates, **3** — Lower Cambrian, **4** — Devonian to Upper Carboniferous, **5** — Triassic, **6** — Jurassic, **7** — Upper Cretaceous, **8** — depth to magneto-telluric basement, **9** — zero line of Wises vectors, **10** — axis of gravimetric minimum, **11** — southern extent of area recognized by boreholes, **12** — Carpathian overthrust, **13** — faults, **14** — occurrences of discussed waters.

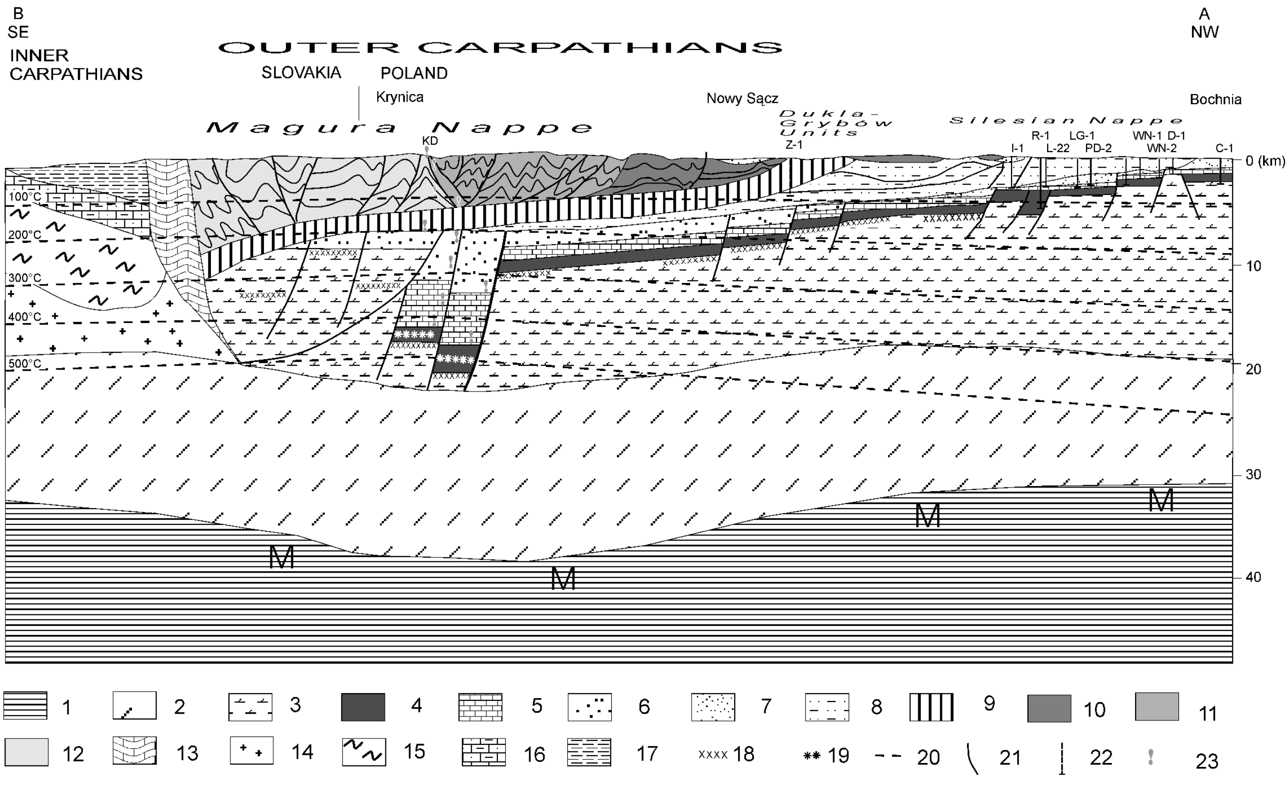

Fig. 3. Deep geological cross-section through the Polish Carpathians. **1** — upper trench, **2** — lower crust, **3** — upper crust, **4** — Paleozoic, **5** — Mesozoic, **6** — Paleogene and Lower Miocene, **7** — Badenian and Sarmatian, **8** — Sub-Silesian and Silesian Units, **9** — Dukla and Grybów Units, **10** — Siary and Rača Subunits of Magura Nappe, **11** — Bystrica Subunit of Magura Nappe, **12** — Krynica Subunit of Magura Nappe, **13** — Pieniny Klippen Belt, **14** — Vahicum, **15** — Tatricum, **16** — Fatricum, **17** — Podhale flysch, **18** — high resistivity basement (after Żytko 1997), **19** — low-resistivity horizon (after Żytko 1997), **20** — isotherms, **21** — faults and overthrusts, **22** — boreholes, **23** — CO_2 ascension, **M** — Moho, **KD** — Krynica dislocation.

the present thickness of flysch sediments is not more than 3 km (springs in Słona and Bieśnik, artesian deep well in Ciężkowice, see Fig. 2).

Numerous andesite dykes and sills occurring in the Czorsztyn-Szczawnica area at the front of the Pieniny Klippen Belt (Fig. 1) cut the Upper Cretaceous-Paleogene rocks of the Magura Nappe (Birkenmajer 1986). These small intrusions are of Middle Miocene age, 11–13 Ma (Birkenmajer & Pécskay 1999), and were formed in the course of the Late Badenian/Sarmatian subduction event. During the post-Sarmatian underplating of the European Platform beneath the Slovak-Pannonian Block, these andesites were probably uprooted from their basement. According to some opinions the CO_2 occurrence in Szczawnica could be related to the presence of the andesite dykes, suggesting its mantle origin. However, both the uprooting of the intrusions and the hydrochemistry of mineral waters in Szczawnica, which show no relation to andesites (Leśniak 1998), contradict that hypothesis.

The basement of the POC represents the epi-Variscan platform and its cover (Fig. 2). The magneto-telluric soundings in the POC revealed a high resistivity horizon (Fig. 3) at the top of the consolidated-crystalline basement (Ryłko & Tomaś 1995; Żytko 1997). On the Bochnia-Krynica geotravers the magneto-telluric basement is inclined to the south from the depths of 5–6 km in the northern, marginal part of the Carpathians, to the depths of 10–12 km south of Nowy Sącz. The depth of the Krynica basement varies from 15 to 20 km, and rises to 8–10 km at the Polish-Slovak boundary (Figs. 2 and 3). The magneto-telluric soundings also reveal a low resistivity zone (0.5–4.0 ohm), which is located south of the gravity minimum. In the Krynica area, this zone has the thickness of about 2.5–3 km and is located in two buried grabens, a few km above the consolidated basement (Fig. 3). According to Jankowski et al. (1985), the low resistivity anomaly indicates the occurrence of highly mineralized waters at great depths, whereas according to Żytko (1997) it results from the graphitization on the contact between the North European Plate and the Slovak Microplate.

A similar anomaly was found at depths of 10–20 km beneath the Island of Taiwan, and was supposed to correlate with the inferred depth of dehydration reactions at the top of the aseismic lower crust (Chen & Chen 1998).

The Krynica Spa is located in the south-eastern part of the Magura Nappe at the boundary between the Bystrica and Krynica Subunits (Figs. 1 and 4). The Bystrica Subunit is built up of the Middle to Upper Eocene Magura Formation (Figs. 4 and 5). The Magura Formation consists of thick-bedded sandstones (Maszkowice Member), variegated shales and thin-bedded turbidites (Mniszek Member), and the Poprad Sandstone Member known only from the deep boreholes (Zuber I–IV). The Krynica Subunit is composed of Upper Cretaceous to Up-

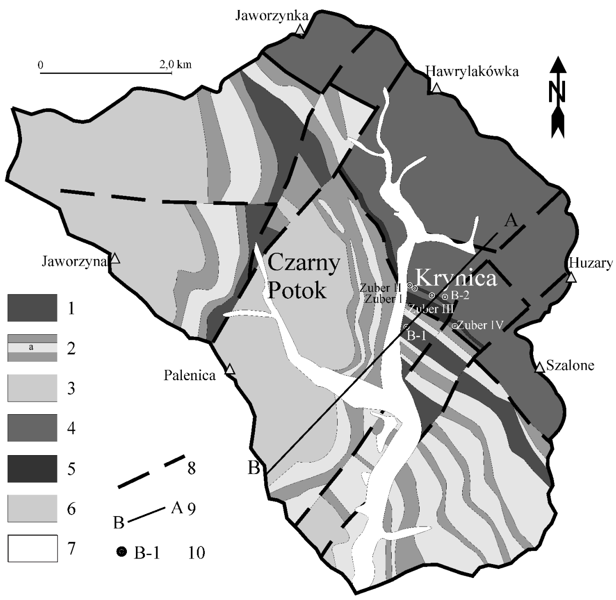

Fig. 4. Geological map of the Krynica area (after Oszczypko et al. 1999). **Krynica Subunit: 1** — Szczawnica Formation, **2** — Zarzecze Formation, **a** — Krynica Sandstone Member, **3** — Magura Formation, Piwniczna Sandstone Member; **Bystrica Subunit:** Magura Formation, **4** — Maszkowice Sandstone Member, **5** — Mniszek Shale Member, **6** — Poprad Sandstone Member, visible only in the cross-section, **7** — Pleistocene, **8** — faults, **9** — cross-section, **10** — selected boreholes.

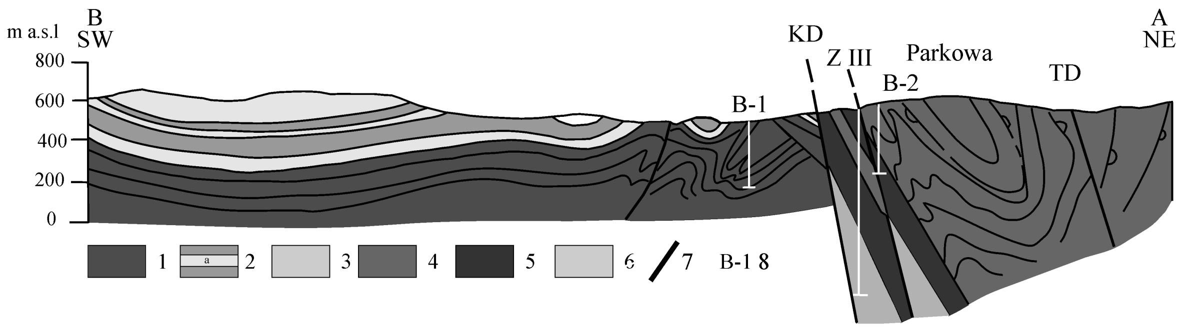

Fig. 5. Geological cross-section (after Oszczypko et al. 1999). **Krynica Subunit: 1** — Szczawnica Formation, **2** — Zarzecze Formation, **a** — Krynica Sandstone Member, **3** — Magura Formation, Piwniczna Sandstone Member; **Bystrica Subunit:** Magura Formation, **4** — Maszkowice Sandstone Member, **5** — Mniszek Shale Member, **6** — Poprad Sandstone Member, **7** — faults, **8** — selected boreholes, **KD** — Krynica dislocation, **TD** — Tylicz dislocation.

per Eocene deposits (Birkenmajer & Oszczypko 1989; Oszczypko et al. 1999). The oldest deposits are known from the Muszyna-Zlockie area, 5 km west of Krynica. They consist of the Turonian-Maastrichtian, deep-water variegated shales (Malinowa Formation) with sporadic intercalations of thin-bedded sandstones (Oszczypko et al. 1990). That formation passes upwards into strongly tectonized, medium to thin-bedded turbidites of the Paleocene and Lower Eocene (Szczawnica Formation), which are rich in calcite veins (Figs. 4, 5). Higher up in the succession, thin-bedded turbidites occur, with intercalations of thick-bedded sandstones and conglomerates of the Lower-Middle Eocene (Zarzecze Formation). In the Krynica Spa the youngest deposits of the Krynica Subunit belong to the thick-bedded sandstones of the Magura Formation (Middle-Upper Eocene). The stratigraphic thickness of the Magura Nappe reaches at least 2.6 km. During overthrust movements and tectonic repetitions, the total thickness of the flysch deposits in the Krynica Subunit increased up to 5.5–7.5 km, as is shown by magneto-telluric investigations (Fig. 3). The Bystrica and Krynica Subunits contact along the sub-vertical thrust fault, which dips to NE (Figs. 4 and 5). Three NE-SW trending transversal faults cut both the Bystrica and Krynica Subunits into several blocks.

The Late Cretaceous to the Upper Eocene flysch formations of the Krynica succession were deposited in a deep-water basin (Oszczypko 1992). Since the Early Eocene, in the southern part of the Magura Basin the sedimentary processes were accompanied by the growth of the accretionary wedge (Oszczypko 1999). Gradual shallowing of the basin started during the Late Eocene. This was followed by the folding and uplifting of the basin after the Late Oligocene–Early Miocene, and prior to the Late Miocene.

The Late Cretaceous-burial history of the Krynica succession of the Magura Basin has been reconstructed using the procedures developed by Angevine et al. (1990) and Allen & Allen (1992). The subsidence plot (Fig. 6) shows the fluctuation of pa-

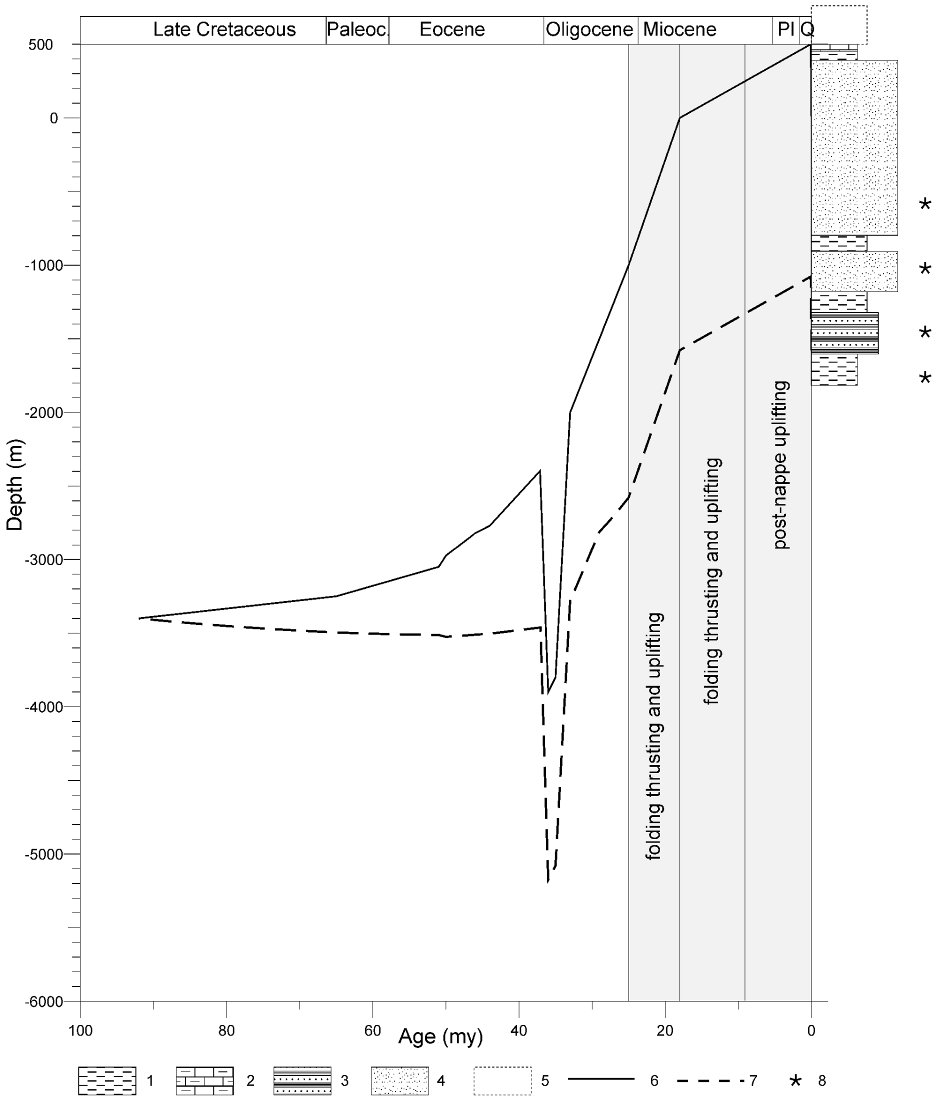

Fig. 6. Backstripped burial diagram of the Krynica succession of the Magura Basin (partly after Oszczypko 1999). **1** — basinal and hemipelagic deposits, **2** — pelagic marls, **3** — thin-bedded turbidites, **4** — thick-bedded turbidites, **5** — eroded part of section (minimal amount), **6** — paleobathymetry, **7** — tectonic subsidence, **8** — strata with mineral waters.

leobathymetry and tectonic subsidence (see also Oszczypko 1999). During the Middle Eocene time the basal portion of the Krynica succession could have been buried at a depth of 6 km beneath the sea level with temperatures of 150–200 °C and pressures of about 100 MPa. The present temperatures at the base of the Magura Nappe in the Krynica area are probably similar to those of the Krynica succession during the maximal burial (Fig. 3), whereas the pressures are probably higher (120–160 MPa). The Krynica Subunit probably covers relatively younger sediments of the Dukla–Grybów Units. These deposits may perhaps still undergo dehydration processes.

Contrary to other tectonic units of the Outer Carpathians, the Magura Nappe is free of hydrocarbons (Karnkowski 1999). Only traces of hydrocarbons were discovered in the saline fluid inclusions of the quartz overgrowths in the Szczawnica Formation (Świerczewska et al. 1999). This suggests that Magura Nappe deposits were buried beneath the lower limit of the main oil generation zone (oil window), with labile kerogen cracked to gas at the temperature exceeding 150 °C (compare Allen & Allen 1993).

The burial depths of the Magura Nappe deposits was probably greater than those of the more external units as it can be assumed from a higher illite to smectite ratio in the Magura Nappe (Dudek & Świerczewska 2001). According to the latter studies the Magura Nappe deposits were affected by the strong diagenesis at temperatures higher than 165 °C in the middle part and about 120–165 °C in other areas of the unit. The advanced diagenesis of the Oligocene deposits of the Grybów–Dukla Units exposed in the tectonic windows in the Magura Nappe was also reported (Dudek & Świerczewska 2001).

The present temperatures at the base of the flysch nappes vary from about 100 °C in the Bochnia area to about 300 °C in the Krynica area (Fig. 3), as deduced from the geothermal gradient of 26 °C/km (Leško et al. 1987).

Hydrogeological setting

Mineral waters discussed within the present work are located along two belts in the Silesian and Magura Nappes. The mineral waters of the Silesian Nappe area occur in the following locations: Słona, Bieśnik, Ciężkowice, Lubatówka, Iwonicz, and Rymanów (Fig. 1). The occurrences of mineral waters in the Magura Nappe can be subdivided into two groups. Waters of Szczawa, Poręba Wielka, Rabka, Sidzina and Sól are strongly related to the tectonic windows of the Dukla–Grybów Units, whereas the waters of Szczawnica, Krościenko, Złockie, Krynica and Wysowa occur in the southern, deep-seated part of the Magura Nappe (Figs. 2, 3 and 5).

In the southern part of the Magura Nappe, abundant carbon dioxide occurrences are observed in both mineral waters and dry exhalations. As discussed further, these CO_2 occurrences are supposed to result from the thermal decomposition of carbonate rocks, which begins at temperatures of 185–190 °C (Mason 1990). The migration of dehydration waters and CO_2 to the surface is enhanced by numerous faults. The upward flow of water results from pressures higher than hydrostatic. No changes in the flow rates of dehydration waters and CO_2 are observable. Therefore, their supply can be regarded as constant in terms of human generations.

In the Krynica Spa particularly favourable conditions exist for the relatively deep penetration of meteoric waters due to many faults and strong folding of the Szczawnica Formation (Paleocene to Lower Eocene, see Figs. 4 and 5). Most probably the faults also play a dominant role in the migration of CO_2 and dehydration waters to the surface. A large amount of CO_2 is also trapped in the Poprad Sandstone Member of the Magura Formation at the depths of 400–1000 m at the tectonic contact of the Bystrica and Krynica Subunits (Fig. 5). In 1938 there was a strong eruption of CO_2 during the drilling of the Zuber II well at the depth of 950 m (Świdziński 1972). In the Krynica area, during the post-nappe time, the long-lasting interaction (around 10 Ma, see Oszczypko 1998) between CO_2-rich waters and rocks caused dissolution of the sandstone cement and an increase of the porosity of sandstones in comparison with other areas. This can be observed in the exposures, where the sandstones and conglomerates of the Krynica Member are weakly consolidated or fully disintegrated to sands and gravels (Oszczypko et al. 1999).

Isotope and chemical data of selected waters of dehydration origin

The typical isotopic composition of CO_2-rich chloride waters from several spas in the POC is shown in Fig. 7. The theoretical ranges of the isotopic composition of metamorphic waters given in Fig. 7 are taken from Taylor (1974) and Kerrich (1987), though Sheppard (1986) reports somewhat wider values to include possible occurrences of dehydration waters of the oceanic crust. CO_2-rich dehydration waters also occur in Slovakia, though to the best knowledge of the authors, their end members with $\delta^{18}O \geq +5.5$ ‰ have not been found so far in that country. However, on the basis of similarity of the Slovak waters to those of the Pacific tectonic belt of the west coast of the United States, Barnes & O'Neil (1976) thought that they contained a metamorphic component.

The Cl^--$\delta^{18}O$ relationships for waters shown in Fig. 7 are given in Fig. 8 (similar relations exist for Cl^--δ^2H). As mentioned above, in spite of similar isotopic composition of the dehydration component, highly different Cl^- contents are observed in different regions, which is difficult to explain by any mixing hypothesis.

In Table 1 chemical and isotope data of selected mineral waters are given. The first group represents examples of the non-Carpathian waters, which are supposed to be of dehydration origin. The second group represents similar waters from the POC. The third group represents chosen examples of oil-field waters in the Polish Carpathians, which most probably contain a dehydration component. The next three groups represent mineral waters of different origin in Poland. They are given to demonstrate typical differences from dehydration waters both in isotopic composition and hydrochemistry. An example from Krosno is also included just to demonstrate the occurrences of chloride waters of other origin in the POC. The last group (VII) represents the chloride waters of Krynica, called the Zuber waters, which are supposed to contain different fractions of a dehydration component as shown further.

In the California Coast Ranges, White et al. (1973) regarded as metamorphic waters only those with a relatively low Cl^-

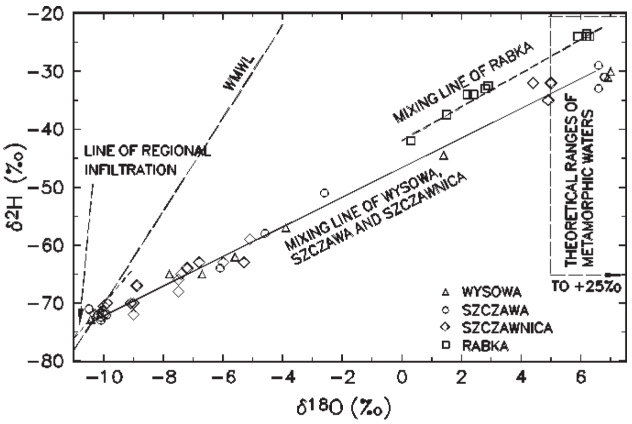

Fig. 7. Isotopic composition of selected Carpathian dehydration waters mixed with local meteoric waters. Note similar compositions of end members. Regional infiltration line after Ciężkowski & Zuber (1995).

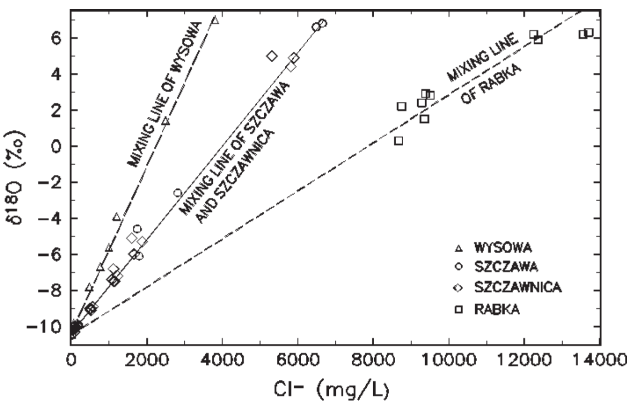

Fig. 8. Cl^--$\delta^{18}O$ relations for selected Carpathian sites showing the mixing of dehydration and local meteoric waters in springs or shallow wells. Note distinctly different Cl^- contents of the end members.

content (up to about 700 mg/l) in the end component (Sulphur Bay Springs, see Table 1). In spite of the same isotopic composition, waters from Wilbur Springs, with Cl^- content close to 10,000 mg/l were supposed to be related to marine waters diluted by ancient meteoric waters. Following White et al. (1973) and Taylor (1974), waters with their end component close to about $\delta^{18}O$ = +6 ‰ and δ^2H = –25 ‰ are often regarded as being of metamorphic origin (e.g. Sheppard 1986; Kerrich 1987). However, contrary to these opinions, in an excellent review, Longstaffe (1987) indicates the possibility of diagenetic origin for such waters. That opinion is mainly based on the results of Yeh & Savin (1976, 1977), and Yeh (1980), obtained for samples taken from deep drill cores of shales and mudstones in the Gulf Coast, and of Suchocki & Land (1983) for samples from the Great Valley sequence in northern California. Findings of these authors can be summarized as follows. The dehydration of argillaceous units mainly results from the transformation of smectite to illite during burial diagenesis at depths of about 3–6 km. Most probably the late-stage dehydration of smectite to illite buffers the oxygen and hydrogen isotope composition of the formation water from that similar to seawater (0 ‰) at shallow depths to values of about +7 ‰ and –25 ‰, respectively, at large depths. The buffering mainly results from dehydration and isotopic exchange, and perhaps also from membrane filtering effects when pore water is pushed out upwards by dehydration water. The dehydration leads to dilution of the pore waters whereas the membrane effects cause the enrichment of the residual water in dissolved constituents as Kharaka & Berry (1973) report. Water-rock interaction undoubtedly also leads to the enrichment in dissolved constituents, especially in the presence of CO_2. In the case of smectite-illite transformation, modelling of formation water in temperatures from 75 to 175 °C yields the $\delta^{18}O$ values from about +5 ‰ to about +9 ‰ (Suchocki & Land 1983; Longstaffe 1987). As no isotopic signatures of the original pore waters (marine or meteoric) are preserved, the final formation water can be regarded as being of dehydration origin. Dehydration waters resulting from diagenesis or metamorphic processes are called within this work diagenetic and metamorphic waters, respectively.

Dehydration waters should not be regarded as free of chemical components because during the smectite illitization not only large amounts of water and OH^- groups, but also Na^+, Ca^{2+}, Mg^{2+} and other ions are released (Boles & Franks 1979). In clay minerals Cl^-, Br^-, and I^- occupy some positions of OH^- ions, and most probably they can also be released. As a consequence, diagenetic waters are mineralized even if the chemical components of the original pore water are not preserved. In any case, the illitization process contributes to the hydrochemistry of diagenetic waters, and high Na/Cl ratios can be expected. In fact the molar ratio of Na^+ to Cl^- is larger than 1 for chloride waters of diagenetic origin, and can serve as a criterion helpful in the identification of such waters (see Table 1). However, caution is needed because that criterion is not unambiguous as values somewhat larger than 1 can also be observed for chloride waters resulting from leaching of salts (see examples of the V group in Table 1). The weight ratio of B to Cl^- shown in Table 1 also seems to be a useful criterion for the identification of chloride waters of diagenetic origin. Its value is larger than 2 ‰ in the case of dehydration waters, and usually below 2 ‰ in other cases. Most probably some amount of boron is also released in the smectite to illite transformation.

In spite of large differences in chemical composition, especially in Cl^- content, all the waters regarded within this work as being of dehydration origin have similar isotopic composition of the non-meteoric end members (Table 1 and Fig. 7). These end members fall within the ranges of the theoretical isotopic composition of metamorphic waters, and, as shown above, are also typical for waters released during burial diagenesis of clay minerals. Such waters also include mixed waters from the South German Molasse Basin, with the non-meteoric end member represented by water from Bad Endorf (Table 1), which results from diagenesis of shales (Stichler 1997). Similarly, no evidence of any regional metamorphism has been found in the POC (deep borehole Kuźmina 1), even at depths of up to 6842 m (Żytko 1989). However, as mentioned above, deep geomagnetic soundings performed in the Western Carpathians suggest the presence of highly mineralized waters in a belt related to two deep grabens seen in Fig. 3. Therefore, the presence of metamorphic processes at large depths cannot be excluded, though it is not regarded as the main source of the discussed waters.

Table 1: Major and selected minor components and the isotopic composition of selected examples of highly mineralized waters in comparison with the Zuber waters of Krynica Spa (except for the samples of group I, Połczyn and Krosno all the other data are based on several determinations characterized by low scatters).

SITE, WELL or SPRING NAME	Na^+ mg/l	K^+ mg/l	Ca^{2+} mg/l	Mg^{2+} mg/l	Cl^- mg/l	Br^- mg/l	I^- mg/l	SO_4^{2-} mg/l	HCO_3^- mg/l	HBO_2 mg/l	CO_2 mg/l	B/Cl ‰	$\delta^{18}O$ ‰	δ^2H ‰
I group. Example of end components of non-Carpathian dehydration waters														
Main Wilbur Spring[a]	8500	440	2.8	38	9700	16	27	390	7130	1255	n.r.	32	+5.3	-22
Sulphur Bay, Ink Spring[a]	n.r.	n.r.	n.r.	n.r.	748	n.r.	n.r.	n.r.	n.r.	n.r.	n.r.	n.r.	+5.6	-24
Sulphur Bay, Geyser Spring[a]	1190	23	20	55	644	1.6	3.2	598	3290	2510	n.r.	963	+3.2	-29
Bad Endorf[b]	7286	72	239	33	8732	12.5	47	72	372	385	150	11	+5.2	-19
II group. End components of shallow Carpathian dehydration waters														
Wysowa, Alexandra well[c,d]	6900	12	314	26	3850	22	5.3	1	13110	990	1690	64	+6.5	-30
Szczawnica, Magdalena[c,d]	7500	125	111	241	5886	31	8.2	Trace	11850	753	890	32	+5.0	-32
Szczawa, Szczawa II well[c,d]	7670	23	116	430	6524	33	7.2	1	11532	528	1740	20	+6.3	-31
Rabka, 18 well[c]	9300	54	80	48	13852	80	16	Trace	1525	395	-	7.0	+6.2	-23
III group. Selected Carpathian oil-field waters with a supposed dehydration component														
Iwonicz, Lubatówka 12[c,d]	6470	40	57	72	7938	32	8.5	10	4132	98	308	3.0	+1.3	-28
Iwonicz, Lubatówka 14[c,d]	6250	33	51	53	7850	32	7.6	8	3713	142	139	4.5	+1.2	-32
Rymanów, Celestyna spring[c,d]	2745	48	83	25	3608	17	2.6	17	1600	190	1030	13	-5.6	-60
Rymanów, Klaudia spring[c,d]	2565	45	176	31	3563	13	3	17	1525	176	790	12	-5.6	-59
IV group. Examples of connate water of the Miocene ocean														
Dębowiec, D-7 well[e]	14900	110	1616	715	28106	170	116	n.d.	149	65	-	0.57	0.0	+2
Zabłocie, Tadeusz well[e]	17100	110	1908	863	32534	184	103	n.d.	142	56	-	0.43	+0.3	-1
V group. Examples of glacial and interglacial waters														
Mateczny, well M-4[c,d]	318	10	142	134	346	n.d.	0.3	794	366	3.8	-	2.7	-10.9	-78
Busko, well 16[f]	4250	110	401	243	6431	20	2.1	1944	422	27	-	1.0	-9.8	-69
VI group. Examples of pre-Quaternary meteoric waters and waters of unclear origin														
Busko, well 15[f]	7750	155	305	379	12800	55	5.3	930	628	45	-	0.87	-6.4	-52
Ustroń, well U-3[g]	22400	405	7791	2410	55593	293	16	380	122	46	-	0.20	-1.2	-22
Goczałkowice, well GN-1[e]	23250	245	4104	1557	47994	248	21	n.d.	117	35	-	0.18	-1.5	-17
Ciechocinek, well XIV[c,h]	14500	155	1292	470	25978	62	1.8	50	365	70	-	0.66	-6.1	-49
Kamień Pomorski, Edward II[c,h]	12400	70	667	260	20913	48	1.3	130	317	57	-	0.67	-8.2	-58
Połczyn, well IG-1[c,h]	24400	55	3178	848	43323	192	1.7	3245	74	62	-	0.35	-3.3	-26
Krosno[g]	16350	35	413	190	25734	88	23	33	1472	78	-	0.75	+2.4	-13
VII group. Zuber waters in Krynica														
Zuber II well[c]	4380	170	190	750	247	2.1	0.7	55	15957	18	2574	18	-9.3	-71
Zuber I well[c]	5700	200	201	480	734	6.8	1.5	33	17364	15	2223	5.0	-7.2	-63
Zuber IV well[c]	6425	265	221	495	870	5.7	1.5	112	19600	9.9	2240	2.8	-8.5	-55
Zuber III well[c]	7000	325	208	378	1136	7.0	2.2	65	19965	17	2061	3.7	-6.9	-56

a) White et al. (1973); b) Stichler (1997); c) chemical data after Jarocka (1976); d) isotope data after Ciężkowski et al. (unpublished); e) Pluta & Zuber (1995); f) Zuber et al. (1997); g) Dowgiałło (1980); h) Zuber & Grabczak (1991); n.r., not reported

All the non-meteoric end members are free of tritium even in the cases of shallow occurrences (e.g. in Wysowa, Szczawnica, Szczawa and Rabka), whereas waters situated along the mixing line(s) with meteoric infiltration (Figs. 7 and 8) usually contain tritium above the detection limit of about 0.5 T.U. That mixing between ascending dehydration waters and modern meteoric waters is a local effect, and usually takes place close to the ground surface.

The dehydration origin of waters cannot be deduced only on the basis of their isotopic composition but the geology of the area and the hydrochemistry must also be considered. Other waters with their end members falling within the ranges of metamorphic waters shown in Fig. 7 are also quite common in different regions of the world. Their discussion is beyond the scope of the present work because they are often associated with oil fields or thermal waters, and their origin is either more complex than just dehydration, or they were subject to secondary changes.

Mineral waters of the Krynica Spa

The mineral waters of meteoric origin in Krynica are of the HCO_3–Ca, HCO_3–Ca–Mg and HCO_3–Mg–Ca types. Waters discharging from several springs and withdrawn from wells up to about 200 m deep contain tritium. Waters withdrawn from wells deeper than about 200 m are tritium free and in some cases have $\delta^{18}O$ and δ^2H values distinctly more negative than the average values of waters rich in tritium, that is $\delta^{18}O \cong -10.5$ ‰ and $\delta^2H \cong -75$ ‰. These distinctly more negative delta values are characteristic for waters in wells about 400 m deep. They do not result from the local altitude effect, because their $\delta^{18}O$ and δ^2H values are more negative than the values found in springs and dug wells at high altitudes (Zuber et al. 1999). Therefore, waters with the most negative delta values are most probably of glacial age, or contain a significant glacial component. Radiocarbon dating and noble gas temperatures cannot support that finding due to high contents of dead CO_2.

Therapeutic waters withdrawn from the four deepest wells with flow rates of 0.8–3.5 m^3/day distinctly differ chemically and isotopically from other waters in Krynica, and, as mentioned, they are called the Zuber waters. Their isotope data neither indicate a common origin, nor fit to a typical mixing line of dehydration waters as seen in Fig. 9. However, a consistent picture is obtained when the relationship between the two most conservative water components is considered, that is between Cl^- and δ^2H, as shown in Fig. 10. In such a case it is possible to draw a straight mixing line which fits the data for the Zuber waters reasonably well. The dehydration end member of that line is assumed to correspond to the highest Cl^- content in the Krynica area, which was measured in water taken from the B-1 well during drilling (Świdziński 1972). The isotopic composition of water from that well was not measured, but under the above assumption the mixing line shows the δ^2H value of about –30 %, which is equal to the value of the end member in nearby Wysowa. The mixing line shown in Fig. 10 can serve for determining the contributions of the dehydration and meteoric components to the Zuber waters in each well. Chloride contents yield the following fractions of the dehydration water: 0.09, 0.26, 0.34 and 0.41, for Z-II, Z-I, Z-IV and Z-III wells, respectively. The fractions of the dehydration water determined from the δ^2H values are 0.08, 0.27, 0.43, and 0.41, respectively. Both methods yield practically the same results except for Z-IV well, as discussed below.

The initial point of the Cl^--δ^2H mixing line corresponds to the mean isotopic composition of hydrogen in local Holocene waters, that is about –75 ‰. However, due to very low outflow rates, high mineralization, and depths larger than the depths of glacial waters, the meteoric member of the Zuber waters cannot be of the Holocene age. As a consequence, an interglacial age can be supposed for that water. Water from the Zuber IV well does not fit the mixing line of three other wells very well and seems to have a meteoric component with somewhat heavier isotopic composition, that is $\delta^2H \cong -65$ ‰ (see Fig. 10). That value suggests an even greater age of the meteoric component because it corresponds to recharge in a pre-Quaternary warm climate. Such pre-Quaternary meteoric waters of the last hydrologic cycle have been found in several regions of Poland (Ciężkowski et

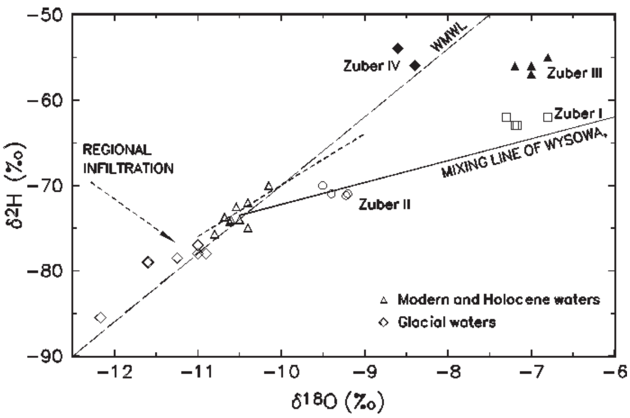

Fig. 9. Isotopic composition of waters exploited in Zuber wells in comparison with the non-chloride CO_2-rich waters of Krynica Spa.

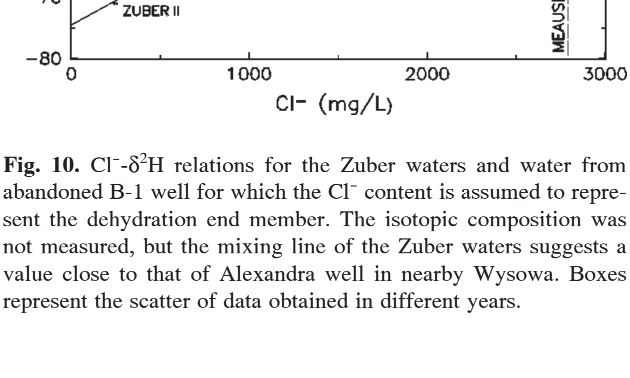

Fig. 10. Cl^--δ^2H relations for the Zuber waters and water from abandoned B-1 well for which the Cl^- content is assumed to represent the dehydration end member. The isotopic composition was not measured, but the mixing line of the Zuber waters suggests a value close to that of Alexandra well in nearby Wysowa. Boxes represent the scatter of data obtained in different years.

al. 1989; Zuber & Grabczak 1985b; Zuber et al. 1997). If a separate mixing line is assumed for the Z-IV well, the fraction of dehydration water is about 0.34.

The shifts of the Zuber waters from the mixing line of dehydration and meteoric waters seen in Fig. 9 can be explained by isotopic exchange of oxygen between large amounts of CO_2 and small volumes of water. Carbon dioxide released from carbonate rocks of marine origin is characterized by $\delta^{18}O$ values of about 0 ‰ in the PDB notation, which corresponds to about +30 ‰ in the SMOW notation (Gat & Gonfiantini 1981). For ^{18}O, the fractionation enrichment between CO_2 and water at the temperature of about 10 °C is –43.5 ‰ (Friedman & O'Neil 1977). Therefore, a small quantity of water affected by a continuous flow of CO_2 will have a tendency to change the isotopic composition of oxygen to be in equilibrium with CO_2, that is to –13.5 ‰. The process of exchange is very fast and takes only several hours (Gat & Gonfiantini 1981). A large amount of CO_2 is indicated by high pressures of CO_2, which are from about 2.1 to 3.2 MPa at closed well heads. Therefore, in the case of the Zuber waters, the masses of through-flowing CO_2 and water are probably comparable, and the isotopic shift of oxygen in water is observed.

The origin of CO_2 in Krynica was also a subject of controversies. In the past, the most common opinion related its origin to volcanic processes (Świdziński 1972). A similar opinion was expressed by Cornides & Kecskés (1982) on the basis of $\delta^{13}C(CO_2)$ measurements for CO_2-rich waters in Slovakia. In general, the distinction between the mantle (volcanic) and crustal (metamorphic) CO_2 is difficult due to overlapping ranges of $\delta^{13}C$ values (e.g. Deines 1980), and the evolution of the isotopic composition of CO_2 during its migration through groundwater reservoirs (Leśniak 1998). However, as $\delta^{13}C(CO_2)$ in the Zuber wells is about –1 ‰ (Leśniak 1985, 1988), the origin of CO_2 can be related to the thermal decomposition of carbonate minerals in the presence of SiO_2 (Maxwell & Sofer 1982). The carbon dioxide is probably derived from the Mesozoic and Paleozoic rocks of the platform basement and partly from the Paleogene and Lower Miocene autochthonous clastic deposits (Oszczypko 1998). The small amount of mantle helium found in all the investigated CO_2-rich waters of the POC (Leśniak et al. 1997) indicates that some contribution of the mantle CO_2 is perhaps possible. However, that contribution, if any, cannot be regarded as significant.

The Zuber waters are chemically unique as indicated by data given in Table 1. Unusually high molar ratios of Na^+ to Cl^-, compensated by high concentrations of HCO_3 ions, are characteristic for the Zuber waters. For these waters, the Na/Cl ratio is evidently independent of the fraction of diagenetic water (see Table 1 and Fig. 10). Therefore, high concentrations of Na^+ probably result from a secondary process related to both components. The decomposition of albite can be supposed as the process responsible for increased Na^+ concentration, though the albite presence is not reported from the Paleocene deposits of the Krynica Subunit, whereas the amount of K-feldspars accounts for 9.5 % (Bromowicz 1986). However, that hypothesis is weak because the deepest non-chloride waters in Krynica, with T.D.S. values reaching about 10 g/l, are of the HCO_3-Ca-Mg type, without an indication of unusually high Na^+ contents. Therefore, the origin of very high Na^+ contents in the Zuber waters remains unclear.

Conclusions

In the Polish Outer Carpathians there are common occurrences of CO_2-rich and CO_2-free chloride waters of non-meteoric origin as deduced from their isotopic composition. In a number of areas these waters migrate to the surface due to pressures higher than hydrostatic, and mix with local meteoric waters yielding similar mixing lines on $\delta^{18}O$-δ^2H diagrams. The mixing lines start at the mean isotopic composition of local meteoric waters, that is $\delta^{18}O \cong -10.2$ ‰ and $\delta^2H \cong -72$ ‰, and end at the values characteristic for dehydration waters, that is $\delta^{18}O \cong +6.5$ ‰ and $\delta^2H \cong -25$ ‰ (Fig. 7). Mixing lines on Cl^--$\delta^{18}O$ (Fig. 8) and Cl^--δ^2H diagrams usually distinctly differ; they are characteristic only for small areas (a spa or village). According to numerous authors (White et al. 1973; Taylor 1974; Leśniak 1980; Sheppard 1986; Kerrich 1987), such waters can be regarded as being released from clay minerals during metamorphism, with high Cl^- contents related to the remnants of marine water. However, it is difficult to explain the same isotopic composition and highly different Cl^- contents for assumed mixing with marine water. It is more reasonable to follow Yeh & Savin (1976, 1977), Yeh (1980), and Suchocki & Land (1983), who investigated two active burial basins in the USA, and whose results were summarized by Longstaffe (1987). These authors showed that the release of bound water and buffering effects during smectite to illite transformation during the burial diagenesis lead to $\delta^{18}O$ and δ^2H values similar to those regarded as being of metamorphic origin. The POC geology and the reconstructed burial history show the possibility of a common existence of diagenetic waters and rather exclude the existence of metamorphic waters. Similarly, chloride waters in the Tertiary Molasse Basin of South Germany, isotopically described by Stichler (1997) can be related to the burial diagenesis.

Smectite illitization is not necessarily an important process in burial diagenesis. The study of pore fluid evolution in the Kimmeridge Clay Formation (mudstone sequence deposited by epicontinetal sea across north-west Europe during the end of Jurassic) showed that other pore waters can also be expected than those presented within the present work (Scotchman 1993).

The origin of chloride waters of the Na-HCO_3 type in Krynica is particularly difficult to determine because their isotope data do not fall on a typical $\delta^{18}O$-δ^2H mixing line of dehydration and meteoric waters in the POC. However, the Cl^--δ^2H relationship is typical for dehydration waters, which suggests that the Zuber waters can be regarded as those resulting from mixing between meteoric and diagenetic waters, with $\delta^{18}O$ shifted to more negative values by isotopic exchange between large quantities of CO_2 and small volumes of water. In Krynica, contrary to other regions, mixing between meteoric and diagenetic waters takes place at relatively large depths (500–1000 m) where slowly penetrating meteoric waters of great ages (interglacial) meet with ascending dehydration waters. That mixing and the long-lasting action of large quantities of CO_2 supposedly lead to the unique chemical composition of the Zuber water and high T.D.S. contents of about 30 g/l.

It is demonstrated that high Na/Cl and B/Cl ratios are characteristic for waters supposed to be released from clay minerals during burial diagenesis. These ratios can be helpful in the identification of diagenetic waters.

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