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Extended Abstracts

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Origin of mineral and thermal waters

title: # On the origin of chloride waters in the Polish flysch Carpathians

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Chloride mineral waters in the Polish flysch Carpathians are exploited for therapeutical purposes in a number of spas; their origin being of interest for the determination of available resources and a proper management. All these waters in the flysch formations of the western part of the area resulted from combined effects of ultrafiltration of sedimentation water and dehydration of clay minerals during burial diagenesis, and possible mixing with meteoric waters during later infiltration stages (Zuber, Chowaniec, 2009). The diagenetic end-members are characteristic for the final stages of diagenesis with $\delta^{18}O \approx (6–7)‰$, $\delta^{2}H \approx –(20–30)‰$, and Cl^- contents of about 3.5 to 25 g/L. In some fault areas, the primary diagenetic waters ascend to the surface and mix with waters of local meteoric origin yielding two-component mixing lines in $\delta^{18}O–\delta^{2}H$ and $\delta^{18}O–Cl^-$ or $\delta^{2}H–Cl^-$ diagrams. The meteoric end-members are usually of modern ages, with $\delta^{18}O \approx –10‰$ and $\delta^{2}H \approx –70‰$.

In the eastern part of the Polish flysch Carpathians, where oil and gas fields exist, the data are not so simple, suggesting possible existence of several different end components of mixing processes (Porowski, 2006). From the data of that author presented in Fig. 1, three examples are selected and shown in Figs. 2 and 3. According to chemical data (Table 3 and 5 in Porowski, 2006) all these waters have TDS contents from several to more than 50 g/L with mNa^+/mCl^- distinctly above 1; the latter indicating the presence of diagenetic water with chemical components being of marine origin changed by ultrafiltration and diagenetic reactions (Zuber, Chowaniec, 2009). The isotope data of Fig. 1a suggest that either marine sedimentation water or highly evaporated meteoric water dominate in a number of cases. However, extrapolated $\delta^{18}O–Cl^-$ relations of examples shown in Figs. 2b and 3b lead to $\delta^{18}O$ values characteristic for the dehydration waters of the final stages of diagenesis with relatively low Cl^- contents. The $\delta^{2}H$ data in Figs. 2a and 3a completely disagree with the hypothetical mixing lines derived from the extrapolated lines given in Figs. 2b and 3b. These disagreements most probably result from shifts of $\delta^{2}H$ to heavier values, if formation water is involved in generation of hydrocarbons. The whole picture is complicated because some waters shown in Fig. 1 do not exhibit the influence of catagenesis, whereas some others have isotopic composition and Cl^- contents indicating intermediate stages of diagenesis.

In conclusion, the chloride components in all mineral waters of the Polish flysch Carpathians are of marine origin, completely changed by diagenesis of clay minerals. Majority of waters in the eastern part, have $\delta^{2}H$ values shifted to heavier values by generation of hydrocarbons.

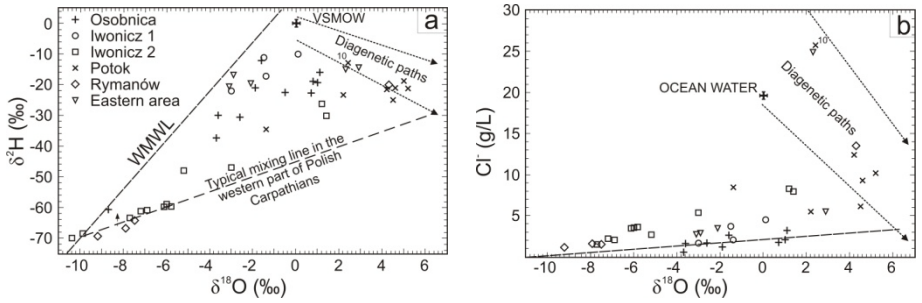

Figure 1. $\delta^{18}O–\delta^{2}H$ (a) and $\delta^{18}O–Cl^-$ (b) data of Central Carpathian Synclinorium (adapted from Porowski 2006, sample 10 from Zuber and Chowaniec 2009).

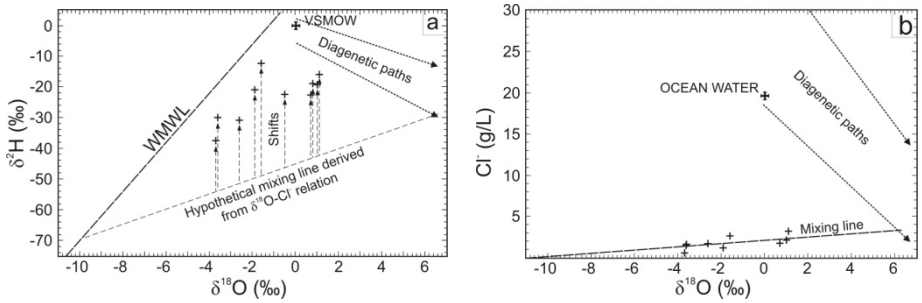

Figure 2. $\delta^{18}O$–$\delta^{2}H$ (a) $\delta^{18}O$–Cl^- (b) data of the Osobnica area selected from Fig. 1. Extrapolated $\delta^{18}O$–Cl^- relationship suggests the heavy end-member to correspond to the final stage of diagenesis whereas the $\delta^{2}H$ values in (a) do not correspond to the expected mixing line due to shifts to heavier values, which is caused by generation of hydrocarbons (catagenesis).

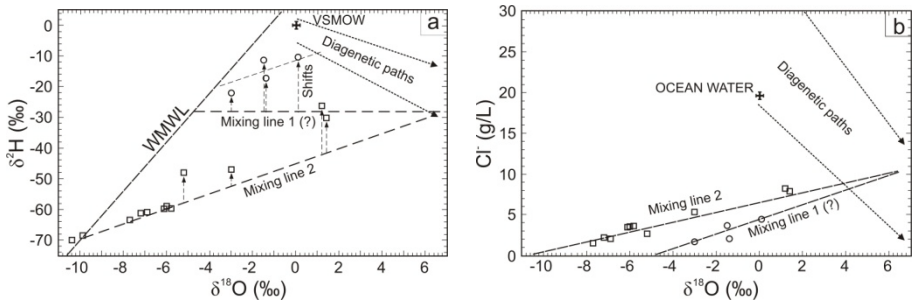

Figure 3. As in Fig. 2, but for the Iwonicz Spa area where two groups of samples can be distinguished. The $\delta^{18}O$–Cl^- relations suggest a similar isotopic heavy end-member as in Fig. 2 but with a higher Cl^- concentration. The mixing lines shown in (a) are deduced from the $\delta^{18}O$ values indicated in (b) in disagreement with the $\delta^{2}H$ values supposedly shifted by catagenesis. The hypothetical meteoric end-member for group 1 corresponds to recharge in a very warm pre-Quaternary climate.

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