Interaction between recent infiltration waters and diagenetic waters in the Wysowa Spa region, southern Poland: insights from combined isotope and geochemical study

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STUDY AREA

The Wysowa Spa is located in southern Poland, in the upper reaches of the Ropa river draining part of the Beskid Niski mountain range. The catchment of Ropa river is underlain by Paleogene-Cretaceous flysch formations covered by Quaternary deposits. Mineral and therapeutic CO_2-rich waters occur in the central part of Wysowa Spa. They are exploited from depth interval of ca. 15 to 100 m by eleven wells distributed over the area of ca. 0.28 km^2.

The exploited mineral waters are mixed waters containing two major components in varying proportions. One end-member, represented by water from Aleksandra well, is highly mineralized diagenetic water of deep circulation, reaching the surface through system of fissures and faults. The second end-member is represented by recent water of local infiltration (W-3 and R-1 in Fig. 1.).

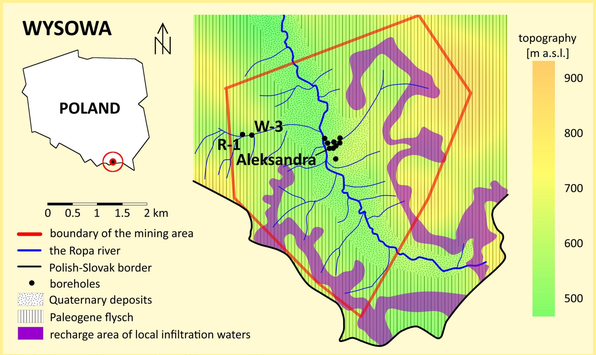


Fig. 1. An overview map of the Wysowa region

Isotope and chemical investigations of mineral waters in the Wysowa Spa region started in 1970s [1-2]. The reported measurement campaign was carried out in October 2017. Nine samples of mineral water were collected during the campaign, supplemented by 2 samples of recent infiltration waters (wells W-3 and R-1). Water chemistry and full isotopic composition of the collected waters (δ^2H, δ^{18}O, δ^{17}O, tritium content) were analysed in the laboratory. In addition, pH, HCO_3, dissolved CO_2 and temperature were measured in the field.

ANALYTICAL METHODS

CHEMICAL COMPOSITION

ICP-MS *Inductively Coupled Plasma Mass Spectrometry*

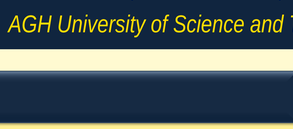


Fig. 2. ICP-MS

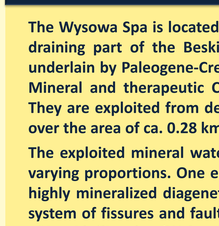


Fig. 3. Picarro L2140-i spectrometer

STABLE ISOTOPES

CRDS *Cavity Ring-Down Spectroscopy*

Analysis of triple isotopic composition of water (δ^2H, δ^{18}O, δ^{17}O) was performed using the Picarro L2140-*i* spectrometer. The results presented in Table 1 and in the figures are averages of several measurement runs. Their uncertainties were estimated as standard deviations of the mean.

TRITIUM

EL-LSS *Electrolytic enrichment combined with liquid scintillation spectrometry*



Fig. 4. Liquid Scintillation Spectrometer "Quantulus"



Fig. 5. Electrolytic enrichment system

RESULTS

Tab. 1. Results of isotopic and chemical analyses on samples obtained in the measurement campaign carried out in October 2017

Well	δ^2H [‰]	δ^{18}O [‰]	δ^{17}O [‰]	d-excess [‰]	Δ^{17}O [per meg]	Tritium [TU]	Cl^- [mg/dm^3]	Na^+ [mg/dm^3]	HCO^-_3 [mg/dm^3]	Ca^{2+} [mg/dm^3]
R-1	-70.43(0.05)	-10.27(0.02)	-5.40(0.02)	11.7(0.2)	31(4)	6.6(0.4)	6	25	323	40
W-3	-69.57(0.04)	-10.17(0.02)	-5.36(0.01)	11.8(0.2)	26 (4)	6.1(0.4)	7	18	305	44
W-24	-69.60(0.09)	-9.32(0.02)	-4.91(0.02)	5.0(0.1)	24(6)	5.0(0.3)	216	390	1159	66
Slone	-66.92(0.03)	-9.29(0.03)	-4.89(0.02)	7.4(0.2)	27(6)	1.8(0.3)	112	202	793	125
Jozef 1	-66.81(0.09)	-8.90(0.03)	-4.69(0.02)	4.4(0.2)	21(10)	4.2(0.3)	242	457	1373	95
Henryk	-66.95(0.16)	-8.30(0.05)	-4.37(0.03)	-0.6(0.3)	24(4)	2.1(0.3)	411	824	2105	121
Wladyslaw	-65.51(0.07)	-8.07(0.02)	-4.25(0.02)	-1.0(0.2)	15(7)	1.5(0.3)	422	746	2318	209
W-15	-64.74(0.07)	-7.14(0.02)	-3.77(0.02)	-7.6(0.1)	11(6)	1.5(0.3)	694	1396	3325	115
Anna	-54.76(0.07)	-3.89(0.03)	-2.05(0.03)	-23.6(0.2)	4(12)	0.0(0.3)	1290	2603	5429	148
Franciszek	-47.35(0.05)	-0.18(0.02)	-0.09(0.02)	-45.9(0.1)	3(7)	0.1(0.3)	2240	4047	7991	189
Aleksandra	-30.14(0.08)	6.63(0.03)	3.48(0.02)	-83.2(0.2)	-14(5)	0.0(0.3)	3928	6000	13115	249

The diagenetic end-member (Aleksandra well) has characteristic stable isotope composition (δ^2H = -30.14±0.08‰, δ^{18}O = 6.63±0.03‰, δ^{17}O = 3.48±0.02‰, d-excess -83.2, Δ^{17}O = -14 per meg) and is devoid of tritium (see Tab. 1.). The recent infiltration end-member (wells W-3 and R-1) reveal high and variable tritium levels and their stable isotope composition (R-1: δ^2H = -70.43±0.05‰, δ^{18}O= -10.27±0.02‰, δ^{17}O= -5.40±0.02‰, W-3: δ^2H = -69.57±0.04‰, δ^{18}O= -10.17±0.02‰, δ^{17}O= -5.36±0.01‰) reflects isotopic signature of local precipitation.

MIXING

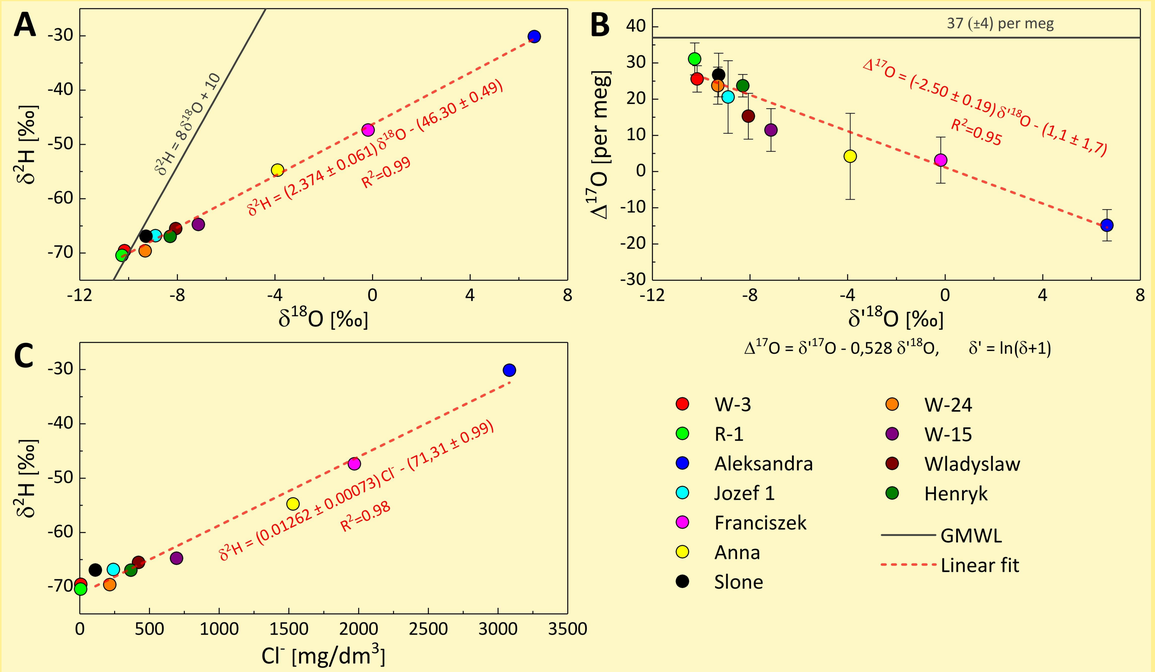


Fig. 6. Mixing lines in 3 different coordinates: δ^2H-δ^{18}O (A), Δ^{17}O-δ'^{18}O (B) and δ^2H-Cl^- (C)

The end-members define a mixing line in the δ^2H-δ^{18}O space (Fig. 6A). Isotope data for the remaining nine wells tightly cluster along this line confirming strong interaction between recent infiltration waters and diagenetic waters in the study area. Also, a strong linear relationship is observed between stable isotope composition and chloride concentration in all studied wells further supporting the occurrence of two-component mixing (Fig. 6C). A mixing pattern is also apparent when Δ^{17}O parameter is plotted as a function of ln(δ^{18}O+1); Δ^{17}O gradually decreases from ca. 30 per meg for recent infiltration component, down to approximately -14 per meg measured in Aleksandra well (Fig. 6B).

CHEMISTRY OF WATERS

Mineral waters of Wysowa Spa are HCO_3-Cl-Na, HCO_3-Na and HCO_3-Na-Ca waters containing trace components with specific pharmacological activity, such as bromine, iodine, iron and metaboric acid. The content of dissolved solid components ranges from 2.3 g/dm^3 in the Jozef I well to 23.4 g/dm^3 in the Alexandera well.

The dominance of the HCO_3 component as well as the variability of the chemical composition of Wysowa waters are clearly visible in the Piper diagram [Fig. 7.]. Water from Aleksandra well is enriched in Cl^- and Na^+ ions and contains geogenic carbon dioxide. In wells W-3 and R-1, representing infiltration water, the participation of Cl^- and Na^+ ions decreases in favor of Ca^{2+} ions.

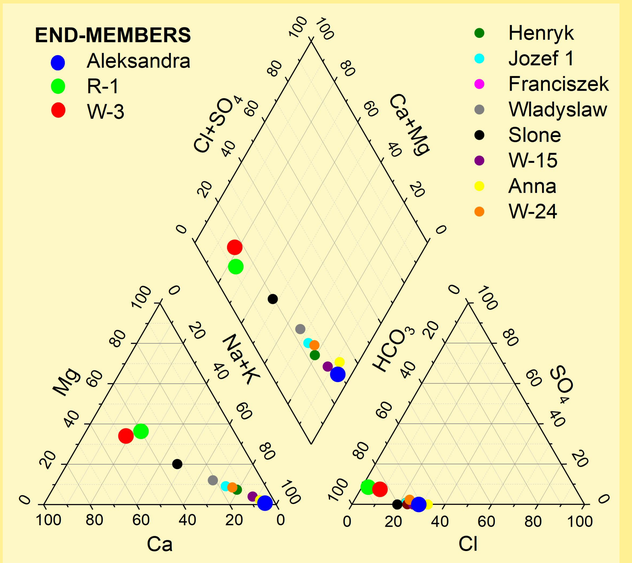


Fig. 7. Piper diagram for Wysowa waters. Aleksandra, W-3 and R-1 end-members are marked with enlarged symbols

CONCLUSIONS

- The mineral waters of the Wysowa Spa region are mixed waters containing two major components in varying proportions: (i) highly mineralized diagenetic water of deep circulation, reaching the surface through system of fissures and faults, and (ii) recent water of local infiltration.
- Isotope and chemical data available for the analysed mineral waters, when plotted in three different space coordinates (δ^2H-δ^{18}O, δ^2H-Cl^-, Δ^{17}O-δ'^{18}O), cluster along mixing lines thus confirming strong interaction between recent infiltration waters and diagenetic waters in the study area.
- The diagenetic end-member (Aleksandra well) reveals distinctly lower Δ^{17}O value (ca. -14 per meg) when compared to the local infiltration water (ca. +30 per meg). It is not clear at the moment what is the origin of this characteristic Δ^{17}O signature. Possible reasons involve: (i) evaporative marine environment in which clay minerals constituting Carpathian flysh were formed, (ii) possible isotope effects during compaction and release of structural water in the course of low-temperature metamorphism, and (iii) possible isotope effects during ultrafiltration process which presence was postulated for the Carpathian flysh [3].

REFERENCES:

[1] Dowgiałło J. (1973) Results of oxygen and hydrogen isotope investigations in groundwaters of the South Poland. Inst. Geol. Biuletyn 277, vol. III, (1973) 319-334 (in Polish)
[2] Leśniak P. (1980) The origin of chloride waters at Wysowa, West Carpathians. Chemical and isotopic approach. Acta Geologica Polonica, 30(4), (1980) 519-550.
[3] Zuber A., Chowaniec, J. (2009). Utrafiltration and diagenesis as important processes controlling isotopic composition and chemistry of waters in some sedimentary basins. Biuletyn Państwowego Instytutu Geologicznego, 436, 575-582 (in Polish)

ACKNOWLEDGEMENTS:

The presented work was supported by National Science Centre (research grant No. 2016/23/B/ST10/00909) and by statutory funds of the AGH University of Science and Technology (project no. 11.11.220.01/1).