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Extended Abstracts

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title: **Two contrasting geothermal systems — towards the identification of geochemical reaction pattern and groundwater temperature, the Sudetes, Poland**

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The Sudetes Mts. (SW Poland) is a region rich in curative mineral waters used in balneotherapy. Two main types of mineral waters occur in the Sudetes Mts.: (1) low-enthalpy CO_2-rich water with various cationic composition (mainly Ca, Mg, Na), and (2) thermal Ca or Na bicarbonate and/or sulphate waters, usually fluoride-rich, containing H_2S and/or Rn. Thermal waters are exploited in two spas: Lądek Spa and Cieplice Spa (Fig. 1).

Figure 1. Location of Lądek and Cieplice spas (The Sudetes Mts., SW Poland). Explanations: 1 — spas with thermal waters in The Sudetes Mts.; 2 — other spas in The Sudetes Mts., which provide low-enthalpy curative waters.

The water temperatures in these spas reach 44°C and 59°C, respectively (Tab. 1).

Table 1. Chemical characteristics of thermal water from Lądek (L-2 borehole) and Cieplice (C-2 borehole), The Sudetes Mts., Poland. Concentrations in ppm.

Parameter	L-2	C-2	Parameter	L-2	C-2
pH	9.22	8.20	Li	0.032	0.182
SEC[1]	777	237	Mg	0.215	0.053
E_H [mV]	-159	-141	Mn	0.010	0.008
T [°C]	44.3	58.8	Na	47.778	169.773
T[2] [°C]	80±5	110±10	Ni	0.002	0.001
$logPCO_2$[3]	-4.50	-2.75	P	0.024	0.026
$logPCO_2$[4]	-2.50	-1.05	Rb	0.010	0.038
Al	0.040	0.052	Si	48.212	85.302
As	0.001	0.047	Sr	0.038	0.205
B	0.043	0.236	Zn	0.105	0.006
Ba	1.577	0.011	F	11.50	12.00
Br	0.041	0.262	Alkalinity[5]	59.568	152.227
Ca	5.822	9.235	SO_4	15.20	148.96
Cs	0.005	0.027	Cl	8.86	43.61
Cu	0.005	0.003	$N-NO_3$	0.007	0.002
Fe	0.033	0.027	$N-NH_4$	0.536	0.008
K	0.772	4.900	H_2S	3.66	<0.01

1 — specific electric conductivity (in µS/cm) compensated for 25°C; 2 — temperatures at depth, estimated; 3 — calculated CO_2 pressure at outflows; 4 — CO_2 pressure at depth, estimated; 5 — alkalinity in $mgCaCO_3/L$

Due to the high cost of drilling and equipment there is a continuous interest in a priori estimation of temperatures in geothermal systems. Most of the developed chemical geothermometers entail only a selected set of water parameters. Moreover, in such an approach all geothermometers are valid only if – even partial and/or local – chemical equilibrium in the system is reached and maintained. At temperature lower than equilibrium temperature and/or if other suit of minerals are in equilibrium with waters the usage of geothermometers might fail. In this study a multi-component chemical calculation of chemical equilibrium proposed by Reed & Spycher (1984) were applied to estimate water temperature at depth.

Two contrasting by temperature and water chemistry geothermal systems in the Sudetes Mts., Poland, were considered. Exploited, most deep waters from wells L-2 and C-2 in Lądek and Cieplice, respectively, represent the chemical end-member compositions. The Cieplice/Lądek thermal waters differ mainly in pH, calculated PCO_2, E_H, and concentration of main solutes (Ca, Mg, Na, SO_4, alkalinity), silica and hydrogen sulphide (Tab. 1). Speciation/solubility modelling and reaction path modelling were performed by using the PHREEQC code (Parkhurst, Appelo, 1999) with LLNL thermodynamic database.

The method of Reed and Spycher (1984) of estimating temperature in the aquifer relies on using the composition of water of interest to find a temperature, where a plausible minerals of the given system are computed to be in equilibrium with aqueous phase. This is provided by plotting the saturation index of minerals versus temperature. This method was adapted previously to the Sudetes thermal waters (Leśniak, Nowak, 1993), although the lack of Al concentration could affect partially the results. Currently obtained temperatures (Figs. 2, 3) are higher than proposed earlier by Ciężkowski at al. (1992), Leśniak & Nowak (1993), and generally are close to the recent estimate by chemical and isotopic geothermometry (Dowgiałło, 2000; Dowgiałło et al., 2005). At calcite equilibrium and $logPCO_2$ of -2.50 and -1.05, respectively, the estimated temperature for Lądek is 80 ±5°C and for Cieplice is 110 ±10°C (Tab. 1).
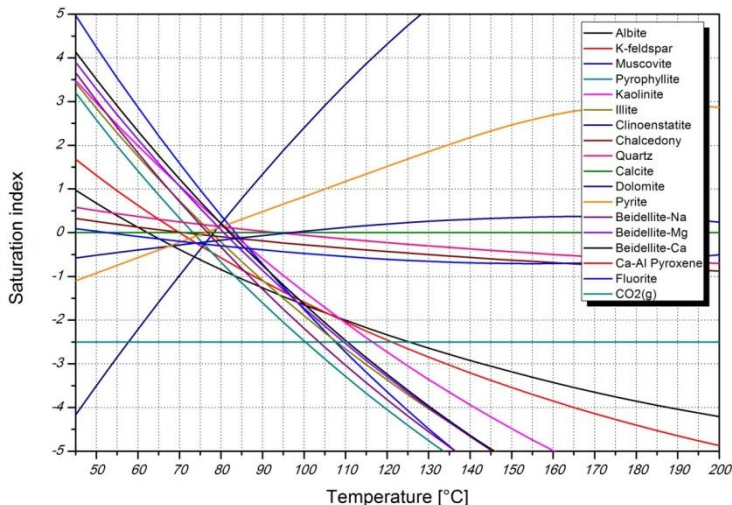

Figure 2. Saturation index for minerals vs. temperature for thermal water from well L-2 in Lądek Spa, equilibrated with calcite, at $logPCO_2$= -2.50.
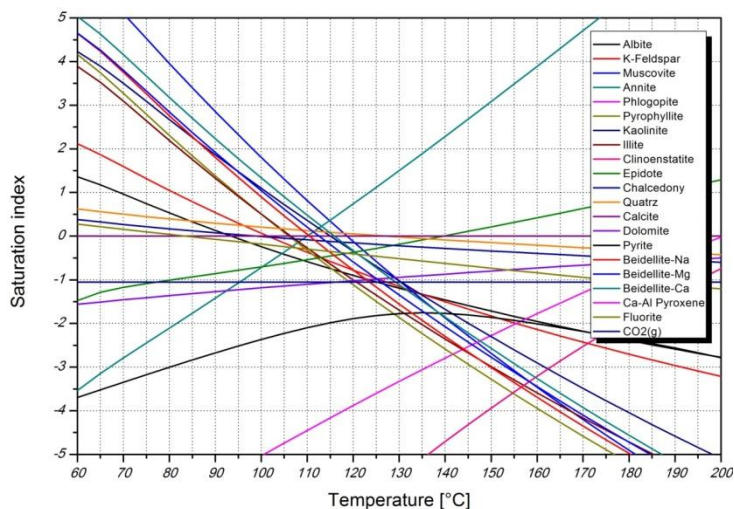
Figure 3. Saturation index for minerals vs. temperature for thermal water from well C-2 in Cieplice Spa, equilibrated with calcite, at logPCO2= -1.05.

In addition to the mineral saturation plots which provide a temperature at depth, a geochemical reaction paths revealing how the chemical composition is formed at a presence of a genuine mineral assemblage have been modelled. Geochemical reaction path modelling has been applied for identifying main chemical reactions which are responsible for formation the chemistry of thermal waters in both systems. Aquifer rocks in the Lądek geothermal system (mainly gneisses) and the Cieplice system (granites) are composed mainly of the same mineral set (plagioclases, K-feldspars, biotites, muscovites). These minerals, with genuine composition, were considered as a preliminary input of source mineral phases in the modelling. The apparent difference is that plagioclases in Lądek gneisses are more sodic (avg. $Ab_{85}An_{15}$) than plagioclases in Cieplice granite (avg. $Ab_{65}An_{35}$). Moreover, the formation of secondary clay minerals, calcite and silica were considered in the models. Fluorite was included in modelling as a source of fluoride, an important constituent of thermal waters. Hydrogen sulphide has been also added to the model of Lądek system because of its distinct presence (Tab. 1).

Logically, reaction path modelling were performed for the same CO_2 pressure and temperature as in the temperature estimation process, i.e., $logPCO_2 = -2.50$, T = 80°C and $logPCO_2 = -1.05$, T = 110°C for Lądek and Cieplice systems, respectively (Tab. 1). Reaction path models which fit the best the field data were found (Figs. 4, 5; Tab. 2) by the trial-and-error method. Species activities in thermal waters were assumed as an end-points of modelled reaction paths. The chemical reaction paths resulted from simulations in $[Na^+]/[H^+]$ vs. $[Si]$, and $[Ca^{2+}]/[H^+]^2$ vs. $[Si]$ scales, lead to the chemical compositions of the thermal waters of interest.
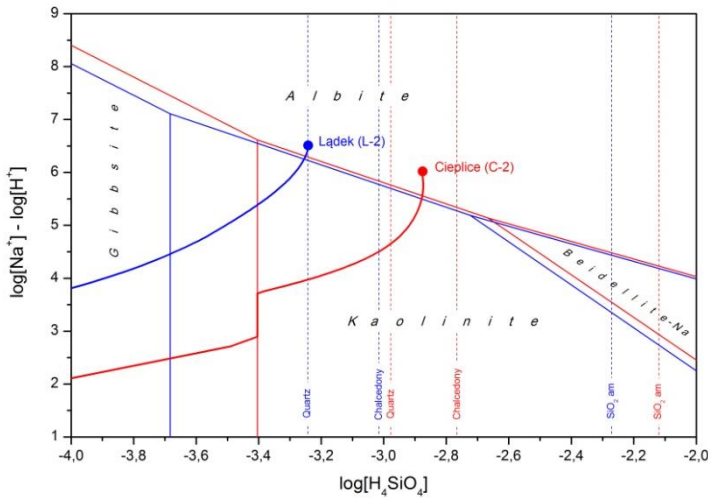
Figure 4. Reaction paths for thermal water from well L-2 (Lądek Spa) and well C-2 (Cieplice Spa) in the Na2O-SiO2-Al2O3-H2O system. Blue lines refer to the Lądek geothermal system, red ones to the Cieplice geothermal system.
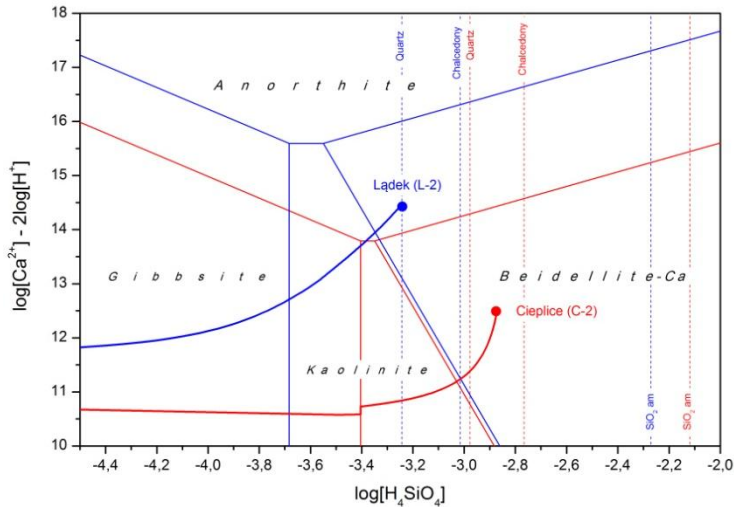
Figure 5. Reaction paths for thermal water from well L-2 (Lądek Spa) and well C-2 (Cieplice Spa) in the CaO-SiO$_2$-Al$_2$O$_3$-H$_2$O system. Explanations as in Fig. 4.

It results, that the main features of the chemistry of the thermal waters in both geothermal systems are probably formed by a similar set of geochemical reactions: dissolution of plagioclases, biotites and fluorites, and formation of Ca-beidellite, calcite and silica. In the Lądek system, Na-beidellite is also forming. The details of the mass transfer of dissolving/precipitating phases can be found in Tab. 2.

Table 2. Phases considered in the geochemical reaction path models with mole transfers.

Lądek L-2			Cieplice C-2		
Phases	**Role in the model**	**Mole transfer ratio with respect to fluorite[1]**	**Phases**	**Role in the model**	**Mole transfer ratio with respect to fluorite[1]**
Plagioclase[2]	Diss	133.33	Plagioclase[3]	Diss	96.67
Biotite[4]	Diss	2.67	Biotite[5]	Diss	8.53
Fluorite	Diss	1	Fluorite	Diss	1
$H_2S(g)$	Diss	3.33			
Beidellite-Na	Prec	46.67			
Beidellite-Ca	Prec	20	Beidellite-Ca	Prec	11.52
Quartz	Prec	90	Quartz	Prec	103.6
Calcite	Prec	76	Calcite	Prec	100.53

Explanations: 1 – according to reaction path modelling fluorite mole transfer has been found to be the lowest one in both models. Average composition of genuine plagioclases and biotites assumed in the model-ling:

2 – $Na_{0.85}Ca_{0.14987}Sr_{0.00013}Al_{1.15}Si_{2.85}O_8$; 3 – $Na_{0.65}Ca_{0.35}Al_{1.35}Si_{2.65}O_8$;

4 – $KFe_{1.495}Mg_{1.495}Mn_{0.007}Zn_{0.003}AlSi_3O_{10}(OH)_{1.629}F_{0.364}Cl_{0.007}$;

5 – $K_{0.8508}Na_{0.0847}Li_{0.0479}Rb_{0.0044}Fe_{1.9874}Mn_{0.0135}Mg_{1.1410}Ca_{0.2441}Th_{0.0002}U_{0.0003}Cu_{0.0008}Zn_{0.0080}Be_{0.0016}Sr_{0.0018}Ba_{0.0274}Sn_{0.0013}Al_{1.2128}Zr_{0.0015}Hf_{0.0001}Si_{2.9544}O_{11.29975}(OH)_{0.7041}F_{0.0050}$.

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