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Extended Abstracts

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title: **Comprehensive geochemical studies of new mineral water found in the Sudetes Mts., Poland. Its origin, age, and reaction rates**

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In Sokołowsko, south of Wałbrzych town (the Intra-Sudetic Synclinorium, the Sudetes Mts., SW Poland), sulphate mineral water has been found. The groundwater does not comply with drinking-water standards, but shows the chemistry unique against a background of the Sudetes Mts., where CO_2-rich mineral water with varied cationic composition dominate. The geochemical investigations which included aqueous chemical and isotopic composition, chemistry of mineral phases, geochemical modelling, and tritium and radiocarbon groundwater dating were performed for: (1) elucidating the origin and the age of mineral water, and fresh groundwater which occur in the same hydrogeological system, and (2) explaining the spatial pattern of the groundwater chemistry.
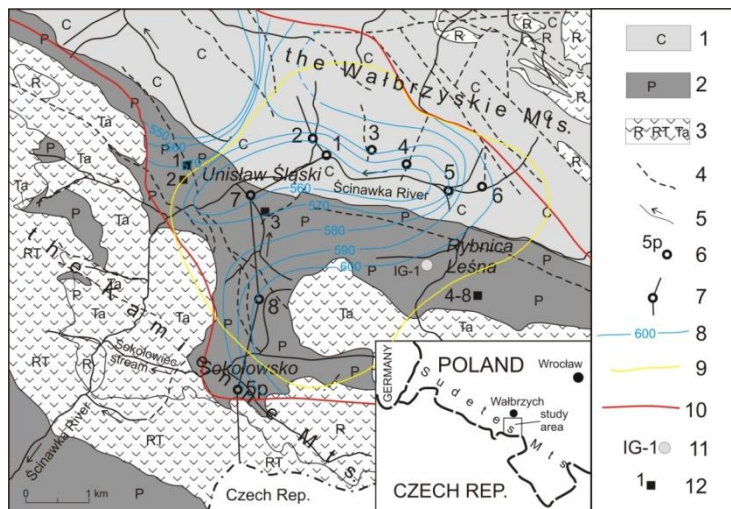
Figure 1. Hydrogeological sketch map of the area studied (after Dobrzyński, 2009). Explanations: 1 — Carboniferous sedimentary rocks; 2 — Permian sedimentary rocks; 3 — volcanic rocks: rhyolites (R), rhyolitic tuffs (RT), trachyandesites (Ta); 4 — faults; 5 — water-courses; 6 — wells; 7 — geological cross-section line (see Fig. 2); 8 — hydroizohypses; 9 — limit of depression cone; 10 — boundary of the hydrogeological unit; 11 — deep borehole; 12 — sites of carbonate rock sampling.

Groundwater was sampled in the well 5p in Sokołowsko and in wells (nos. 2, 1, 7, 8) located in the vicinity of the village of Unisław Śląski (Fig. 1). Physico-chemical analysis of groundwater comprises: field measurement (T, pH, E_H, specific electric conductivity (SEC), and gases (O_2, H_2S)), determination of main anion and cation solutes, and trace elements. Isotopic research covered stable ($\delta^{34}S$-SO_4, $\delta^{13}C$-DIC, $\delta^{18}O$, δ^2H) and unstable (^3H, ^{14}C) isotopes in groundwater, $\delta^{13}C$ and $\delta^{18}O$ in carbonate minerals, and $\delta^{34}S$ and $\delta^{18}O$ in gypsum. Determination of radiocarbon activity was performed by the AMS method, and tritium by liquid scintillation spectrometry. The lumped-parameter approach (the FLOWPC code; Małoszewski & Zuber, 1996, 2002) was applied to obtain the mean tritium ages of water and the age distribution functions. Tritium input function was prepared upon tritium data in precipitation (from Cracow station, extrapolated to Vienna and Ottawa data (the GNIP database) using correlation parameters (Duliński et al., 2001, IAEA, 2002)), and monthly precipitation records from the nearest station. The PHREEQC code has been applied for the geochemical modelling of groundwater.
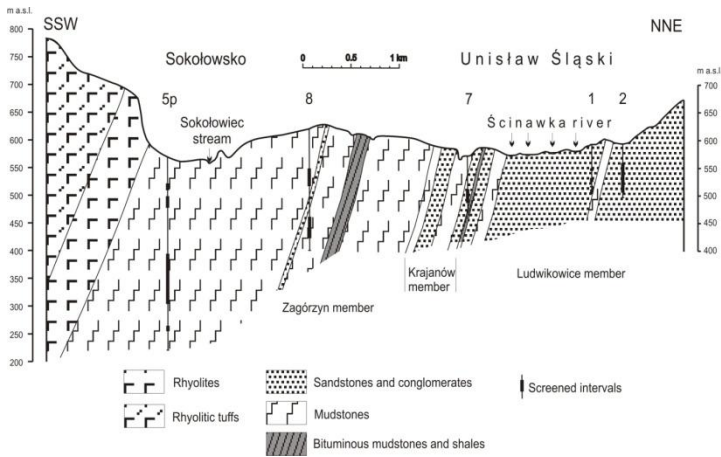
Figure 2. Schematic geological cross-section (after Dobrzyński, 2007a).

The Intra-Sudetic Synclinorium is filled by a thick complex (up to 10 km) of Carboniferous-Permian terrestrial clastic sediments with volcanogenic rocks. The Carboniferous-Permian succession is locally overlain by a thin cover of terrestrial Lower Triassic sandstones and Upper Cretaceous marine deposits. In the study area the bedrocks are conglomerates, sandstones, mudstones with clays and limestones of Late Carboniferous-Early Permian ages (Fig. 1) comprising the Ludwikowice Member (Upper Stefanian), and the Krajanów and Zagórzyn members (Lower Autunian) (Fig. 2). In the southern part of the area, Permian volcanogenic rocks occur. Sulphate mineral water in Sokołowsko occur in mudstones and claystones, with sandstones. Argillaceous-siliceous and ferrous cements are dominant in bedrock. The most reactive phases in the aquifer rocks are gypsum, calcite, dolomite, siderite, illite, kaolinite, and dispersed pyrite and organic matter.

The chemical and isotopic data acquired evidence gradual changes of groundwater composition (Table 1), from fresh water in well 2 (in an unconfined part of the aquifer) to mineral water in well 5p. The salinity of the groundwater and the concentration of most solutes increase southwards, towards the centre of the sedimentary basin. The wells (2, 1, 7, 8, 5p) are situated along the dip of the beds. However, the hydrogeological conditions indicate that wells are not located on the same single flow path, and the groundwater chemistry pattern could not be considered to be a result of chemical evolution.

The studied hydrogeological system is treated as a system of flows of two end-member waters: (1) the modern, tritium-bearing, fresh groundwater (MTW), and (2) the pre H-bomb, Holocene sulphate mineral water (SMW) (Dobrzyński, 2007b). The mixing of these components is the main process responsible for the spatial pattern of aqueous chemistry. Observation during pumping in well 5p and isotope evidences revealed that the MTW component occurs also in the sulphate mineral water horizon (Dobrzyński, 2007a, 2009). The ratio of mixing components was quantified by using geochemical modelling. The SMW to the MTW component ratio in the well 5p was estimated to be 0.65/0.35 (Dobrzyński, 2007b).

Table 1. Selected physico-chemical parameters of groundwater. Concentrations in mg/L (for complete isotopic data see Dobrzyński, 2009).

| Parameter	Well no. 2	Well no. 1	Well no. 7	Well no. 8	Well no. 5p
T [°C]	11.2	9.3	10.1	15.46	15.3
pH	7.73	7.80	7.47	7.74	7.60
pe	6.373	6.151	5.969	5.556	1.278
SEC_{25} [µS/cm]	249	460	598	1230	2070
DOX	4.47	2.32	2.87	<0.01	0.60
H_2S	<0.01	<0.01	0.03	0.01	0.44
SiO_2	17.0	18.0	17.3	30.4	19.8
SO_4	38.8	126	205	625	1113
HCO_3	84	111	123	95	116
Cl	7.12	9.5	2.4	0.2	0.2
F	0.11	0.10	0.10	0.01	0.01
NO_3	8.11	8.9	4.46	1.94	0.00
Ca	33.5	56.5	98.4	197.7	322.9
Mg	5.8	16.6	9.4	25.9	20.2
Na	6.0	12.6	16.1	54.9	129.5
K	1.1	1.5	1.9	0.3	1.5
Al	0.004	0.010	0.006	0.006	0.045
As	0.0062	0.0036	0.0092	0.0887	0.1023
B	0.022	0.048	0.144	0.304	1.114
Ba	0.127	0.044	0.038	0.017	0.011
Fe	0.005	0.010	0.010	0.060	0.66
Li	0.005	0.011	0.031	0.035	0.121
Mn	0.0005	0.001	0.011	0.086	0.126
NH_4	<0.05	<0.05	<0.05	<0.05	0.13
Sr	0.086	0.291	1.045	8.942	7.836
Zn	0.016	0.018	0.054	0.017	1.052
[3]H [TU]	10.18 ÷ 9.59	10.62 ÷ 7.55	16.20 ÷ 6.50	4.00 ÷ 2.86	3.20 ÷ 2.44
[14]C [pmC]	56.39 (±0.23)	46.19 (±0.26)	36.79 (±0.19)	41.68 (±0.27)	26.94 (±0.19)
PCC[1]	Ca-HCO₃-SO₄	Ca-Mg-SO₄-HCO₃	Ca-SO₄-HCO₃	Ca-SO₄	Ca-Na-SO₄

[1]prevalent chemical character according to ion concentrations exceeding 20% meq/L.

Main reactions which formed chemistry of the SMW component were quantified by applying inverse mass balance modelling, which was performed between recharge fresh groundwater (input water) and sulphate groundwater (output water). The chemical composition of the groundwater from well 2 was taken as representative of fresh groundwater recharging the system (Dobrzyński, 2008). The chemistry of the mineral water from well 5p was equilibrated with gypsum, and in this way modified composition assumed as composition of output water in the inverse modelling (Dobrzyński, 2009). Solid, gas and exchange phases are included in the mass balance model. Dissolution of gypsum and Mg, Fe, Mn, Zn-bearing carbonates was included. The sulphate mineral water is supersaturated with respect to calcite and barite and the minerals are assumed to be precipitating. Both celestite and strontianite minerals were considered as source phases for strontium. Of silicate phases, biotite (phlogopite), chlorite and kaolinite were included in the model. Organic matter is incorporated into the model as CH_2O. The sulphate mineral water contains H_2S and is supersaturated with pyrite (SI=16.6), which mineral is considered as a possible sink phase for iron released from siderite. Ion exchange between sodium (adsorbed onto clay minerals) and calcium solute is assumed to be a sodium source. Precipitation of halite and fluorite is not thermodynamically possible (SI<0), but both minerals are incorporated as sink phases for explaining the decrease in chloride and fluoride, respec-

tively. Sulphur and carbon stable isotopes on aqueous and solid phases (after the author's own and cited data — Dobrzyński, 2009) have also been included in the inverse model for balancing the chemical reactions. According to the two inverse models found (Dobrzyński, 2009), the main chemical features of the sulphate mineral water are controlled by gypsum dissolution, dedolomitization, organic matter decomposition and cation exchange. Sulphate solutes are reduced by bacterial mediation with the decomposition of organic matter, and iron sulphide might form. Sulphate reduction raises pH and additionally contributes to calcite supersaturation. The models found differ in the source phase for strontium. Model with strontianite dissolution as a source of strontium, probably better fits the sulphate mineral water than model with celestite dissolution. Investigation of carbonate chemical composition shows that carbonates from the study area contain about 0.5% of Sr, whereas gypsum is very poor in strontium (ca. 0.03% mol.) (Dobrzyński, 2009). Therefore, dissolution of carbonates is assumed to be a main source of Fe, Mn, Zn, and Sr solutes in the sulphate groundwater. The increase in porosity due to the reactions which formed chemistry of SMW is calculated to be lower than 0.04%. Dedolomitization driven by gypsum dissolution is a well recognized process, and has been documented in several aquifers on a regional scale (e.g., in Mexico, USA, Spain). In the study area, similar significant effects of gypsum dissolution and dedolomitization on groundwater quality have been found on a much smaller, local aquifer.

The tritium age of MTW component in well 5p was calculated by using lumped-parameter approach (e.g., Małoszewski & Zuber, 1982). Tritium data from the sulphate mineral water horizons in well 5p fit best the dispersion model (with $\beta=0.65$, $P_D=0.20$, $\Sigma=0.125$) and the exponential-piston flow model ($\beta=0.65$, $\eta=1.38$, $\Sigma=0.131$) with a mean residence time (MRT) of 98.3 years and of 126.4 years, respectively (where β — extra water component with zero tritium concentration, from the mixing geochemical modelling; P_D — the dispersion parameter (reciprocal of the Peclet number); η — the ratio of the total water volume to the volume with the exponential distribution of transit times; Σ — goodness of fit in the FLOWPC code defined by Małoszewski & Zuber (1996)). Dispersion model is more adequate to local hydrogeological conditions. The MRT larger than the period of the H-bomb era arises from assumed flow model (flow distribution) in the lumped-parameter approach. The presence of flow lines with groundwater of residence time of hundreds of years seem to be realistic and might result from retarded draining of small fissures and matrix micropores.

The radiocarbon age of the SMW component was estimated after complex corrections. Initial ^{14}C activity in recharge zone was assumed for two variants, for closed and semi-closed conditions with respect to soil-CO_2. Effects of mixing (MTW and SMW waters) and chemical water-rock reactions in saturation zone (after inverse mass balance modelling), as well as calibration for variations of atmospheric ^{14}C in the Holocene were taken into account. The calibrated radiocarbon-age of SMW is estimated to be of 5.9($\pm$0.3) ka BP and 12.4($\pm$0.5) ka BP for closed and semi-closed systems, respectively. Inverse mass balance models indicate system closed with CO_2, and it much better fit radiocarbon activity (Fig. 3). Consequently, the radiocarbon age of 5.9($\pm$0.3) ka BP was assumed as more adequate for the SMW component.
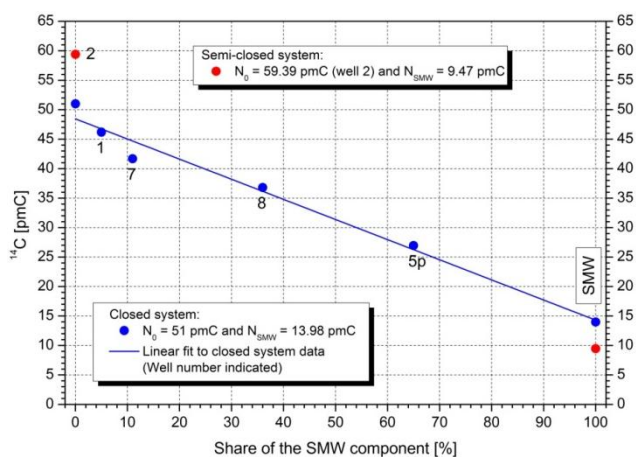
Figure 3. Radiocarbon activity in groundwater versus water mixing ratio (after Dobrzyński, 2009)

The mean apparent reaction rates for the chemistry of SMW were estimated based on phase mole transfers (from inverse model) and radiocarbon dating, and are calculated to be: dissolution of gypsum (2.85 µmol/L/year) and dolomite (0.21 µmol/L/year), calcite precipitation (0.20 µmol/L/year), and organic matter decomposition (0.08 µmol/L/year) (Dobrzyński, 2009). The studied hydrogeological system has about 40 km² only. One should be noticeable that the reaction rates found are well consistent with the reaction rates for a vast regional Madison aquifer, USA (e.g., Busby et al., 1991), where a very similar set of geochemical reactions is currently responsible for groundwater quality formation.

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