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Isotope Temperature Indicators of Thermal Waters in South - Western Poland

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ABSTRACT

Thermal springs occur or have occurred in the past in crystalline formations of the Sudetes Mountains. At all these sites, water was used for centuries as a therapeutic factor. In order to increase its temperature and available resources, boreholes up to 2000 m deep were carried out and the results are promising. However, in order to substantiate further drilling, temperatures in the deeper parts of particular hydrogeothermal systems have to be estimated. The paper presents the preliminary results of the application of SO_4-H_2O isotope geothermometer to three separate hydrogeothernal systems of Sudetes Mountains, namely: Duszniki, Ladek and Cieplice, where spring water temperatures range between 20 – 45°C. It was found that equilibrium was reached only in waters at Cieplice in the reservoir temperature of about 100°C. Such equilibria don't exist in thermal waters at Duszniki and Lądek, where secondary processes take place as for example, the mixing with shallow groundwaters, oxygen isotope shift due to very high CO_2/H_2O ratio (Duszniki), and reduction of sulfates (Lądek).

1. INTRODUCTION

A number of hydrogeothermal systems have been recognized in the Sudetes Mountains. both on the Polish and Czech sides of the border. Their general hydrogeological description may be found in Dowgiałło (1976), while the paper by Dowgiałło (2002) is devoted in particular to thermal waters occurring within the Polish territory.

At Cieplice, Duszniki and Lądek (Fig.1) renowned spas were developed during the 18-20 centuries, based initially mainly on natural mineral and thermal water springs. The highest temperature of spring water was known at Cieplice (up to 45^0C), the lowest one, only slightly exceeding 20^0C (but still deserving the qualification "thermal") was that of carbonated water springs at Duszniki. In course of time drilling was applied in order to increase available water amount and its temperature. Initially the depth of boreholes did not exceed 200 m (Duszniki). Only in the second half of the 20th century they attained the depth from 700 m (Lądek) up to 2000 m (Cieplice). Drilling often resulted in the reduction of natural springs yield or even in their disappearance, but the outcome was in general positive as far as the available water volume and its temperature are concerned.

Thermal water systems under consideration are linked to crystalline formations. At Cieplice the host rock is fissured Carboniferous monzonitic granite, while at Duszniki and Lądek thermal water is circulating in Proterozoic schists and gneisses. Detailed studies have shown, that the presence of hot springs is always connected with faults and accompanying fissure systems. Areas of faults crossing are particularly favorable to warm springs occurrence (Dowgiałło and Fistek, 1995; Zuber et al., 1995; Dowgiałło and Fistek, 2003).

The existence of distinct positive anomalies of conductive heat flow has not been ascertained so far in any of the above-mentioned sites (Bruszewska, 2000; Dowgiałło, 2002). The water temperatures are due mainly to deep penetration of the meteoric recharge fluid. This deep circulation is the result of the generally deep-reaching high fissurity of crystalline rocks and considerable differences in altitude between the recharge areas and the warm spring discharge areas. These differences vary between about 1200 m (Cieplice) and 500 m. (Duszniki). Temperatures attained at depths by waters under consideration seem to be connected mainly with geothermal gradients close to average values. Convection plays probably an important role in forming the measured surface heat flow values not exceeding 79 mWm^{-2} (Cieplice).

In all these sites further development of spa treatment is planned. Thermal water is also supposed to be used for recreation and space heating. This requires a drilling program to be implemented. In order to substantiate this program all possible methods including the isotopic ones have to be used to estimate the temperatures at depths.

2. WATER SAMPLING AND ANALYSIS

Water samples for isotopic analyses were taken from 15 springs and boreholes at Lądek-Spa, Duszniki-Spa and Cieplice-Spa. Untreated 30 ml water aliquots for oxygen and hydrogen isotope determination were collected in glass bottles. The isotopic compositions were performed at the Institute of Geological Sciences PAS, Warsaw, using the method of CO_2 equilibration for $\delta^{18}O$ and water reduction on zinc for δD. The determinations were done by means of Finnigan-Mat Delta-Plus mass spectrometer. The analytical errors is $\pm 0.1^o/_{oo}$ for $\delta^{18}O$ and $\pm 1^o/_{oo}$ for δD.

Samples for the determination of $\delta^{18}O$ in sulfates were prepared in the field by precipitating $BaSO_4$ in polyethylene bottles containing 1.5 l aliquots of water. At the laboratory the precipitate was collected by means of nylon filters, rinsed and dried. 15 mg of the precipitate was taken for reduction with carbon to CO and subsequently to CO_2 following the method proposed by Mizutani (1971). Sulfate oxygen isotopes determinations were done at the Institute of Physics UMCS, Lublin. Reproducibility of measurements is $\pm 0.1^o/_{oo}$.

For a few samples of thermal waters from Lądek the preliminary results of determination of sulfur isotopes in sulfates are presented (Table 2). For these measurements, $BaSO_4$ precipitated in the field was used. Prior to its precipitation H_2S was removed from acidified samples by bubbling nitrogen (Carmody et al., 1998). Collected $BaSO_4$ was converted to SO_2 with $NaPO_3$ at 850^0C according to Halas and Szaran (2001). Sulfur isotopic composition was measured at the Institute of Physics UMCS, Lublin. Reproducibility of measurements is ±0.1‰.

Chemical data of waters under consideration (Table 1) were taken from archival records. New analyses of 5 water samples were done at the Central Chemical Laboratory, Polish Geological Institute, Warsaw. High performance liquid chromatography (HPLC) was applied for anion analysis and inductively coupled plasma-atomic emission spectrometry (ICP-AES) for cation analysis in samples acidified to pH 2.

Indicatory measurements of pH and temperature were done in the field for all waters considered by means of portable pH-meters with automatic temperature compensation.

3. RESULTS AND DISCUSSION

Tables 1 and 2 present chemical and isotopic characteristics of thermal waters at the considered localities in the Sudetes Mts. The thermal waters are situated above the GMWL except some water samples from Cieplice (Fig.2).

Local Meteoric Water Line (LMWL), calculated by Ciężkowski (1990) for 76 shallow groundwaters of the Sudetes Mts. is the following:

$$\delta D = 5.28\ \delta^{18}O - 15.83, \quad R = 0.93 \qquad (1)$$

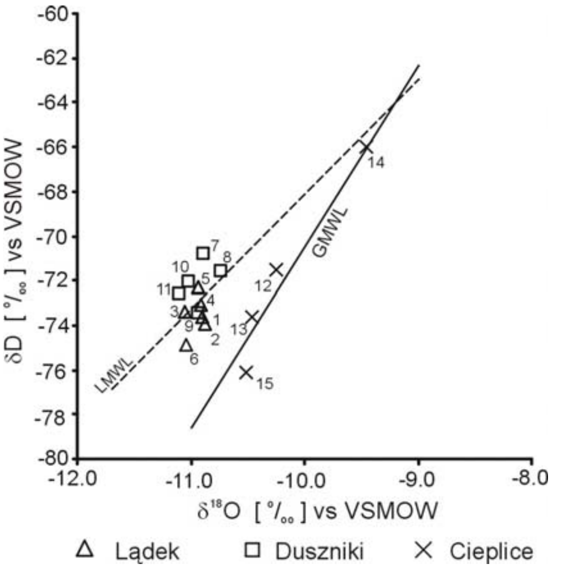

Figure 2: Oxygen and hydrogen isotopic composition of thermal waters. Global Meteoric Water Line (GMWL) after Różański et al. (1993); Local Meteoric Water Line (LMWL) after Ciężkowski (1990). Numbering of wells and springs according to Table 1. For more explanations see the text.

The isotopic compositions of thermal waters considered here lie along the LMWL. In the case of some waters at Duszniki, which are plotted above the LMWL, the oxygen shift should be taken into account as shown by Zuber (1987) for deep carbonated waters at Krynica Spa, (Carpathian Mts., Poland). This negative $\delta^{18}O$ shift is caused by the large water content of CO_2 rich in the heavy oxygen isotope. This forces water's oxygen composition to lighter values. Ciężkowski (1990) estimated the mean value of $\delta^{18}O$ shift in carbonated waters at Duszniki as -0.36‰. Application of this correction would move the position of the waters to the right, closer to the LMWL.

Tritium content in thermal waters of all sites considered is evidence that modern meteoric water can play an important role in their recharge. Present day tritium content in precipitation in Poland is ca 10 TU. Thermal waters at depths of 700 m and more contain almost no tritium. At moderate depths, up to 200 m, the content of tritium rises considerably, exceeding even values typical for present day precipitation. At springs or shallow wells the contents of tritium vary significantly from 0.0 to 16.6 TU (Ciężkowski et al. 1996).

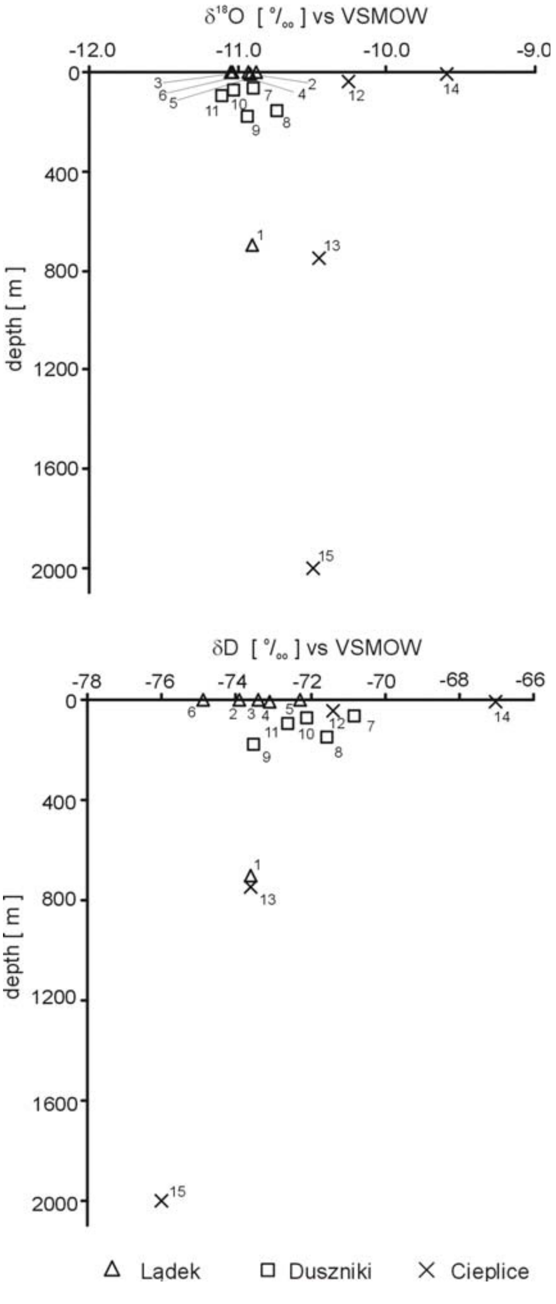

Figure 3: The isotopic composition of thermal waters plotted against depth. Numbering according to Table 1.

There is no linear relationship between tritium content and thermal water temperature at the outflow. Probably, deep hot waters during ascending to the surface mix with different proportion of shallow water of the modern hydrological cycle. The deepest thermal water with temperature of 86.7°C at the outflow (well C-1 at Cieplice), coming from the depth range 1650 - 2000 m (geophysical logging) has -76‰ for δD, -10.5 for $\delta^{18}O$, and no tritium (Fig. 3).

In particular, δD values show that waters that occur deeper are isotopically lighter (Fig. 3). Such a trend might mean that the water occurring deeper infiltrated under climatic conditions colder than the present one (Ciężkowski et al., 1992). The impact of the altitude effect is also possible (Dowgiałło and Fistek, 1995).

Such a shift may not be quite clear on $\delta^{18}O$ which seems to be justified because some, deep-seated water (for instance from C-1 well) might be warmed enough and flow slowly enough to at least start an exchange of their oxygen isotopes with rocks constituting the geothermal reservoir. However, there are positive premises that in favorable geological settings we can obtain deep, old water with no younger admixtures. The presence of such old waters, possibly of glacial age, was confirmed by ^{14}C measurement at Cieplice and Lądek (Dowgiałło et al. 1974).

To predict reservoir temperature of waters in particular hydrgeothermal field the oxygen isotope geothermometer in the sulfate – water system was tested. The geothermometer utilizes the fact that the exchange of oxygen isotopes between SO_4^{2-} and H_2O is a function of temperature. This temperature indicator is counted among the most useful ones for water-dominated geothermal fields and was successfully applied in many geothermal systems in the range of temperatures 100 – 350°C (Mizutani and Rafter 1969; Mizutani 1972; Cortecci 1974; Cortecci and Dowgiałło 1975; McKenzie and Truesdell 1977).

The rate of the oxygen isotopic exchange between sulfate and water in acid and neutral thermal waters of temperature above 100°C is sufficiently fast to expect that sulfates are in isotopic equilibrium with the reservoir waters. Below 100°C the rate of this exchange is much slower. For instance, according to the equation proposed by Lloyd (1968) for half-time of the exchange

$$\text{Log } t_{1/2} = 2.54\ (1000/T) + b$$

where $t_{1/2}$, T and b are the half-time of the exchange in hours, temperature in °K, coefficient equal –1.17 at pH 7, respectively, the time for 99.9% isotopic exchange to equilibrium is about 18 years at 200°C and about 500 years at 100°C.

However, in some groundwaters the residence time of SO_4^{2-} ion may be long enough to attain the isotopic equilibrium with water at temperatures even much below 100°C. The first evidence of such equilibrium was found by Halas et al., (1993) in the study of postglacial waters from deep horizons under the Baltic Sea bottom, Eastern Pomerania, Poland.

The results of application of SO_4–H_2O oxygen isotope geothermometer to thermal waters of Sudetes are summarized in Table 3 and plotted in Fig.4. The equilibrium temperatures based on the Mizutani and Rafter (1969a) scale of equation:

$$1000\ln\alpha = 2.88(10^6/T^2) - 4.1$$

are presented as those best fitted to thermal waters considered.

For all waters considered, there is no common, linear relationship between $\delta^{18}O$ of water and $\delta^{18}O$ of sulfates fitting equilibrium conditions in a particular temperature. The waters from different localities create rather distinct groups which seem to fit equilibrium conditions in different temperatures. It is justified because these waters belong to separate hydrogeothermal systems where the depth of water circulation and the velocity of flow are different.

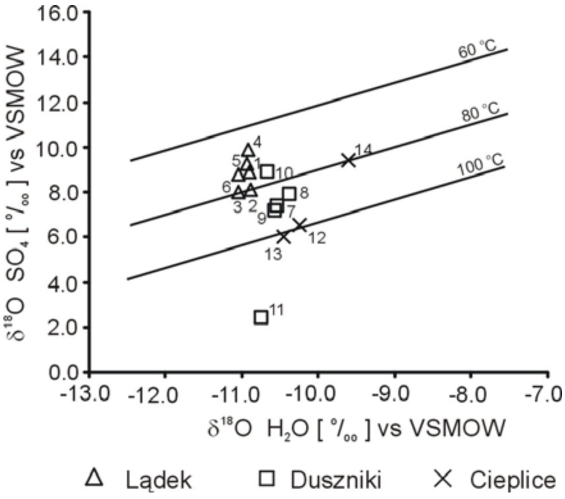

Figure 4: Relationship between $\delta^{18}O$ of water and $\delta^{18}O$ of dissolved sulfates for thermal waters of Sudetes. Solid lines: isotherms after Mizutani and Rafter (1969a). Oxygen shift in the mean value –0.36‰ was applied for waters of Duszniki. Numbering according to Table 1. For more explanation see the text.

All waters under consideration have similar values of $\delta^{18}O$ of water – generally within the range –11.0‰ - –9.6‰. Differentiation on $\delta^{18}O$ of dissolved sulfates is less than 2‰ for each group excluding water from Sobieski spring, at Cieplice, which contain a considerable amount of local precipitation, and water from spring B-3, at Duszniki, where the determined value of $\delta^{18}O$ of sulfates may be erroneous and needs to be checked. Taking into account waters of all localities, the $\delta^{18}O$ of dissolved sulfates scatter from 6.0‰ to 9.9‰.

Isotopic temperatures of waters obtained by applying the fractionation factor proposed by Mizutani and Rafter (1969a) are higher than those measured at the outflow. As can be seen on Fig. 4, waters from Cieplice (excluding the water from Sobieski spring) are plotted almost directly on the isotherm 100°C, whereas waters from Lądek are close to the isotherm 80°C and above it. The carbonated waters at Duszniki are between the waters of Cieplice and Lądek.

We suggest that in the case of thermal waters at Cieplice the equilibrium between oxygen isotopes of water and sulfates was reached in the reservoir at temperatures indicated by the fractionation factor of Mizutani and Rafter (1969a). Such equilibria don't exist in thermal waters at Duszniki and Lądek. However, it cannot be told that the equilibrium did not exist at all. Probably, in these waters we are dealing with secondary processes which cause the disequilibrium observed.

The chemical composition of waters in every particular geothermal system is considerably uniform irrespective of the depth and temperature at the outflow. The waters at Cieplice are of the SO_4-HCO_3-Na type with TDS seldom exceeding 620 mg/l; at Lądek the waters are of the HCO_3-CO_3-Na type with TDS about 200 mg/l whereas at Duszniki the waters are of the HCO_3-Ca-Na + CO_2 type with TDS up to about 3000 mg/l. The highest TDS of waters at Duszniki is connected with the content of CO_2 and is caused mainly by the content of HCO_3^- ion. Carbonated waters at Duszniki are rather young (considerable content of tritium). Due to high CO_2 content, low temperature exchange with carbon dioxide can occur, falsifying the equilibrium picture in the sulfate – water system.

As can be seen on Fig. 5, the relationship between concentration of Cl^- and SO_4^{2-} suggests the regional dilution process.

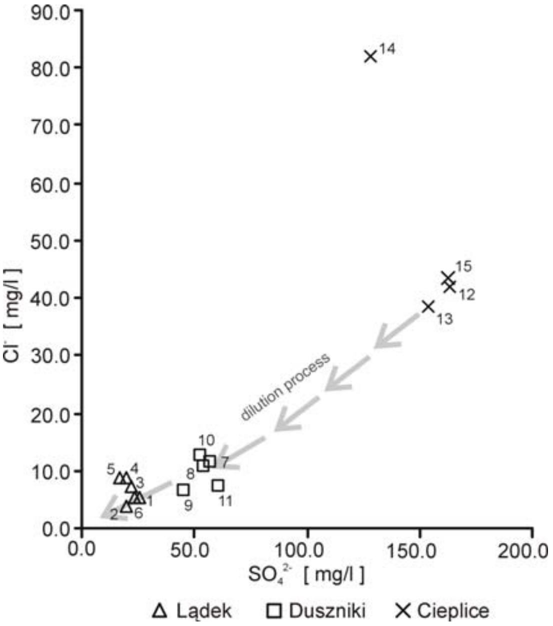

Figure 5: The relationship between Cl^- and SO_4^{2-} concentration in Sudetic thermal waters. Numbering according to Table 1.

The thermal waters at Cieplice contain the highest amount of chlorides and sulfates, and should be considered as those residing in the deepest part of the reservoir for the longest time. Such dilution trend is corroborated by the relationship between concentration of Cl^- and $\delta^{18}O$ of water (Fig. 6a).

The relationship between concentration of Cl^- and $\delta^{18}O$ of sulfates is also noticeable (Fig. 6b). The less the chlorides content, the highest the value of $\delta^{18}O$ of sulfates. The highest values are characteristic for waters at Lądek. In the case of waters at Duszniki and Lądek such relationship is not obvious suggesting the influence of other processes affecting the ^{18}O composition of sulfates like for example reduction of sulfates or oxidation of sulfides.

The relationship between $\delta^{34}S$ and $\delta^{18}O$ of sulfates for a few waters at Cieplice and Lądek suggests processes of bacterial reduction of sulfates (Halas and Mioduchowski, 1978), (Fig. 7). This is corroborated by the occurrence of H_2S in thermal waters of Lądek. The existence of such correlation may indicate that before the sulfate reduction process both the isotopic composition of sulfates and oxygen isotopic composition of water were similar in all waters (Mizutani and Rafter, 1969b; Halas and Mioduchowski, 1978).

All these facts seem to corroborate our hypothesis that among hydrogeothermal fields under consideration isotopic equilibrium in the sulfate – water system can be observed only in thermal waters at Cieplice. This may be finally verified once the water sample from the deepest borehole C-1 is taken.

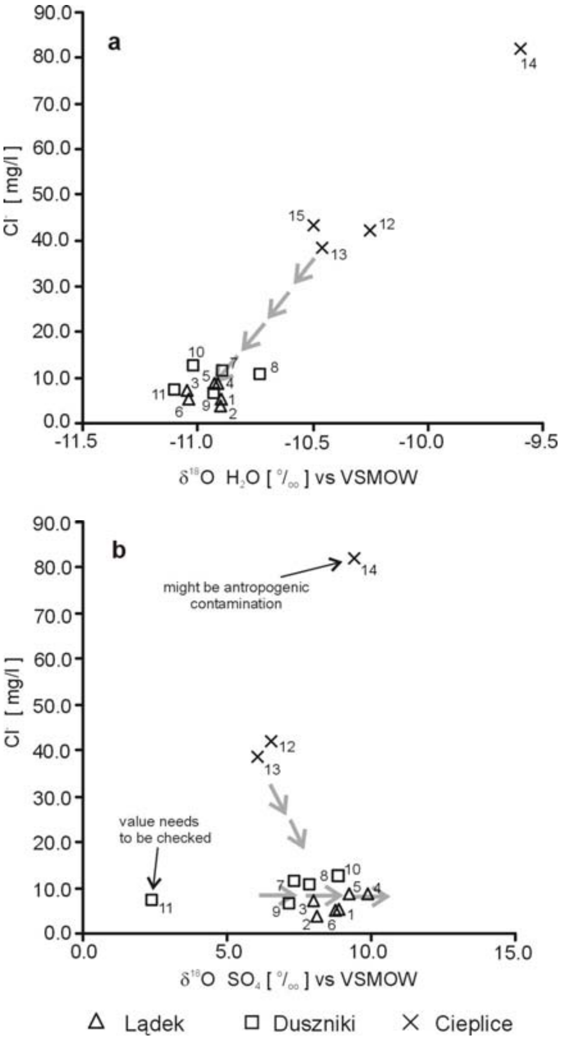

Figure 6: The relationship between concentration of Cl^- and $\delta^{18}O$ of water (a) and $\delta^{18}O$ of sulfates (b) in Sudetic thermal waters. Numbering according to Table 1.

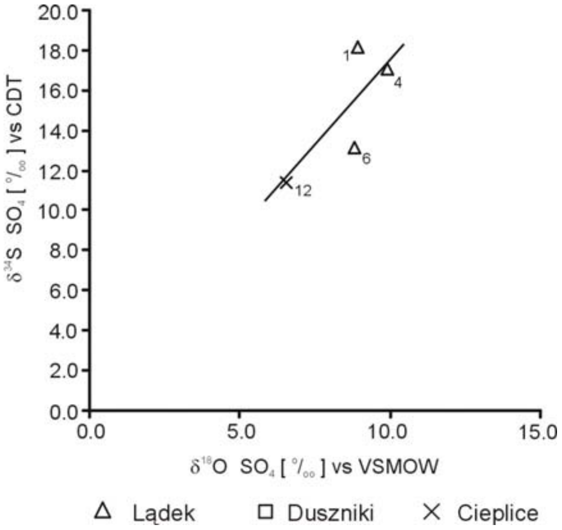

Figure 7: The relationship between $\delta^{18}O$ and $\delta^{34}S$ of sulfates for same thermal waters at Cieplice and Lądek. Numbering according to Table 1.

Nevertheless, the temperature of water in this borehole measured at the outflow reaches 86.7°C whereas that measured at the bottom amounts to 96.1°C. This is in good agreement with water temperature in the reservoir calculated applying SO_4-H_2O oxygen isotopic geothermometer to water from wells C-2 and Nowe, much shallower but certainly belonging to the same circulating system. Moreover, the estimated reservoir temperatures are in good agreement with temperatures obtained by the alkali geothermometers as well as chalcedony (Table 3). Such good agreement between temperature values calculated by all applied geothermometers is observed only for the hydrogeothermal field at Cieplice but not at Lądek or Duszniki.

4. CONCLUSIONS

The investigations carried out so far suggest that the sulfate–water oxygen isotope geothermometer can be satisfactorily applied to thermal waters of the Sudetes Mountains.

The oxygen isotope fractionation factor in sulfate – water system proposed by Mizutani and Rafter (1969a) fits the best the temperature conditions of the hydrogeothermal system at Cieplice, already measured and calculated by other means. This strongly suggests that oxygen isotope equilibrium in sulfate-water system is reached and is not disturbed considerably during the flow up. It means that waters here come from deep parts of the reservoir where they reside sufficiently long time in temperatures exceeding 100^oC.

At Lądek and Duszniki the oxygen isotope equilibrium in sulfate-water system is not observed. There are many secondary processes, which could cause the observed disequilibrium in the sulfate-water system. At Duszniki the high content of tritium suggests a considerable admixture of shallow modern groundwaters, but at Lądek, where there is almost no tritium, waters may reside in a reservoir which is not sufficiently hot and/or their flow velocities are too high Thus, at Lądek and Duszniki the probability of finding waters with temperatures exceeding 80^oC at depths not exceeding 1000 m is low.

For technical reasons water samples for isotopic determinations could not be taken from the deep boreholes at Cieplice (C-1, 2002.5 m) and Duszniki (GT-1, 1650 m). This difficulty is going to be overcome and sampling will be possible soon.

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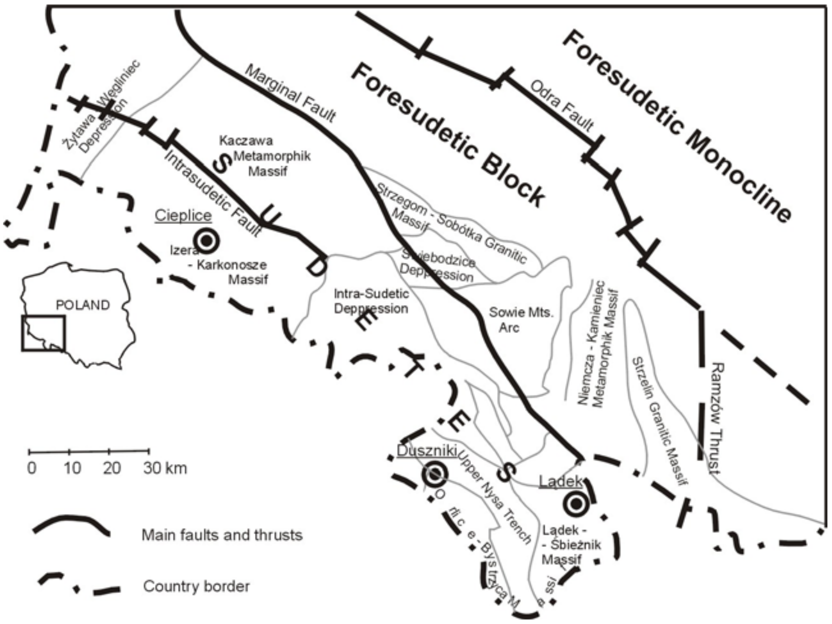

Figure 1: Geological sketch of the study area (after Bruszewska, 2000).

Table 2: Isotopic composition of thermal waters from three geothermal systems in the Sudetes. Blank fields mean: “not measured”

No	Name of well	Site	$\delta^{18}O\ SO_4^{2-}$ $[^{o}/_{oo}]$ vs VSMOW	$\delta^{18}O\ H_2O$ $[^{o}/_{oo}]$ vs VSMOW	$\delta^{2}H\ H_2O$ $[^{o}/_{oo}]$ vs VSMOW	$\delta^{34}S\ SO_4^{2-}$ $[^{o}/_{oo}]$ vs CDT	$\delta^{34}S\ H_2S$ $[^{o}/_{oo}]$ vs CDT	^{3}H [1] [TU]
1	L-2	Ladek	8.9	-10.9	-73.6	18.2	-7.6	0.0 [b]
2	Jerzy		8.1	-10.9	-73.9			0.3 [b]
3	M. Curie-Skłodowska		8.0	-11.1	-73.4			1.0 [c]
			9.9	-10.9	-73.1	17.1	6.4	0.0 [b]
4	Chrobry		9.2	-10.9	-72.3			0.4 [b]
5	Dąbrówka							
6	Wojciech		8.8	-11.0	-74.9	13.1	-9.3	1.0 [c]
7	Pieniawa Chopina	Duszniki	7.4	-10.9	-70.8			12.0 [b]
8	Jan Kazimierz		7.9	-10.7	-71.6			14.7 [b]
9	B-39		7.2	-10.9	-73.5			11.8 [b]
10	B-4		8.9	-11.0	-72.1			2.3 [b]
11	B-3		2.4	-11.1	-72.6			11.3 [b]
12	Nowe	Cieplice	6.5	-10.3	-71.5	11.6 [e]		1.7 [a]
13	C-2		6.0	-10.5	-73.6			1.3 [a]
14	Sobieski		9.4	-9.6	-67.0			16.6 [b]
15	C-1[d]			-10.5	-76.0			0.0 [a]

[a] – data after Zuber et al., (1989);
[b] – data after Ciężkowski et al., (1996);
[c] – data after Dowgiałło et al. (1974)
[d] – data after Dowgiałło (2000)
[e] – data after Cortecci and Dowgiałło (1975)

Table 3: Comparison of calculated reservoir temperatures for thermal waters of the Sudetes. Blank fields mean: “not measured”

No	Name of well	Site	T_o [°C]	T_{MR} SO_4-H_20 [°C]	T_{HP} SO_4-H_20 [°C]	$T_{Na\text{-}K}$ [°C]	T_{SiO2} [°C]	$T_{Na\text{-}K\text{-}Ca\text{-}(Mg)}$ [°C]
1	L-2	Ladek	43.9	74	34	77	68	56
2	Jerzy		27.9	80	39	89	56	48
3	M. Curie-Skłodowska		25.5	80	39	57	55	36
4	Chrobry		26.5	67	28	61	53	45
5	Dąbrówka		19.1	72	32	64	51	40
6	Wojciech		29.2	74	34	81	61	50
7	Pieniawa Chopina	Duszniki	18.1	89	46	na	67	71
8	Jan Kazimierz		17.0	86	44	na	55	80
9	B-39		18.6	90	47	na	82	86
10	B-4		16.6	76	36	na	67	69
11	B-3		12.8	135	84	na	27	63
12	Nowe	Cieplice	27.6	98	54	114	90	96
13	C-2		63.5	101	56	98	105	94
14	Sobieski		21.5	80	39	na	66	143
15	C-1		86.7			98	64	115

T_o – temperature measured at theoutflow;
T_{MR} - temperature based on Mizutani and Rafter (1969) scale;
T_{HP} – temperature based on Halas and Pluta (2000) scale**;**
$T_{Na\text{-}K}$ – temperature based on Na-K geothermometer (Arnorsson et al. 1983)
T_{SiO2} – temperature based on chalcedony geothermometer (Arnorsson et al. 1983)
$T_{Na\text{-}K\text{-}Ca\text{-}(Mg)}$ – temperature based on Na-K-Ca (Mg corrected) geothermometer (Fournier and Potter, 1979)
na – not applicable due to unrealistically high figure

Table 1. Hydrochemical characteristics of thermal

No	Name of well	Site	D_T [m]	T [°C]	Q_E [m^3/d]	pH_f	Na^+	K^+	Ca^{2+}	Mg^{2+}	Sr^{2+}	Fe^{2+}	B^{3+}	Cl^-	HCO_3^- + CO_3^{2-}	SO_4^{2-}	F^-	SiO_2	H_2S	CO_2	TDS [mg/l]
1	L-2	Lądek	700.0	43.9	370.0	9.40	47.10	1.00	3.40	0.10	0.03			5.29	60.00	25.90	12.90	44.60	2.89		200.22
2	Jerzy		0.0	27.9	340.0	8.92	38.00	1.00	4.70	0.30	0.03			3.80	51.00	19.50	10.10	34.10	3.06		162.53
3	M. Curie-Skłodowsk		2.0	25.5	90.0	9.09	44.00	0.65	5.04	0.59				7.09	52.50	21.9	9.00	35.00	1.70		175.77
4	Chrobry		9.6	26.5	32.0	9.15	47.50	0.75	3.88	0.71	0.50	0.06		8.86	54.66	20.00	10.00	31.55	2.55		178.47
5	Dąbrówka		3.5	19.1	12.0	9.07	44.50	0.75	5.03	0.47	0.50	0.14		8.86	57.61	16.50	9.00	30.01	3.57		173.37
6	Wojciech		2.0	29.2	95.0	9.04	43.70	1.00	4.30	0.20	0.04	0.01		5.19	60.00	23.50	11.20	38.50	2.55		187.64
7	Pieniawa Chopina	Duszniki	70.0	18.1	464.4	5.96	166.00	84.00	232.6	71.7				11.53	1590.00	57.00	0.40	45.00		2100	2258.23
8	Jan Kazimierz		162.0	17.0	104.4	5.82	126.00	66.00	164.70	45.90				10.60	1101.00	53.90	0.45	35.00		1950	1603.55
9	B-39		180.0	18.6	288.0	5.99	122.30	81.00	198.40	54.90	0.64	8.84	0.06	6.48	1281.00	45.20		60.30			1859.21
10	B-4		76.0	16.6	104.4	6.10	216.00	108.00	269.40	89.40				12.4	1958.00	52.90	0.40	45.01		2260	2751.51
11	B-3		96.0	12.8	10.1	6.02	73.00	35.00	296.20	94.08		6.90		7.09	1552.41	60.80		16.01	1.19	2460	2141.59
12	Nowe (Nr 4)	Cieplice	34.5	27.6	24.0	7.82	157.50	6.00	13.63	0.47		0.06	0.50	42.10	158.53	163.20	11.00	70.02			623.21
13	C-2		750.0	63.5	240.0	7.85	165.70	5.00	11.50	0.30	0.24	0.01	0.26	38.50	157.00	154.00	13.30	93.30	0.34		639.11
14	Sobieski (Nr 2)		6.2	21.5	1.0	6.83	119.00	44.00	78.29	9.41		0.12		81.99	359.28	128.00	2.00	42.32			864.81
15	C-1		2002.5	86.7		8.70	160.00	4.84	8.42	0.82				43.31	164.70	162.30	13.00	42.50			620.00

Concentrations in mg/l; D_T – well (spring) depth, T- water temperature at the outflow, Q_E – yield, pH_f - field measured pH, TDS – total dissolved solids; blank fields means ‘not measured’ or ‘below detection limit’