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Factors controlling chemical composition of chloride CO_2-rich waters within Magura Unit occurring in Krynica-Wysowa-Cigel'ka area

ABSTRACT OF DOCTORAL THESIS

The main aim of this thesis was to precisely determine all hydrogeochemical processes affecting chemical composition of CO_2-rich waters in Krynica-Wysowa-Cigel'ka area. The study area is located in the cross-border region of Polish and Slovak Outer Carpathians, within Magura Unit. The Outer Carpathians are mainly built of Createceous and Paleogene flysch sediments that are strongly folded and dissected by numerous deep-reaching faults. The abundance of many types of mineral and specific waters in the area under study is a result geological structures complexity and considerable tectonic disruption. This thesis is focused on the Krynica-Wysowa-Cigel'ka area, where common CO_2-rich and chloride CO_2-rich waters coexist. The thorough understanding of the chloride CO_2-rich waters origin is very important as they pose related elements of the transboundary hydrogeological system.

Comprehensive assessment of factors controlling chemical composition of chloride CO_2-rich waters exploited in Polish-Slovak border zone was a relatively difficult task which required selection and application of various scientific methods. Not only the analytical techniques common in the field of hydrogeology, but also some advanced tools typical for mineralogy, chemistry and physics has been applied. During the field work, the author has collected water and precipitates' samples, described precisely each point, measured unstable parameters of waters and free CO_2 concentration and made photographic documentation. The accurate physicochemical analyses of 41 water samples, as well as the isotopic analyses of $\delta^{18}O$, $\delta^{2}H$, $\delta^{37}Cl$ and radioactive elements (tritium, uranium, radium) have been conducted. The obtained results constituted the input data for hydrogeochemical modeling realized with the help of *Phreeqc* and *Geochemist's Workbench Standard ver 8.0* programs.

Despite the fact that all analyzed waters were classified to the one group of CO_2-rich waters, their physicochemical parameters significantly vary. The mineralization differs from 859.91 mg/dm^3 to 28525.60 mg/dm^3. The pH of groundwaters under observation is included between 5.3

and 7.5, though the most frequently varies within acidic values. A common feature of the discussed CO_2-rich waters is the occurrence of the HCO_3^- as the major anion and Na^+ as the major cation. The concentrations of HCO_3^- range from 568.52 mg/dm^3 to 15834.40 mg/dm^3, while Na^+ concentrations were recorded between 56.63 mg/dm^3 and 8011.60 mg/dm^3. The analyzed waters contain high amounts of Cl^-, which concentration was measured in the range from 7.09 mg/dm^3 to 4148.29 mg/dm^3. Significant amounts of free CO_2 were found in all waters in which they change from 750 mg/dm^3 to 3437 mg/dm^3. Apart from mineralization and free CO_2, iodine and iron are also the specific components in some of the investigated waters. The hydrogeochemical type of the examined waters changes from HCO_3-Cl-Na through HCO_3-Cl-Na-(Ca)-(Mg) and HCO_3-Na-(Ca)-(Mg) to HCO_3-Na.

Investigations of natural radioactivity of selected CO_2-rich waters have shown that the concentrations of radium isotopes change from 29 mBq/dm^3 to 622 mBq/dm^3 for ^{226}Ra and from 30 mBq/dm^3 to 635 mBq/dm^3 in case of ^{228}Ra. For the majority of the analyzed waters uranium isotope concentrations are low and range from the detection limit (0.5 mBq/dm^3) up to 13 mBq/dm^3 for ^{238}U and from 0.3 mBq/dm^3 to 33.4 mBq/dm^3 for ^{234}U.

The isotopic composition of the analyzed CO_2-rich waters, determined on the basis of the performed tests and the results of archive data, is characterized by δ^{18}O and δ^2H values in the ranges of -9.6 ‰ to -0.1 ‰ and -82.4 ‰ to -29.3 ‰, respectively. The content of tritium were recorded from 0 to 8.1 TU. The waters exploited from the *Aleksandra* borehole in Wysowa and *CH-1* borehole in Cigel'ka are the most enriched in the ^{18}O isotope and they contain the highest chlorides concentrations. It was assumed that they are the closest to typical diagenetic waters and according to that they may be the initial solution for remaining CO_2-rich waters occurring in the investigated area, that are at various stages of diluting diagenetic waters by infiltration waters.

The measurements of ^{37}Cl/^{35}Cl isotope ratios have been carried out in attempt to solve the problem of Cl^- origin. These analyses are crucial and innovative element of the conducted study, since they were performed for the first time for CO_2-rich waters occurring in the investigated area. It was observed that the δ^{37}Cl values and and Cl^- concentrations in all analyzed waters are lower than in marine water, considered as a starting substance for the examined groundwaters. It might be caused by the processes accompanying the burial diagenesis, e.g. ion exchange, diffusion through low permeable clay layers or inflow of infiltration waters. If we consider the geological structure and proximity of the subduction zone, it cannot be denied that fluids released from the subduction zones may supposedly be responsible for low values of δ^{37}Cl (<-1 ‰) noted in following boreholes: *Zuber I* and *Zuber III* in Krynica, *Z-3** in Zubrzyk and *Alžbeta* in Bardejovské Kúpele.

The collected archival physicochemical data from the years 1916-2014 and the results of analyses conducted by author during this study have been used to assess chemical stability of the waters. Temporal evaluation of variability of the waters' chemical composition shows that most of the analyzed parameters are within the limits of permissible fluctuations. Nonetheless, the main ions are closely distributed about the mean, while the concentrations of specific components, including mineralization, fluctuates more widely. It was observed that the chemistry compositions of CO_2-rich waters from following boreholes: *Zuber I–IV* in Krynica, *Zofia II* in Żegiestów and *Aleksandra* in Wysowa were stable throughout the whole exploitation period. On the other hand, a statistically significant downward trend was noted for mineralization in the case of other CO_2-rich waters exploited in Wysowa. Decrease of mineralization as well as Cl^- and Na^+ share, with simultaneously increase of HCO_3^- concentration, may be caused by boosting influx of infiltration waters.

Within spring niches or along headwater outflows of CO2-rich waters some precipitates resembling ochres occur. Based on mineralogical analyses, the sediments were divided into three types. Most precipitates were classified as ferruginous or ferruginous-carbonate type. These precipitates are rusty-coloured and their main components are iron hydroxides (ferrihydrite, goethite), sometimes accompanied by carbonate minerals (calcite, aragonite, dolomite, siderite). For the first time, the third group including pure carbonate precipitates was identified. This type of precipitates is even macroscopically distinguishable from the others due to white or whitish colours. Furthermore mineralogical analyses have shown that besides the basic carbonate minerals, these precipitates compose of rare minerals, such as nesquehonite or monohydrocalcite.

The inflow of subduction CO_2 plays a significant role in modifying the waters' chemical composition. The presence of CO_2 influences on the carbonate equilibrium, determines enhanced concentrations of selected ions (higher TDS) and changes physicochemical properties of waters. Based on the hydrogeochemical modeling results, it was ascertained that CO_2 affects the thermodynamic state of the solution, especially SI values determined for carbonate minerals. What is more, it was observed that the waters with the highest mineralization (*Aleksandra, CH-1, Zuber I-IV, Złockie 6* and *Z-3**), show saturation with respect to basic carbonate minerals, i.e. aragonite, calcite, dolomite, magnesite and siderite. It was also found that the free carbon dioxide ($CO_{2(g)}$) to dissolved carbon dioxide ($CO_{2(aq)}$) ratio decreases with increasing water mineralization. In other words, the groundwaters with the greater share of infiltration component has higher $CO_{2(g)}$ to $CO_{2(aq)}$ ratio than waters in which diagenetic water predominates.

In the light of all the results, it was ascertained that the final chloride CO_2-rich waters' chemical composition in Krynica-Wysowa-Cigel'ka area depends primarily on interactions between water, rocks and gas. The CO_2-rich waters occurring within the boundaries of the research area can be categorized into three genetic groups: diagenetic waters, infiltration waters and mixed waters. The hydrogeochemical water types are varied mainly due to replacing of mineralized diagenetic waters with fresh infiltration waters. Although this mechanism is extremely important for final chemical composition of analyzed chloride CO_2-rich waters, the other processes cannot be definitively excluded. According to obtained results, it is probable that solutions released from the subduction zones, hydrothermal solutions and perhaps Cl-Na waters coming from the strata underlying the Magura Unit, might influence on chemistry of waters in question.

The analysed CO_2-rich waters are important deposits used by bottling plants for the production of natural mineral waters. A crucial aspect is, that they are also commonly utilized in medical treatment, e.g. healing baths, crenotherapy. Due to their valuable properties, they consist important mineral raw for many health resorts, where they are used as therapeutic waters. Four localities in the research area (Żegiestów-Zdrój, Krynica-Zdrój, Wysowa-Zdrój and Bardejovské Kúpele) are proud to be statutory health resorts. Moreover, there was also a very well-known spa center in Cigel'ka that was closed as a result of the II World War outbreak.