

## Article

# Determination of Reservoir Temperatures of Low-Enthalpy Geothermal Systems in the Sudetes (SW Poland) Using Multicomponent Geothermometers

Barbara Kielczawa 

Faculty of Geoengineering, Mining and Geology, Wrocław University of Science and Technology, Wybrzeże S. Wyspiańskiego 27, 50-370 Wrocław, Poland; barbara.kielczawa@pwr.edu.pl

**Abstract:** Thermal waters from deep circulation systems are mixed with cold shallow system components during their ascent to drainage zones. In the current research, classic chemical geothermometers and geothermometric modeling using the GeoT app were employed to determine the temperatures of geothermal reservoirs in the Sudetic region. Moreover, models of primary deep components mixed with cold shallow circulation system components were used to determine their proportions, particularly water deposits. In the studied geothermal systems, the proportion of the cold component ranged from c. 46% to c. 75%. Classic cation thermometers (Na-K, Na-K-Ca) indicated a very wide temperature range and they proved rather unreliable. The reservoir temperatures estimated with silica thermometers ranged from 52 °C to 141 °C and they can be deemed more reliable. The temperatures obtained from modeling ( $54.5 \pm 3$ – $120 \pm 4$ ) were adopted as temperatures of waters pre-cooled conductively and then mixed with cold components. The temperatures of primary deep waters (74–225 °C) were adopted as geothermal system temperatures.

**Keywords:** geothermometers; thermal waters; crystalline massifs; hydrochemistry; Sudetes Mountains; Poland



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## 1. Introduction

Reservoir temperatures can be estimated using sets of equations referred to as chemical geothermometers [1–7]. They are based on analysis results of the chemical and isotope compositions of geothermal waters and gases. The most popular of them are so-called classic chemical geothermometers using concentrations of dissolved silica (SiO<sub>2</sub>) or ionic ratios, e.g., Na-K, Na-K-Ca, K-Mg [8–10]. The basic assumption while using these equations is the thermodynamic equilibrium between the fluid and rock medium, or a state close to this equilibrium. Moreover, it is assumed that this equilibrium is maintained along the whole path of water movement to drainage zones (water intakes of flowing wells) [11]. The consequence of this assumption is the “sensitivity” of the equations to the precipitation of secondary minerals (e.g., calcite or silica) or the presence of CO<sub>2</sub> in the system. In such cases, water–rock–gas systems are subject to re-equilibration (e.g., after cooling the primary fluid or as a result of its boiling). Moreover, mixing with waters from shallow circulation systems influences ion ratios, which results in temperature miscalculations [12]. Additionally, the accuracy of the performed analyses is of key importance, especially with regard to the determination of aluminum and magnesium ions, whose concentrations are often close to the accuracy of analytical determination [13].

In situations when geothermal waters do not reach full thermodynamic equilibrium, more reliable reservoir temperatures are obtained by analyzing their saturation with respect to aquifer minerals. A detailed description of this method was provided by Reed [14], Reed and Spycher [15], Pang and Reed [16], and Spycher et al. [17]. Generally, it consists of determining the saturation indices (SI) of the studied waters with respect to the chosen

complex of rock-forming minerals in a given temperature range. The value of the equilibrium temperature of the system is adopted as the temperature of the water reservoir [18,19]. The GeoT app based on the above method additionally enables the reconstruction of water composition in the deep circulation system before calculating the values of SI indices. Moreover, it makes it possible to optimize the concentrations of inaccurately determined water components ( $\text{Al}^{3+}$ ,  $\text{Mg}^{2+}$ ) [19].

The Sudetic region was chosen for the research in view of its long tradition of exploiting thermal waters for balneotherapeutic purposes and hence the availability of water analysis results, but also because these waters occur in lithologically varied aquifers. These waters have been the subject of research for many years. The characteristics and potential possibilities of capturing thermal waters within the Lower Silesian block were described by Dowgiałło [20,21], Ciężkowski et al. [22–24], Przylibski et al. [25]. Based on research into the composition of stable isotopes of oxygen and hydrogen, Ciężkowski et al. [26,27], Zuber et al. [28], and Dowgiałło et al. [29] have determined the meteoric origin of Sudetic thermal waters.

The estimation of deposit temperatures of Sudetic thermal waters was initiated by Dowgiałło [30,31]. Using classic chemical geothermometers, he estimated the subsurface temperatures of the Jelenia Góra-Cieplice and Łądek-Zdrój geothermal systems as ranging from 74 to 217 °C and from 53 to 140 °C, respectively. Porowski [32], and Porowski and Dowgiałło [33], also using chemical geothermometers, obtained wide ranges of deposit temperatures for geothermal systems of Łądek-Zdrój, Jelenia Góra-Cieplice, and Duszniki-Zdrój: 36.7–78.9 °C, 50.2–99.9 °C, 106.3–140.6 °C, respectively. However, as they pointed out, the values obtained for Duszniki-Zdrój were rather unlikely. Dowgiałło et al. [29] reported temperatures in the range of 64–115 °C for Jelenia Góra-Cieplice and 34–77 °C for Łądek-Zdrój. Recently, based on results from silica and cation thermometers, Liber-Makowska and Kielczawa [34], Kielczawa and Liber-Makowska [35], and Kielczawa et al. [36] have estimated the deposit temperatures of Łądek-Zdrój waters as ranging from 55.8 to 97.2 °C. In the case of Jelenia Góra-Cieplice, they suggest temperatures in the range of 78–139 °C and reliable temperatures of Duszniki-Zdrój waters—from 107 °C to 136 °C. Earlier, Leśniak and Nowak [37], and Dobrzyński and Leśniak [38], having analyzed the variation in saturation indices, suggested that the temperatures of Łądek-Zdrój and Duszniki-Zdrój systems might reach 95 °C. In their opinion, waters with temperatures of  $110 \pm 10$  °C can be obtained in Jelenia Góra-Cieplice.

Considering such wide variations in estimated deposit temperatures, research aimed at obtaining better insight into geothermal systems and verification of their temperatures based on multicomponent chemical geothermometers and mixing models has been conducted. The current report is the first one to use reconstruction of geothermal fluids for a more accurate determination of the temperatures of Sudetic low-enthalpy thermal systems.

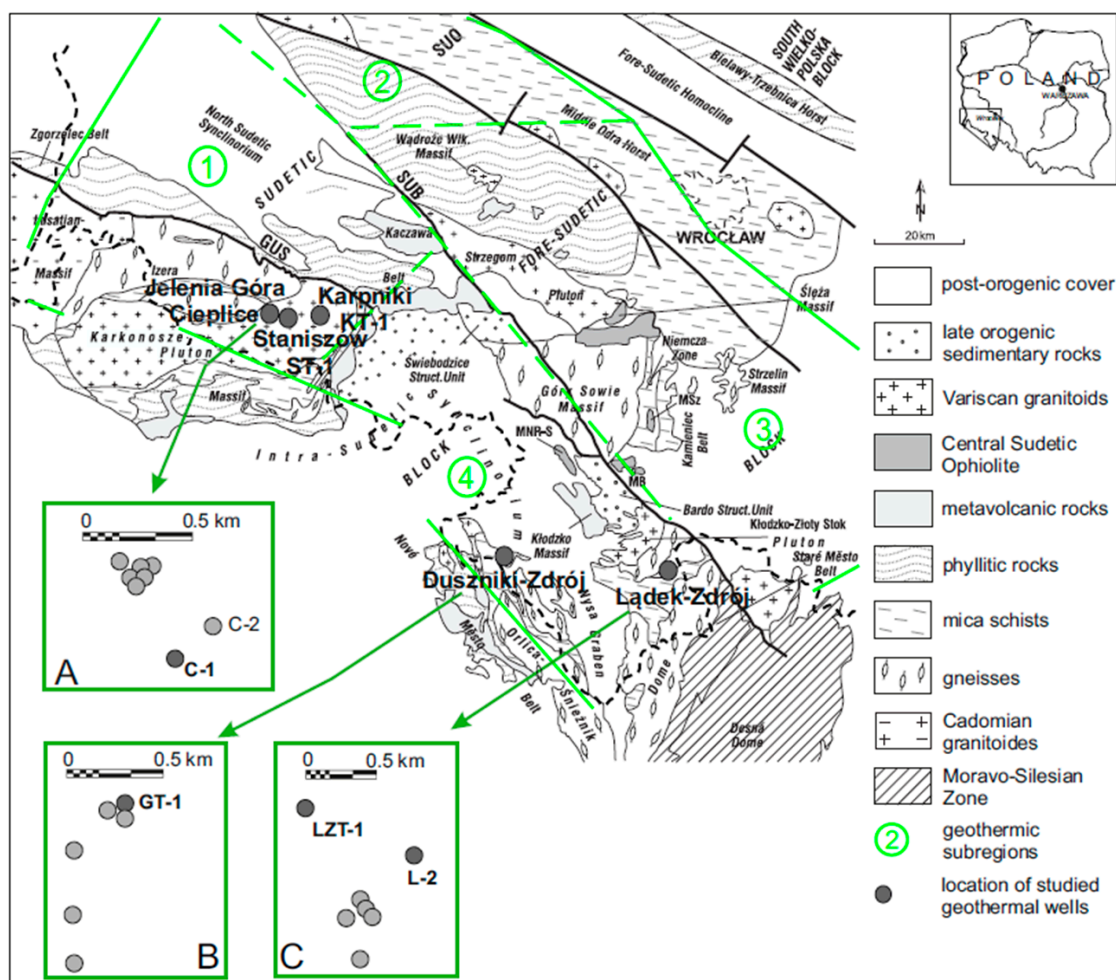
## 2. Study area

### 2.1. Hydrogeological Conditions

The area of southwestern Poland is built predominantly of crystalline rocks forming smaller tectonic block units gradually descending to the northeast. The most elevated unit is the massif of the Sudetes, followed by the lower Fore-Sudetic block, and then by the Fore-Sudetic monocline (Figure 1). The Sudetes and the Fore-Sudetic block bear similarities in their geological structure and hydrogeological conditions. Hence, in the literature, they are jointly referred to as the so-called Lower-Silesian block [39,40].

In the area of the granite Karkonosze massif, geothermal waters are exploited in Jelenia Góra-Cieplice and Karpniki. In the former locality, six springs supply waters with temperatures in the range of 20–44 °C. In two drilled wells, C-1 and C-2 with respective depths of 2002.5 and 750 m, these are waters with outflow temperatures of 26 (C-2)—c. 87 °C (well C-1). Chemically, these are  $\text{Na-SO}_4\text{-HCO}_3$  waters (Table 1) with increased fluorine (2–13.5 mg/L) and metasilicic acid (59–141 mg/L) content and TDS in the range of

0.4–1.0 g/L. These waters are used mainly for balneotherapeutic treatments and recreation [34].



**Figure 1.** Location of deep wells capturing thermal waters in the Lower-Silesian block (based on [25,40,41]). Abbreviations: GUS—main intra-Sudetic fault; MB—Brasowice–Brzeźnica massif; MNR-S—Nowa Ruda–Ślupiec massif; MSz—Szklary massif; NK—Kłodzko thrust; RC—Czerwieńczyce graben; SUB—marginal Sudetic fault; SUD—Dolsko fault zone; SUL—the Elbe fault zone; SUO—the Odra fault zone; geothermic subregions: 1—Jelenia Góra, 2—Legnica, 3—Świdnica–Niemodlin, 4—Wałbrzych–Kłodzko.

In late 2013 and early 2014, a 1997 m deep well was drilled in Karpniki, 13 km east of Jelenia Góra-Cieplice (Figure 1), supplying geothermal waters with TDS content of 0.5 g/L and an outflow temperature of c. 53 °C (Table 1) [42]. These are Na-HCO<sub>3</sub>-SO<sub>4</sub> waters containing increased concentrations of F<sup>−</sup> ions (11.4–16 mg/L), metasilicic acid (up to c. 68.0 mg/L), and radon (290 Bq/L) [43]. They are utilized in the investor’s hotel facilities [42].

At the same time, a 1501 m deep well was drilled in Stanisławów, 4 km east of Jelenia Góra-Cieplice (Figure 1), where Na-HCO<sub>3</sub>-SO<sub>4</sub> waters with TDS content of 0.5 g/L and increased concentrations of H<sub>2</sub>S (2.5 mg/L) and radon activity (116–174 Bq/L) were found. The temperature of water at the outflow is 37.3 °C (Table 1) [43]. At the moment, work on intake development is underway.

The described deposits lie in the NE part of the Karkonosze-Izera crystalline massif of the Sudetes. Their circulation within the Karkonosze granite is possible thanks to deep tectonic zones of the regional extent [44].

**Table 1.** Main characteristics of the studied thermal water deposits [20,34,45–49].

Location (Number of Intakes)	Intake Depth (m)	Available Reserves (m³/h)	Water Temperature (°C)		Main Water Type	Geothermal Gradient (°C/100 m)
			At the Outflow	At the Well Bottom (Name of Well)		
The Karkonosze massif (granite)						
Jelenia Góra-Cieplice (9)	4–2002.5	0.04–45	20.0–87.7	97.7 <sup>a</sup> (C-1)	Na-SO <sub>4</sub> -HCO <sub>3</sub> F, Si	2.8–3.4
Karpniki (1)	1997	44.0	53.0	59.1 (KT-1)	Na-HCO <sub>3</sub> -SO <sub>4</sub> F, Rn	2.7–2.85
Staniszków (1)	1501	20.5	37.3	45.0 (ST-1) <sup>b</sup>	Na-HCO <sub>3</sub> -SO <sub>4</sub> F, Rn, H <sub>2</sub> S	2.37
The Orlica-Śnieżnik dome (mica schists, gneisses)						
Duszniki-Zdrój (9)	1695	39	35	55.8 <sup>c</sup> (GT-1)	Ca-Mg-HCO <sub>3</sub> Si, Fe, CO <sub>2</sub>	3.0
Łądek-Zdrój (8)	0.3–2500	1.22–30	20.0–44.0	58.9 (LZT-1) <sup>b</sup>	Na-HCO <sub>3</sub> -SO <sub>4</sub> Rn, F, S	1.83–6.53 <sup>d</sup>

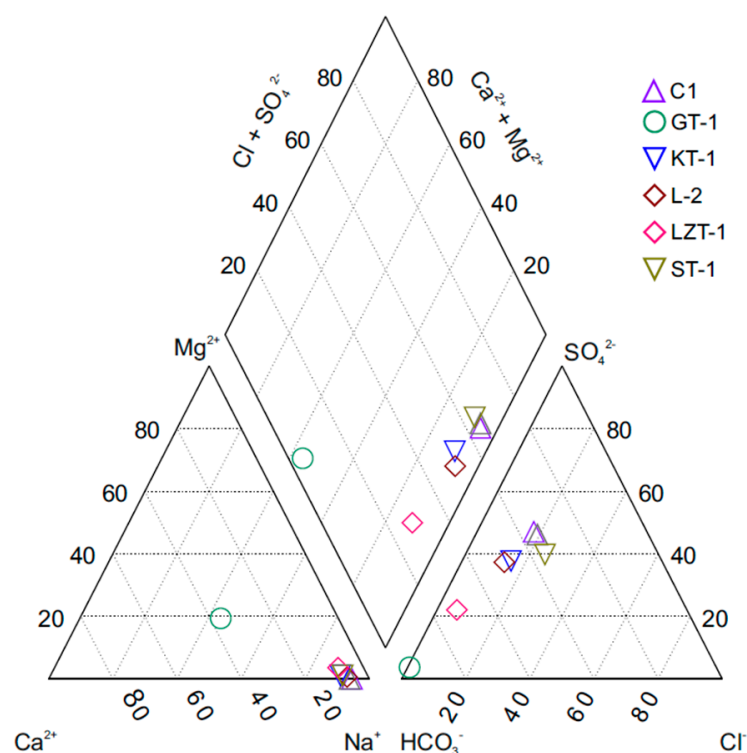
Notes: <sup>a</sup>—at a depth of 1640 m below ground level; <sup>b</sup>—unused well; <sup>c</sup>—at a depth of 1870 m below ground level; <sup>d</sup>—local thermal anomaly.

In the Sudetic region, geothermal water deposits are also found in Duszniki-Zdrój and Łądek-Zdrój (Figure 1). In the former locality, the temperatures of waters exploited for balneotherapeutic purposes do not exceed 20 °C. In 2000–2002, a borehole designated as GT-1 was drilled to a depth of 1695 m. It provided access to geothermal CO<sub>2</sub>-rich waters occurring in two fractured zones, at depths of 193.5–534 m, and 552.2–1695 m (below the depth of 552.5 m the hole is without casing). The upper horizon supplies waters with an outflow temperature of 29 °C and the chemical type Ca-Na-Mg-HCO<sub>3</sub>. The water is characterized by TDS, CO<sub>2</sub>, and metasilicic acid content of 3.2 g/L, 2.2 g/L, and c. 127 mg/L, respectively. The water flows out automatically at a rate of 20 m<sup>3</sup>/h. The lower zone contains Ca-Mg-HCO<sub>3</sub>-type waters with a TDS range of 3.3–3.5 g/L and H<sub>2</sub>SiO<sub>3</sub> content of up to 135 mg/L. Their temperature at the outflow does not exceed 35 °C [50,51]. The available reserves are estimated at 39 m<sup>3</sup>/h [21,46,52]. These waters circulate within fractured mica schists and gneisses of the western part of the Orlica-Śnieżnik dome (Figure 1) [48]. They have not been exploited yet.

In the eastern part of the above tectonic unit, thermal waters occur within a gneiss series in the area of Łądek-Zdrój. Flowing wells (five encased springs) are associated with areas of intersecting dislocations of varying prominence (deep faults and minor transverse discontinuities). These waters are also exploited from a 700 m deep borehole L-2 [53]. They are characterized by very low TDS values (0.15–0.27 g/L), the chemical type Na-HCO<sub>3</sub>-F-SO<sub>4</sub>, and increased concentrations of fluorine ions (7–13 mg/L), H<sub>2</sub>S (0.2–5.1 mg/L), and Rn activity (94–1336 Bq/L). The temperatures of spring waters oscillate from 20.3 °C to 28.3 °C, while those of water from the L-2 borehole—from 41 °C to 44 °C [36,54,55]. In 2018–2019, a 2.5 km deep borehole was drilled in Łądek-Zdrój, capturing Na-HCO<sub>3</sub>-SO<sub>4</sub>, Rn, F, S waters with TDS content of 0.2 g/L. Their temperature at the outflow is 37 °C, but the available reserves are not known [36]. The borehole is currently being surveyed and developed.

The discussed water deposits in the Sudetes generally comprise two main chemical groups of water: Ca-Mg-HCO<sub>3</sub> (captured in GT-1 borehole) and Na-SO<sub>4</sub>-HCO<sub>3</sub>—in the remaining intakes (Figure 2).

Concentrations of stable isotopes of oxygen (<sup>18</sup>O) and hydrogen (<sup>2</sup>H) in the studied waters range from (−10.84) to (−10.5)δ<sup>18</sup>O and from (−75.7) to (72.8)δ<sup>2</sup>H (Table 2).



**Figure 2.** Piper diagram with chemical characteristics of thermal waters (based on [42,43,49,56]).

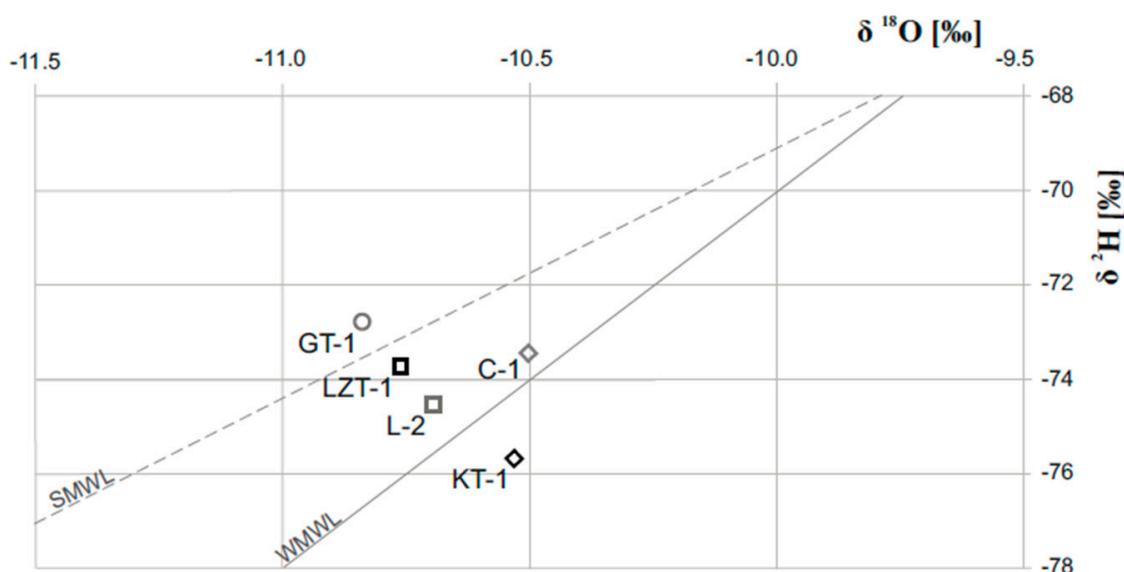
**Table 2.** Chemical and isotopic composition of thermal waters (based on [42,43,49,56]); J.G.-Cieplce—Jelenia Góra-Cieplce; concentration of elements in mg/L, radon activity in Bq/L.

Location Name of Intake	J.G.-Cieplce C-1	Karpniki KT-1	Staniszów ST-1	Duszniki-Zdrój GT-1	Lądek-Zdrój L-2	LZT-1
pH	8.7	8.27	8.3	6.7	9.5	9.6
TDS	663.0	492.6	471.0	3430.0	206.0	189.0
HCO <sub>3</sub> <sup>−</sup>	146.0	151.9	122.0	2330.0	33.60	97.6
SO <sub>4</sub> <sup>2−</sup>	153.0	95.76	107.8	72.2	20.0	20.0
Cl <sup>−</sup>	425.0	28.7	49.6	8.92	5.30	<5
F <sup>−</sup>	11.8	11.39	12.7	38.0	11.0	11.1
Br <sup>−</sup>	0.27	n.d.	n.d.	0.06	0.04	0.023
H <sub>2</sub> SiO <sub>3</sub>	141.0	68.2	31.25	127.0	57.9	35.7
Na <sup>+</sup>	153.0	122.5	133.35	301.0	48.3	49.6
K <sup>+</sup>	5.08	3.46	1.39 <sup>a</sup>	182.0	0.77	2.51
Mg <sup>2+</sup>	0.02	<1.0	<1.0	95.10	0.18	<1.2
Ca <sup>2+</sup>	7.82	10.02	10.02	297.0	3.13	4.01
Al <sup>3+</sup>	0.05	n.d.	n.d.	1.1	0.02	0.234
Fe <sup>2+</sup>	0.02	0.05	n.d.	9.1	n.d.	0.148
Li <sup>+</sup>	0.18	n.d.	n.d.	0.44	0.03	0.003
Sr <sup>2+</sup>	0.21	n.d.	n.d.	1.14	n.d.	0.06
Rn	n.d.	290.1	116.4	b.d.	133.0	93.9
δ <sup>18</sup> O	−10.5	−10.54	n.d.	−10.84	−10.68	−10.76
δ <sup>2</sup> H	−73.4	−75.7	n.d.	−72.8	−74.5	−73.7

Notes: <sup>a</sup>—information obtained during a field excursion during the 8th Symposium “Contemporary Problems of Hydrogeology”, Wojanów 8–10.11.2017; n.d.—no data available.

Figure 3 presents the isotopic composition of waters from particular locations; points corresponding to particular wells lie near the World Meteoric Water Line (WMWL) and the local Sudetic Meteoric Water Line (SMWL), which proves the meteoric origin of the discussed waters.





**Figure 3.** Isotopic composition of thermal waters from particular locations (based on [42,44,49,56]).

The waters from GT-1 and LZT-1 are situated closer to the SMWL, which indicates the participation of cold waters from a shallower circulation system in these deposits. A minor negative oxygen shift of Duszniki-Zdrój waters may indicate isotope exchange with  $\text{CO}_2$  [57]. A slight positive oxygen shift of Jelenia Góra-Cieplce and Karpniki waters (Figure 3) suggests probable isotope exchange with a rock medium in higher temperatures [57–60].

## 2.2. Thermal Conditions

The area of the Lower-Silesian block comprises the so-called Sudetic geothermal region divided into subregions of Jelenia Góra, Wałbrzych-Kłodzko, Legnica, and Świdnica-Niemodlin (Figure 1) [41]. The vast majority of Sudetic thermal water deposits are associated with crystalline rock formations, and the outflows of these waters are located in the areas of tectonic zones or at their intersections. The outflow temperatures of these waters reach nearly  $87^\circ\text{C}$ , with maximum intake discharges of even  $200\text{ m}^3/\text{h}$  [53].

In well C-1 in Jelenia Góra-Cieplce, zones of waters with increased temperatures are found at depths of 1590–1602 m and 1840–1895 m. The highest temperature in this well,  $97.7^\circ\text{C}$ , was recorded at a depth of 1870 m, while at the bottom it reached  $96^\circ\text{C}$ . In the borehole profile, there is a marked dependence of water temperature on the depth of its circulation and the presence of tectonic disturbance zones at depths of 1601–1800 m and 1826–1970 m (Figure 4). The mean geothermal gradient determined on the basis of borehole tests is from  $2.8$  to  $3.4^\circ\text{C}/100\text{ m}$  (Table 1) [20]. Dowgiałło [61] suggests that intense fractures facilitate the circulation of these waters to a depth of at least 3 km.

For boreholes KT-1 in Karpniki and ST-1 in Stanisławów, Dąbrowski [45] determined geothermal gradients values as  $2.85^\circ\text{C}/100\text{ m}$  and  $2.37^\circ\text{C}/100\text{ m}$ , respectively (Table 1.). However, as the author emphasizes, due to unstable conditions during temperature measurements, these values do not reflect the actual thermal conditions in the orogen. While the values of the discussed parameter in Jelenia Góra-Cieplce and Karpniki are comparable, lower values recorded in Stanisławów suggest an intensive influx of cold waters from shallow circulation systems. At the bottom of the Stanisławów well (ST-1), a temperature of  $45^\circ\text{C}$  was recorded [45]. In Karpniki (KT-1), inflows of water with the highest temperatures (about  $59^\circ\text{C}$ ) were observed at a depth range of 1792–1850 m. The geothermal gradient determined during temperature profiling was  $2.7^\circ\text{C}/100$  [42].



**Figure 4.** Temperature profiles in particular wells in the Sudetic region (based on [20,47,49,54]).

According to results obtained by Bruszevska [62], the average geothermal gradient in the areas of Duszniki-Zdrój and Łądek-Zdrój ranges from 2.3 to 3.0 °C/100 m, with temperatures at a depth of 1500 m in the ranges of 44–46 °C and 40–42 °C, respectively. During the drilling of well GT-1 in Duszniki-Zdrój, a temperature of 55.8 °C was observed at a depth of 1640 m (Table 1, Figure 4). The calculated geothermal gradient was 2.0 °C/100 m, but it was probably significantly underestimated owing to technical problems during the measurements [47]. At the same time, the geothermal gradient in Łądek-Zdrój, calculated on the basis of temperature variation in the L-2 borehole profile (Figure 4), was 6.53 °C/100 m, with the maximum temperature of 45.7 °C at the bottom of the well. What is noteworthy at this point is a distinct local thermal anomaly observed in this locality, with a temperature gradient of 18 °C/100 m [54]. However, the observed anomalous gradients should not be generalized or adopted as representative of other regions in the Sudetes. This has been confirmed by measurements conducted in the LZT-1 borehole, at whose bottom a temperature of 58.9 °C was obtained (Table 1, Figure 4) and the geothermal gradient was 1.83 °C/100 m [49].

The Sudetic region is characterized by radiogenic heat in rocks ranging from c. 2.0 to 5.1  $\mu\text{W}/\text{m}^2$ , but it does not significantly affect the value of surface heat flux (from 45 to 64.73  $\text{mW}/\text{m}^2$ ) [63]. The highest values of heat flux density, 79  $\text{mW}/\text{m}^2$  and 71.2  $\text{mW}/\text{m}^2$ , were found in Jelenia Góra-Cieplice (borehole C-1) and Łądek-Zdrój (borehole L-2), respectively [41]. It should be noted that the temperature gradient in SW Poland varies in the range of 2.0–3.5  $^{\circ}\text{C}/100\text{ m}$ , with the highest values observed south of Łądek-Zdrój [62].

### 3. Materials and Methods

Reservoir temperatures have been estimated on the basis of available archival materials and published results of physicochemical analyses of water. The authors used data from intakes providing access to geothermal waters from the deepest aquifers in particular localities (Table 2). For temperature calculations with classic chemical geothermometers (Equations (1)–(5)), mineral compositions of deposit fluids obtained as final solutions in saturation modeling were used. Reservoir temperature was calculated from commonly used chemical geothermometers [3,5,7]:

$$T_Q = \frac{1309}{5.19 - \log \text{SiO}_{2(\text{aq})}} - 273.15, \quad (1)$$

$$T_{\text{Ch}_1} = \frac{1032}{4.69 - \log \text{SiO}_{2(\text{aq})}} - 273.15, \quad (2)$$

$$T_{\text{Ch}_2} = \frac{1112}{4.91 - \log \text{SiO}_{2(\text{aq})}} - 273.15, \quad (3)$$

$$T_{\text{Na-K}} = \frac{933}{0.993 + \log\left(\frac{\text{Na}}{\text{K}}\right)} - 273.15, \quad (4)$$

$$T_{\text{Na-K-Ca}} = \frac{1647}{\log\left(\frac{\text{Na}}{\text{K}}\right) + \beta \cdot \log\left(\frac{\sqrt{\text{Ca}}}{\text{Na}}\right) + 2.24} - 273.15, \quad (5)$$

where  $T_Q$  is the silica geothermometer,  $T_{\text{Ch}_1}$  and  $T_{\text{Ch}_2}$  are the chalcedony geothermometers,  $T_{\text{Na-K}}$  is the Na-K geothermometer and  $T_{\text{Na-K-Ca}}$  is the Na-K-Ca geothermometer;  $\text{SiO}_{2(\text{aq})}$  concentrations in  $\text{mg}/\text{L}$  and Na, K and Ca concentrations in  $\text{mol}/\text{kgH}_2\text{O}$ .

The triangular Giggenbach diagram was used to determine which of the studied waters had reached complete or partial equilibrium with a rock medium [9,59]. The location of points in the field of immature waters suggests that waters are mixed, and then the results of temperature estimation using classic chemical thermometers should be taken with reserve.

The calculations of water-medium equilibrium and estimation, on their basis, of deposit temperatures were conducted using the GeoT app [18]. The detailed procedure of this method was discussed by Reed and Spycher [15], and Spycher et al. [17]. Generally, the reservoir/deposit temperature is determined on the basis of the chemical equilibrium of the analyzed water with a complex of rock-forming minerals. The app works using a thermodynamic database SOLTHERM.H06. At the same time as saturation indices in given thermal conditions, statistical characteristics (RMED—median, MEAN—mean, SDEV—standard deviation, and RMSE—mean root square error) are calculated. The temperature at which all the statistics have minimum values is adopted as the deposit temperature.

To estimate the probable primary temperature of a hot deep circulation component, a graphic method based on variation in  $\text{SiO}_2$  concentration depending on solution enthalpy was used. It was assumed that the primary concentration of silica in a hot component at large depths is controlled by the dissolution of quartz and that during water migration (before it is mixed with a shallow circulation component), further dissolution or precipitation of  $\text{SiO}_2$  does not occur [3,64,65]. Curves in the diagram (in the results and discussion section) illustrate changes in quartz solubility and the maximum gas/steam loss.



SiO<sub>2</sub>-H (enthalpy) diagrams for water were also used to determine the ratio of the system components (hot and cold).

When water moves slowly or indirectly (ascends) to a drainage zone, there is a large probability of conductive cooling [3] and then a quartz dissolution curve is used. For waters from which steam/gases have probably been released, the primary component temperature is estimated based on the maximum steam loss curve.

$$H_s = H_c X + H_h \cdot (1 - X), \quad (6)$$

$$\text{SiO}_{2s} = \text{SiO}_{2c} \cdot X + \text{SiO}_{2h} \cdot (1 - X), \quad (7)$$

where  $X$  is the proportion of the cool component,  $H$  is the enthalpy of  $H_c$ —cold water,  $H_h$ —hot water,  $H_s$ —mixture (at intake outflow); SiO<sub>2</sub> is silica concentration in SiO<sub>2c</sub>—cold waters, SiO<sub>2h</sub>—deep hot waters, and SiO<sub>2s</sub>—mixed waters (at intake outflow).

Using the above equations and the graphic method, the component ratio and the temperature of the deep circulation component were determined based on mixing models.

To estimate the enthalpy of waters from Łądek-Zdrój, Jelenia Góra-Cieplice, Karpniki, and Stanisław deposits, a model without a pre-mixing gas loss was adopted. For this purpose, a quartz dissolution curve and points illustrating the concentration of silica in thermal and ordinary waters from particular locations were used.

When it comes to Duszniki-Zdrój waters, due to considerable quantities of CO<sub>2</sub> dissolved in them and a large probability of their de-gassing along the flow path, the model of conductive cooling was not adopted. In order to estimate the enthalpy of the primary deep component, the maximum steam loss curve was used (the diagram can be found in the Results and discussion section). A detailed description of the method can be found in works by Fourier [3], Fournier and Truesdell [64], and Truesdell and Fournier [65].

#### 4. Results and Discussion

A modified Giggenbach diagram (Figure 5) presents the proportions of major cations in the analyzed waters.

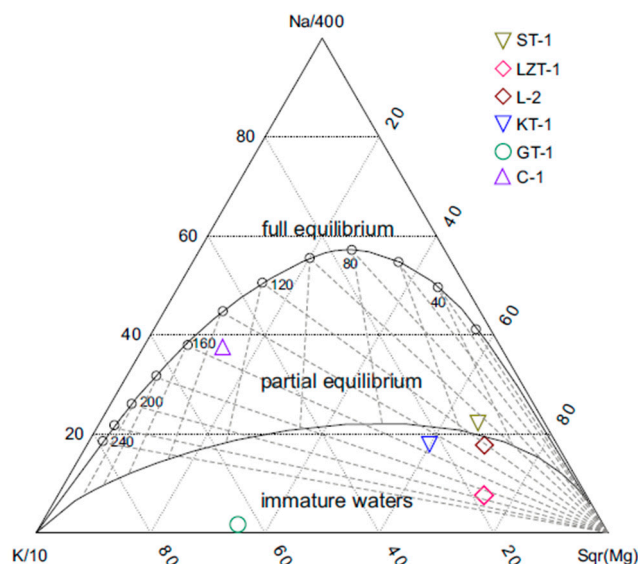


Figure 5. Analyzed waters on a modified triangular Na-K-Mg diagram (based on [59]).

It can be seen that the bicarbonate CO<sub>2</sub>-rich waters from Duszniki-Zdrój (GT-1) are located in the “immature waters” field, which proves the lack of thermodynamic equilibrium in this system. According to Giggenbach’s and Corrales Soto’s [59] hypothesis for waters with the dominant HCO<sub>3</sub><sup>−</sup> ion and characterized by a pH close to neutral (waters from GT-1 have pH 6.7—Table 2), temperatures can be estimated based on K<sup>+</sup> and Mg<sup>2+</sup>

ion content. Hence, in the case of waters from the GT-1 well, a temperature of c. 112 °C (Figure 5), which is higher than that measured at the outflow (Table 1), was obtained.

Closer to the boundary of the partial equilibrium field, there are waters from the KT-1, ST-1, and L-2 intakes with estimated deposit temperatures of c. 70 °C (KT-1) and 50 °C (ST-1 and L-2). The highest degree of equilibrium and temperatures of c. 137 °C are observed in waters from the Jelenia Góra-Cieplie deposit (C-1) (Table 3, Figure 5).

**Table 3.** Reservoir temperatures estimated using classic geothermometers, Giggenbach and Corrales Soto's diagram [59], and modeling of equilibrium between water and the rock medium (GeoT); temperature in °C.

Intake	Q	Ch <sub>1</sub>	Ch <sub>2</sub>	Na-K	Na-K-Ca	Giggenbach and Corrales Soto's Diagram	GeoT
C-1	141	115	113	73	136	137	120 ± 4
KT-1	104	74	75	63	123	70	74 ± 3
ST-1	83	52	54	18	86	50	54.5 ± 3
GT-1	135	108	107	373	290	112	114 ± 11
L-2	96	66	68	36	95	50	65.5 ± 3
LZT-1	91	60	62	97	140	62	88 ± 16

Notes: Q—SiO<sub>2</sub>(aq) concentration in mg/L; Ch<sub>1</sub>—SiO<sub>2</sub>(aq) concentrations in mg/L; Ch<sub>2</sub>—SiO<sub>2</sub>(aq) concentration in mg/L; Na-K—Na and K concentrations in mol/kg H<sub>2</sub>O; and Na-K-Ca—Na, K and Ca concentrations in mol/kg H<sub>2</sub>O.

#### 4.1. Silica Thermometers (Q, Ch<sub>1</sub>, and Ch<sub>2</sub>)

In the process of determining deposit temperatures using silica thermometers, the quartz thermometer (Q) showed temperatures in the range of 83–141 °C for waters in the Jelenia Góra-Cieplie area (the Karkonosze granite), and from 91 °C to 135 °C for waters in Łądek-Zdrój and Duszniki-Zdrój (the Orlica-Śnieżnik metamorphic complex). Slightly lower temperatures were obtained using chalcedony thermometers (Ch<sub>1</sub> and Ch<sub>2</sub>). For the analyzed areas they fall in the ranges of 52–115 °C and 60–108 °C, respectively. Overall, the chalcedony and quartz geothermometers give results differing from each other in the range of about 30 °C. The temperature obtained from the latter is higher than that obtained from the former (Table 3).

#### 4.2. Na-K and Na-K-Ca Thermometers

In the case of the Duszniki-Zdrój deposit, one should expect the significant amounts of CO<sub>2</sub> to intensify the mutual interaction of the water–rock–gas system. This undoubtedly translates into the chemical composition of these waters and hence the values of temperatures obtained using cation Na-K and Na-K-Ca geothermometers. The calculated respective temperatures are 373 °C and 290 °C (Table 3) and they are probably considerably overestimated. High values (97 °C and 140 °C) were also obtained for the LZT-1 well in Łądek-Zdrój, which might be due to the fact that in low-enthalpy systems equilibrium is reached either with potassium or sodium feldspar [66]. The temperatures of waters from the C-1, ST-1, and L-2 intakes (73 °C, 18 °C, and 36 °C, respectively) obtained using the Na-K geothermometer are lower than those observed at outflows/wellheads. The atypically low value obtained for the ST-1, due to a very low concentration of potassium ions in these waters, is contaminated with gross error. This confirms Nicholson's thesis [67] that this thermometer does not work efficiently in low-temperature systems (<120 °C). On the other hand, cold waters flowing to intakes from shallow circulation systems undoubtedly change ion ratios (Na-K-Ca), which consequently affects the estimated temperatures [66]. Temperatures obtained with the Na-K-Ca thermometer are significantly different from these values (Table 3).

#### 4.3. Temperature Estimation Using GeoT App

A large complex of rock-forming minerals was selected for the simulation. The minerals of the Karkonosze massif and the Orlica-Śnieżnik metamorphic complex were

selected on the basis of Borkowska [68], Rasała et al. [46], and Szczepański [69]. The most important of them are quartz, potassium feldspar (microcline), chalcedony, calcite, sodium plagioclase (albite), kaolin, muscovite, and phlogopite. To reduce the impact of re-equilibration in the case of low concentrations of  $\text{Al}^{3+}$  ions, concentrations of the above ions were stabilized by equilibrating the studied waters with microcline or kaolin [70].

The chemical composition of waters from deep circulation systems can change during their flow to the terrain surface as a result of their mixing with waters from more shallow zones, dilution, boiling, or re-equilibration with the rock medium and inflowing gases [60]. Moreover, in the presence of a water-and-gas (e.g.,  $\text{CO}_2$ ) mixture in a well, the temperature observed at the outflow cannot be considered representative, as it is affected by gas pressure, which, in turn, depends on the flow conditions in the rock medium and the well [71]. Considering these determinants and the possibility of considerable degassing of Duszniki-Zdrój waters along their flow path or during sampling, equilibrating them with calcite at outflow temperature was analyzed. The pH (5.8) of water obtained in this way was adopted for further simulations. An appropriate amount of gas was added to the water to maintain its pH, and concentrations of bicarbonate and aluminum ions were stabilized by equilibrating the solution with calcite and microcline.

The waters from Łądek-Zdrój were also equilibrated with calcite and microcline. The waters from the LZT-1 well were additionally concentrated by disposing of 100 g/1 kg water.

The waters from Jelenia Góra-Cieplice (C-1) and Karpniki (KT-1) deposits did not require reconstruction, while those from Stanisław (ST-1) showed slight dilution, so they were concentrated by disposing of 350 g/1 kg water.

The results of such modeling produced a very good cluster of solution equilibration curves with selected groups of minerals. The closest to zero values of all the statistical parameters (RMED, RMSE, SDEV and MEAN) of the saturation index (SI) indicate the highest estimated temperatures for particular deposits (Figure 6). For the thermal waters from intakes in the Karkonosze granite unit: C-1 (Jelenia Góra-Cieplice), ST-1 (Stanisław), and KT-1 (Karpniki), temperatures of  $120 \pm 4$  °C,  $54.5 \pm 3$  °C and  $74 \pm 3$  °C were obtained, respectively. For the waters from Duszniki-Zdrój (GT-1) and Łądek-Zdrój (L-2 and LZT-1), circulating within the Orlica-Śnieżnik metamorphic complex, respective values of  $114 \pm 11$  °C,  $65.5 \pm 3$  and  $88 \pm 16$  °C were obtained (Table 3).

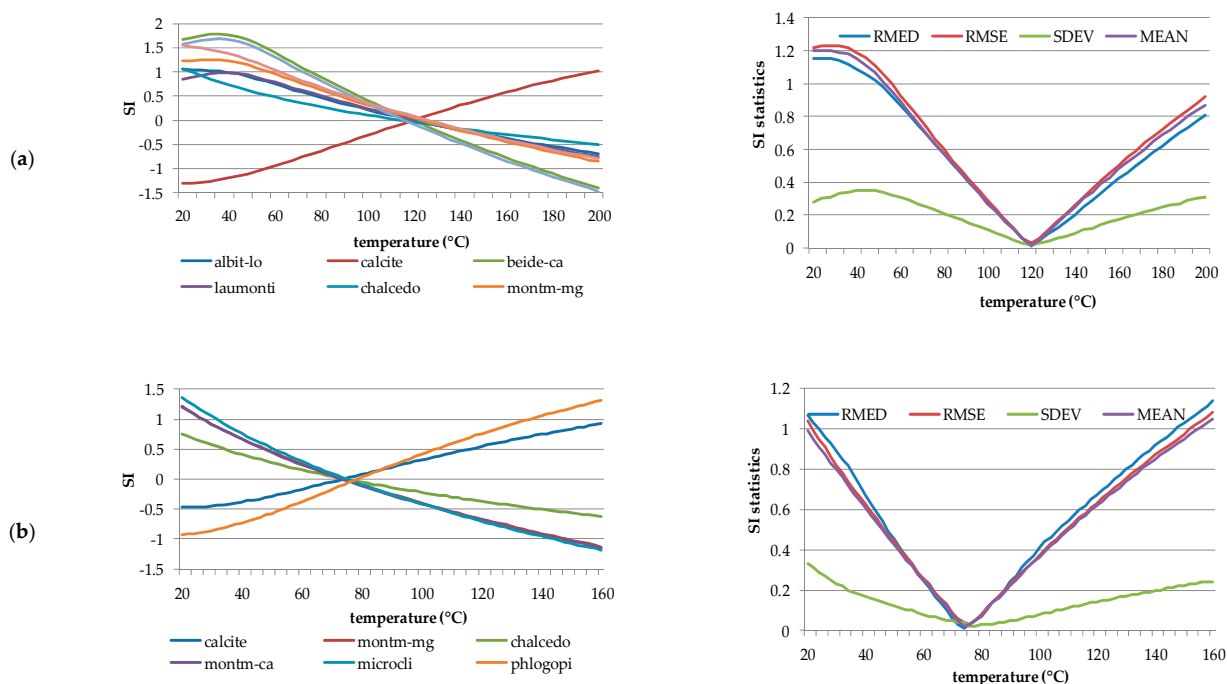
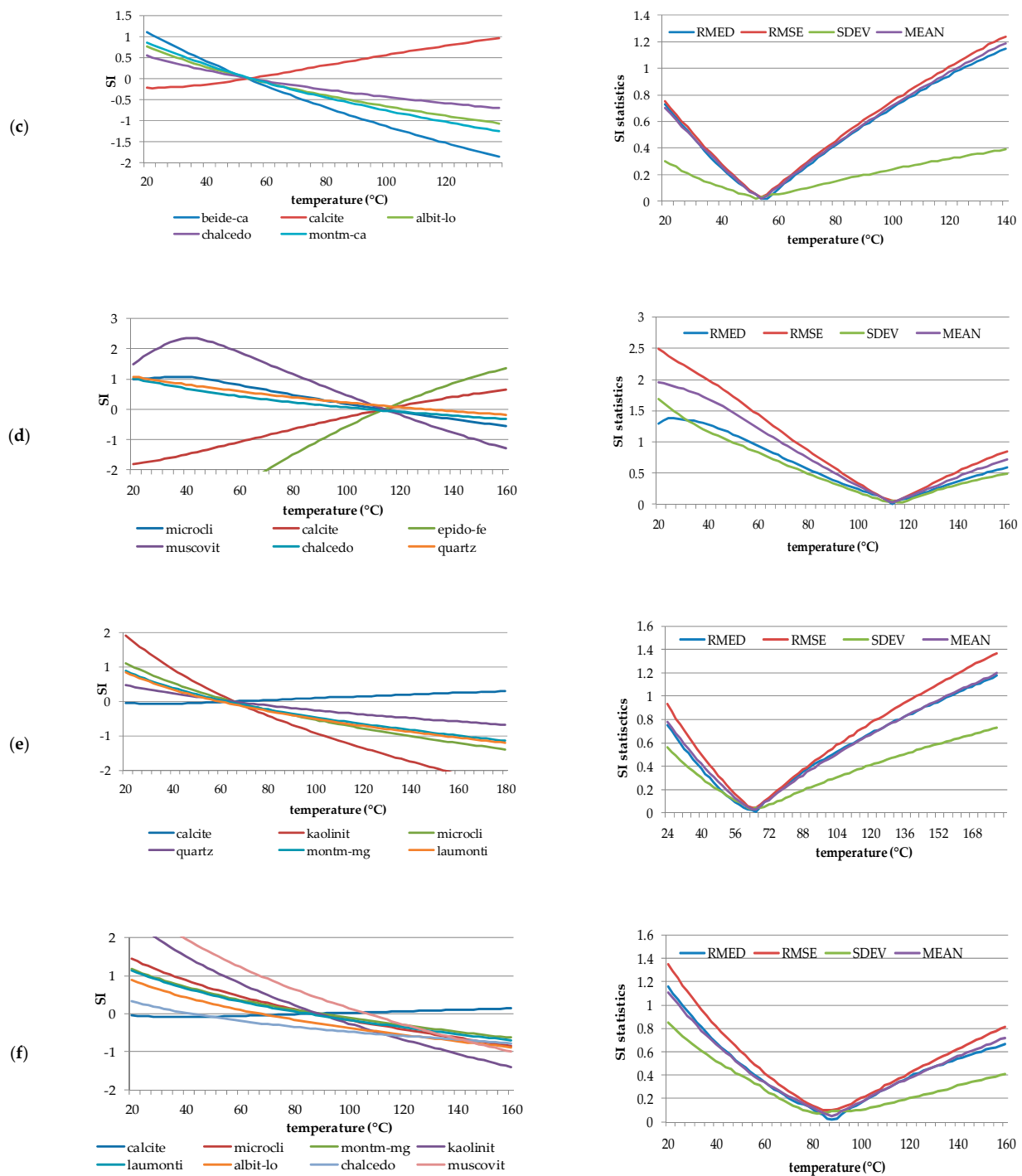


Figure 6. Cont.



**Figure 6.** Changes in the saturation indices (SI) and SI statistics: median (RMED), mean (MEAN), standard deviation (SDEV) and mean root square error (RMSE) of absolute  $\log(Q/K)$  values as a function of model reservoir temperature; (a)—C-1, (b)—KT-1, (c)—ST-1, (d)—GT-1, (e)—L-2, (f)—LZT-1.

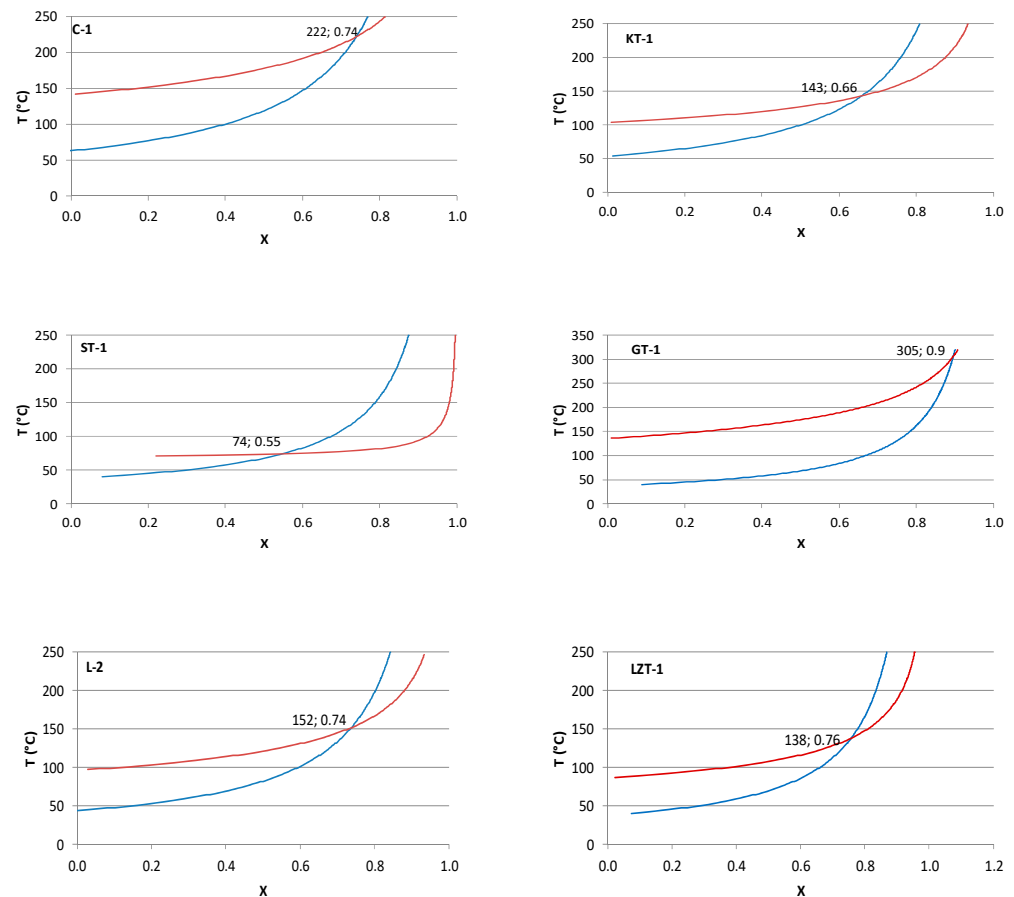
It can be observed that the temperatures obtained as a result of this modeling, allowing for an error range, are not substantially different from those estimated using classic chalcedony thermometers (Table 3).

#### 4.4. Deep Component Temperatures Determined Based on Mixing Models

In many cases, geothermal waters are mixtures of hot waters from deep systems and much colder shallow-system waters. Hot water ascends to drainage zones along faults and fissures. At the mixing depth, the pressure difference makes the cold component flow into

the hot component's fissures/system [64]. As a result, mixtures of the two components are observed in particular intakes. Partial or total chemical equilibrium of such mixtures may be established after the mixing of both components, and then chemical geothermometers indicate the temperature of the mixture and not of the deep component.

In view of the above, temperatures were estimated based on the proportion of the cold component in mixtures and the mixing models (Figure 7, Table 4). Proportions of the components were determined using Equations (6) and (7).

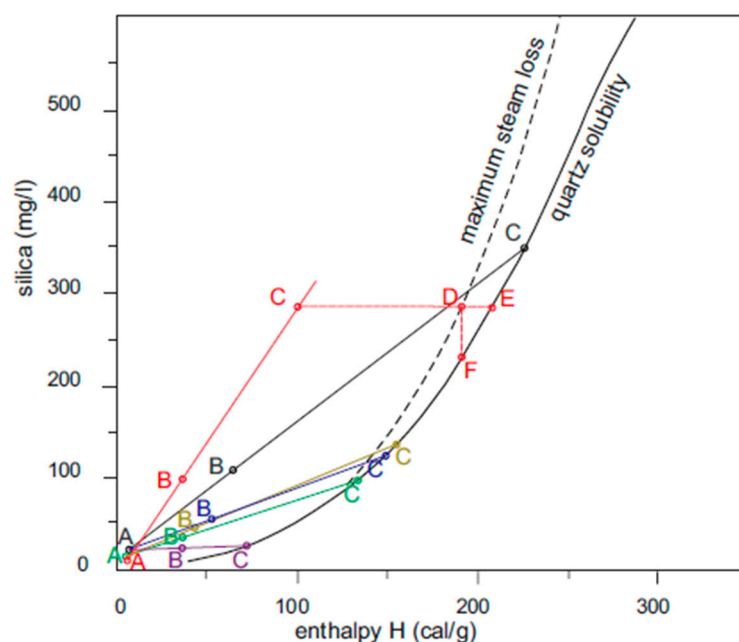


**Figure 7.** The proportion of cold waters (X) in thermal water mixtures in particular locations, and the temperatures (T) of hot deep components; the blue line—the proportion of cold waters based on enthalpy/temperature changes, the red line—the proportion of cold waters based on variation in silica concentrations (T-X graph).

**Table 4.** Reservoir temperatures determined on the basis of the dependence of silica dissolution on the enthalpy of thermal waters (based on the determined enthalpy [72] and Figures 7 and 8); temperature in °C.

Intake	Enthalpy H ( $\times 4.1868$ J/kg)	SiO <sub>2</sub> (mg/L)	T (°C)		Fraction of Cold Water (%)	
			Enthalpy H	T-X Graph	T-X Graph	SiO <sub>2</sub> -H Equation
C-1	226.4	348	220.5	222	74	73.5
KT-1	149.7	123.6	148.5	143	66	70
ST-1	72.5	25.7	72.5	74	55	45.9
GT-1	206.4	230	202.5	305	90	60
L-2	156	135	155	152	74	75.1
LZT-1	133.6	92.1	133	138	76	72.7





**Figure 8.** Diagram of dissolved silica ( $\text{SiO}_2$ ) versus enthalpy ( $H$ ) in mixed thermal and cold waters (based on [3]); points and lines: red—GT-1, black—C-1, blue—KT-1, purple—ST-1, green—LZT-1, yellow—L-2; A—concentration of silica in ordinary waters (black—for waters from Jelenia Góra-Cieplice area, green—for Łądek-Zdrój waters, red—for Duszniki-Zdrój waters); B—concentrations of silica in thermal waters; C—concentrations of silica in primary deep waters except for GT-1, indicated by point F; D—enthalpy at steam loss temperature; E—silica concentration at the assumed steam separation temperature.

In the Jelenia Góra-Cieplice (C-1) and Karpniki (KT-1) systems, the proportion of the cold component reaches 70–74%. In Stanisławów waters (ST-1), it can be assumed to range from 46% to 55%. The estimated temperatures of the hot deep system component are c. 74 °C for ST-1, 143 °C for KT-1 and 222 °C for C-1 (Table 4, Figure 7). A much lower temperature of water from the ST-1 well is probably due to the much shallower horizontal circulation system.

The thermal water systems of the Orlica-Śnieżnik dome are colder. The temperature of the deep component of Łądek-Zdrój waters ranges from 138 °C (LZT-1) to 152 °C (L-2) with a c. 73–76% share of cold water (Table 4, Figure 7).

It can be observed that the enthalpies of the primary deep circulation component are very different from the temperatures estimated using classic chemical thermometers and the modeling of the water saturation state (Table 3, Figure 8).

It should be noted that for waters with temperatures below 100 °C, the value of water enthalpy expressed in (cal/g) is generally equal to that of water temperature. The temperatures of waters with higher enthalpy values were obtained from thermodynamic tables [72].

Except for waters from the GT-1 well in Duszniki-Zdrój, the temperatures of the studied systems can be estimated using the adopted model of conductive cooling of deep system waters during their ascending flow to drainage zones. Consequently, using the quartz dissolution curve (Figure 8) for the waters from the Jelenia Góra-Cieplice area, a temperature of 220.5 °C was obtained for the C-1 well, 148.5 °C—for the KT-1 well and 72.5 °C—for the ST-1. For the Łądek-Zdrój system, values in the range of 133 °C (LZT-1)–155 °C (L-2) were obtained.

In the case of Duszniki-Zdrój (well GT-1), the lack of intersection with the quartz dissolution curve (Figure 8) implies that the primary deep component had lost  $\text{CO}_2$  before it was mixed with a shallower circulation component, so the considerable reduction in the temperature of this component had taken place before its mixing with shallow cold

waters [3]. The temperature of 305 °C determined for this system by using the graphic method (Figure 7) and the 90% share of cold waters from a shallower system are doubtful in this case. It should be remembered that this method is based exclusively on variation in silica concentrations depending on water temperature, without taking into account the presence of CO<sub>2</sub> dissolved in waters. Therefore it is not possible to take into account the conditions of loss/release of this gas from the system during water migration. Consequently, the author considers a temperature of 202.5 °C for the primary deep component and a 60% share of a cold component more reliable.

Only slight differences (3–4 °C) in the temperatures determined with the graphic method and based on mixture enthalpies are notable. For the waters from the GT-1 well (Duszniki-Zdrój), which are “immature”, a much bigger temperature difference, i.e., c. 103 °C (Table 4) was obtained.

## 5. Discussion

Chemical geothermometers for the liquid phase do not work properly and/or involve difficult interpretation. This is because waters in thermal springs/wells rarely flow out directly from reservoirs without re-equilibration, dilution, or mixing with waters of shallower systems [73].

In systems with temperatures in the range of 50–180 °C, waters are close to saturation with chalcedony [2,71], so it can be assumed that temperatures obtained using chalcedony thermometers (Ch<sub>1</sub> and Ch<sub>2</sub>) are more reliable than the values obtained with the quartz geothermometer.

In the case of the Duszniki-Zdrój system, the results of temperature estimation with classic geothermometers (283 °C, 373 °C) are substantially overestimated. This is the result of the impact of the CO<sub>2</sub> present in this deposit on the rock medium and the formation of decay products in the form of increased concentrations of Na<sup>+</sup>, Ca<sup>2+</sup>, and HCO<sub>3</sub><sup>−</sup> ions, and silica [74]. These reactions lead to the precipitation of secondary calcite in the zones of cold water inflow to the main stream of geothermal waters from a deep circulation system. This makes these waters “immature” and the temperatures estimated by means of classic cation thermometers are not particularly reliable. According to Pfeiffer et al. [60], such waters are typical of young geothermal systems and their chemical compositions are formed as a result of re-equilibration established along the flow path.

The temperature determined on the basis of Fournier and Truesdel [64] mixing models is probably the minimum temperature in this system. The deep component, moving inside the orogen and cooled adiabatically, is reached by inflowing CO<sub>2</sub>, which dissolves in it. The deep component moves to drainage zones, but before it is mixed with the cold shallower system component, the gas phase is partly released from water. The inflow of cold waters from a shallower system results in the formation of a mixture with a temperature of c. 114 °C. As a result of further migration, water with a temperature of 55.8 °C flows into the GT-1 well (Table 5). The release of gas from the system may be indicated by dry exhalations of CO<sub>2</sub> in the area of intakes in Duszniki-Zdrój [75].

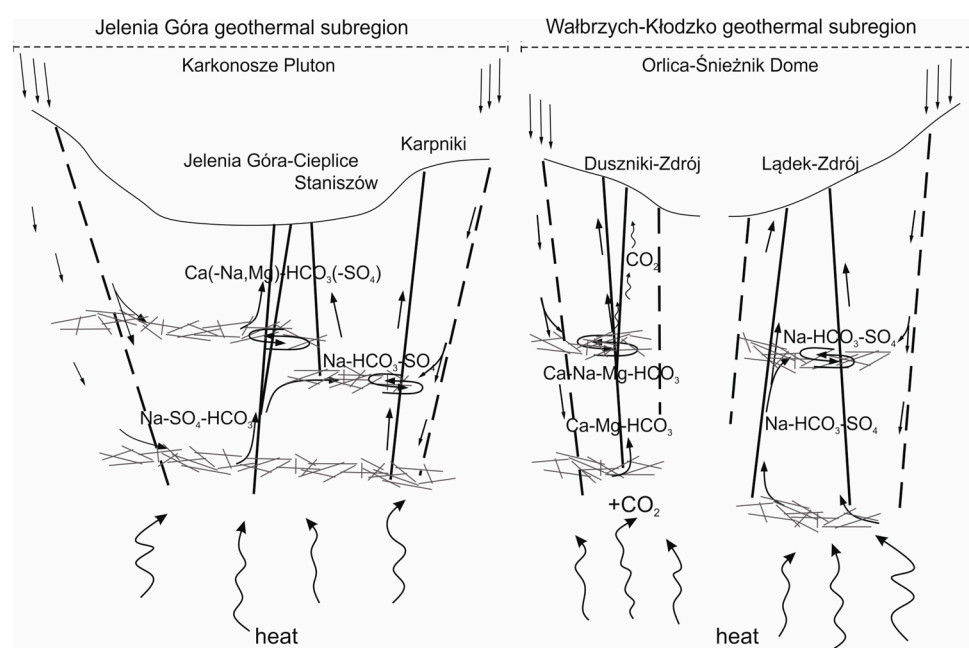
**Table 5.** An overview of the temperatures of thermal water deep components, their temperatures after cooling, and the temperatures of the mixture flowing into the well and out of the intake; temperature in °C.

Temperature	Intake					
	C-1	KT-1	ST-1	GT-1	L-2	LZT-1
at the outflow	87.7	53.0	37.3	34.7	44.0	37.4
mixture flowing into the well	97.7	59.1	45.0	55.8	-	58.9
after cooling	120 ± 4	74 ± 3	54.5 ± 3	114 ± 11	65.5 ± 3	88 ± 16
deep component	220.5–222	143–148.5	72.5–74	202.5	152–155	133–138

It should be noted that among the studied thermal water deposits, only Łądek-Zdrój waters are in equilibrium with chalcedony below the equilibrium temperature for potassium and sodium feldspar and muscovite (Figure 6). Therefore the proportion of silica in this deposit is probably buffered by its precipitation in temperatures close to those measured in intakes. Plagioclases and muscovite have probably reached equilibrium with waters from this deposit in temperatures higher than those determined by the estimation, i.e., above 65.5 °C in the L-2 well and 88 °C in LZT-1 (Table 3). This implies that they have not been re-equilibrated or have been to a small extent, as waters from this deposit exhibit equilibration “memory” in higher temperatures [15].

Geologic settings of geothermal systems are different from one country to another. Italy, Iceland, and New Zealand are very shallow geothermal reservoirs with short pathways to the surface. In such systems high (above 100 °C) reservoir temperatures are typical [73]. In the case of intracontinental systems located outside the range of active volcanic zones, subduction zones, or shallow hot spots, such parameters are unlikely to be obtained. An example is the Black Forest geothermal system with parameters very similar to the Sudetic systems (water extracted from granitic rocks, reservoir temperature from 63 to 101 °C, and a reservoir depth of 3–4 km) [76].

The temperatures of deep components suggest considerable depths of their circulation. Conceptual models of the deep geothermal reservoirs in the Jelenia Góra and the Wałbrzych-Kłodzko geothermal subregions are presented in Figure 9.



**Figure 9.** Simplified schematic cross-sections of the Jelenia Góra and the Wałbrzych-Kłodzko geothermal subregions (based on [49,77]).

In the case of the discussed geothermal systems associated with crystalline rocks, circulation to a depth of 6–8 km is rather unlikely, although it is not completely improbable in fault zones. Stober et al. [76] suggested that in the Black Forest heat is transported along flow channels/tectonic zones.

It should be remembered that it is in such zones where the discussed waters occur. It is noteworthy that modeling research by Bujakowski et al. [78] demonstrated that in the NE part of the Karkonosze pluton, at a depth of c. 6.2 km, the maximum temperatures can in places exceed 225 °C. On the other hand, given the Neogene volcanic activity (basaltic magmatism) in SW Poland and the infiltration origin of the studied waters, it is possible that the primary deep components gained heat while moving conductively from magmatic bodies. Dowgiałło [79] suggested that these heat focuses have not been cooled to this

day. The observed minor “oxygen shifts” in isotopic compositions of the Łądek-Zdrój and Jelenia Góra-Cieplce waters might be due to isotopic exchange with the surrounding rocks leading to the enrichment of waters in  $^{18}\text{O}$ .

## 6. Conclusions

The Orlica-Śnieżnik dome in the Sudetes contains thermal  $\text{Na-HCO}_3\text{-SO}_4$  waters and  $\text{CO}_2$ -rich thermal  $\text{Ca-Mg-HCO}_3$  waters. Thermal waters within the Karkonosze granite are  $\text{Na-HCO}_3\text{-SO}_4$ -type waters.

All the studied waters are of meteoric origin, so their thermal water systems are formed as a result of the infiltration of precipitation, heating at considerable depths, and the ascent along faults and fissures.

The reservoir temperatures estimated with silica thermometers range from 52 °C to 141 °C for the waters in the Jelenia Góra-Cieplce area (C-1, KT-1, ST-1), and from 62 °C to 96 °C for those in Łądek-Zdrój (LZT-1, L-2).

Classic cation geothermometers showed considerable differences in the estimated temperatures, indicating a lack of thermodynamic equilibrium of the studied waters. It is not possible to select a single geothermometer as the best one for estimating the temperature of a particular geothermal system.

The varied results obtained in Łądek-Zdrój may be due to inaccurate sampling of the new LZT-1 intake or the waters from the studied wells may represent two geothermal water systems. Although the latter hypothesis is not improbable, given the varied depths from which the waters flow into the wells (1304–2500 m in LZT-1, and 700 m in L-2) and their locations (LZT-1 is situated c. 700 m NE of L-2), the close similarity of the parameters of waters from Łądek intakes rather indicates that the well was sampled in unstable thermal conditions.

The small ranges (3–4 °C) of variation in the temperatures determined with the GeoT app for the Jelenia Góra-Cieplce (C-1), Karpniki (KT-1), Stanisławów (ST-1), and Łądek-Zdrój (L-2) deposits suggest minor variations in the chemical types within the main  $\text{Na-HCO}_3\text{-SO}_4$  type and a similar history of geochemical processes forming their composition [80].

The lowest temperatures of the deep component, only 72.5–74 °C (Table 5), are characteristic of the Stanisławów system (ST-1). Most likely, this is the result of an extensive horizontal flow system, which causes significant cooling of this component. The deep components in Jelenia Góra-Cieplce (C-1) and Duszniki-Zdrój (GT-1) are the warmest, with temperatures of 220.5–222 °C and 202.5 °C, respectively, but during their migration to drainage zones, they are already significantly cooled. Additionally, in Duszniki-Zdrój, considerable quantities of  $\text{CO}_2$  flow into these waters along faults.

The analysis of the remaining thermal water deposits suggests that the temperatures obtained from saturation modeling relate to waters pre-cooled conductively and then mixed with inflowing colder water, as the enthalpy values obtained from estimations with mixing models suggest much warmer primary components.

The proportion of colder waters of more shallow circulation in the geothermal systems of both units, i.e., the Karkonosze granite (C-1, KT-1) and the Orlica-Śnieżnik metamorphic complex (GT-1, L-2, LZT-1), falls within the ranges of 66–74% and 60–76%, respectively. Slightly lower values, 46–55%, were obtained for the Stanisławów waters (ST-1). The relatively smaller proportions of the hot components despite the considerable depths of the wells should not raise doubts given the location of these intakes in tectonic zones. On the one hand, faults facilitate the ascent of hot deep waters, but on the other, they are zones of their intensive mixing with colder waters.

The chemical compositions of the deep waters reflect water–rock interaction along the circulation paths from the recharge areas to the drainage zones. The expected geochemical processes in which the geothermal waters take part are the dissolution of aluminosilicates as well as mixing and ion exchange reactions. Therefore, precipitation of a secondary calcite and scaling problems may play an essential role in future studies.

Analysis of some trace elements, such as cesium, lithium, rubidium, strontium, etc., could confirm the estimated reservoir temperatures.

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