Chair of Mining Engineering and Mineral Economics

Master's Thesis

Estimation of the reservoir temperatures on the example of selected geothermal systems of Austria and Poland.

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MONTANUNIVERSITÄT LEOBEN

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AFFIDAVIT

I declare on oath that I wrote this thesis independently, did not use other than the specified sources and aids, and did not otherwise use any unauthorized aids.

I declare that I have read, understood, and complied with the guidelines of the senate of the Montanuniversität Leoben for "Good Scientific Practice".

Furthermore, I declare that the electronic and printed version of the submitted thesis are identical, both, formally and with regard to content.

Date 27.03.2023

Signature Author

Kamila Kozyra

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1. Introduction

The geothermal energy is one of the most important and efficient energy resources at the disposal of mankind, and its extraction has relatively few harmful environmental impacts. In many countries where geological, hydrological and geophysical conditions are favourable for the establishment of geothermal systems, geothermal energy has proven to be a viable alternative energy source (Arnórsson, 2000). The global supply of geothermal energy in 2010 was 10,897 MW, but this increased to 15,950 MW in 2020 and is predicted to reach 19,361 MW in 2025 (Benti et al., 2023).

Research on the geothermal energy are important and constantly evolving, because it is classified as one of the most important natural resources of Central Europe and with every year it gains more and more significance in the energetic and climatic policy of the European Union (Rman & Lapanje, 2013). Although, this is especially the case in the active volcanic regions, where there are noticeably high geothermal gradients, the economic geothermal reservoirs were additionally discovered in sedimentary strata and fractured volcanics outside the areas where recent volcanism has occurred (Arnórsson, 2000).

The majority of countries that exploit geothermal resources have focused on using them to generate electricity. However, certain countries use geothermal water on a large scale, especially for a space heating (Arnórsson, 2000). The commercial use of them is closely linked to their quantity of usable heat (Albu et al., 1997).

Temperature of the groundwater to a depth of about 50 m is influenced by the air temperature. Below this level, additional heat is supplied from the rocks with which the water comes into contact (Albu et al., 1997).

The reservoir temperature is the main factor which determined the possible use of particular geothermal resource (Arnórsson, 2000). Interest in the use of geothermal energy is growing year by year, therefore estimating reservoir temperatures has a future-proof application (Benti et al., 2023).

1.1. Aim of the thesis

The aim of this study was to estimate the geothermal reservoir temperatures of selected systems from Austria and Poland and to compare the parameters of these systems. The selection of the studied geothermal systems was based on the lithology, which determines the mineral composition of the water. All the wells and spring are characterised by different depths (Chochołów PIG-1: 3572 m, Biała Tatrzańska GT-1: 2500 m, Szymoszkowa GT-1: 1737 m, Marienquelle (Baden): 450 m, Oberlaa Thermal 1: 933 m, Bad Radkersburg II: 1932 m), but common feature is that they are all in carbonated rock systems. Obtained estimated temperatures can be applied to analyses of further sustainable exploitation and use of these resources.

1.2. Scope of the thesis

The scope of the study refers to all procedures leading to the estimation of the reservoir temperatures on the example of selected geothermal systems in two countries. To obtain the estimated temperatures of three Austrian and three Polish systems, firstly, the analyses of the chemical components and properties of selected geothermal waters in those country were done. In addition, estimation of the reservoir temperature by using classic chemical geothermometers and based on thermodynamic equilibrium (GeoT) was conducted. Lastly, comparison of the obtained results from 3 different regions and various depths (Podhale Basin, Vienna Basin, Bad Radkersburg-Hodoš pilot area) with similar lithology was made.

2. Study area

This work concerns the estimation of the reservoir temperature of geothermal systems in Austria and Poland. The locations were selected on the basis of lithology, which determines the mineral composition of the water.

2.1. The Polish Carpathians systems

The location of the selected Polish geothermal systems in the Podhale Trough is presented in *Figure 1* and *Figure 2*.

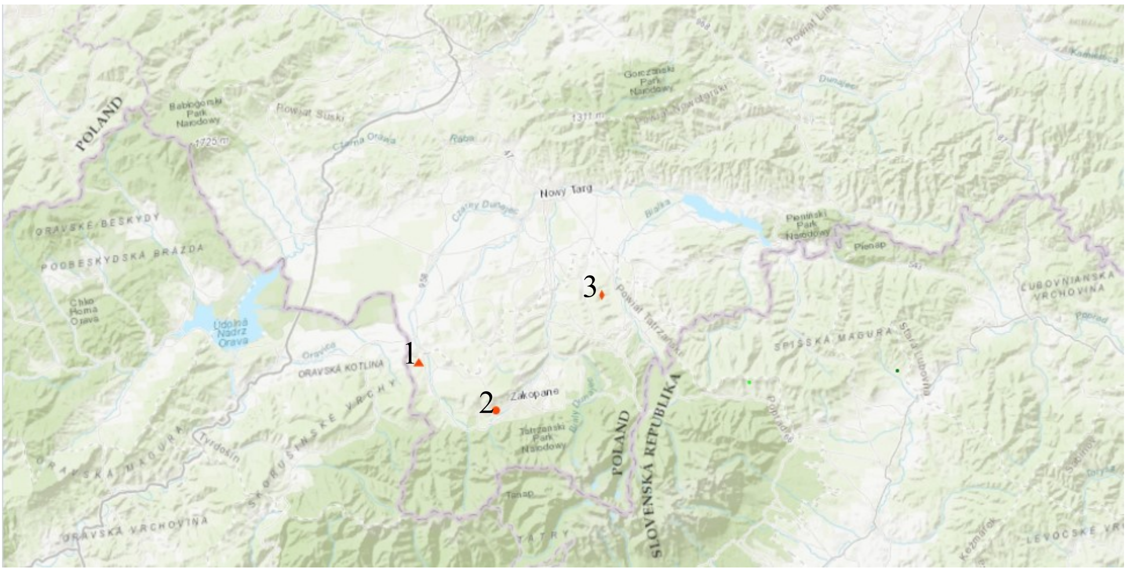

Figure 1. The location of the selected Polish geothermal systems: 1- Chochołów, 2- Szymoszkowa, 3- Białka Tatrzańska (https://geoera.eu/projects/hover8/hover-map-viewer/, 2023, modified).

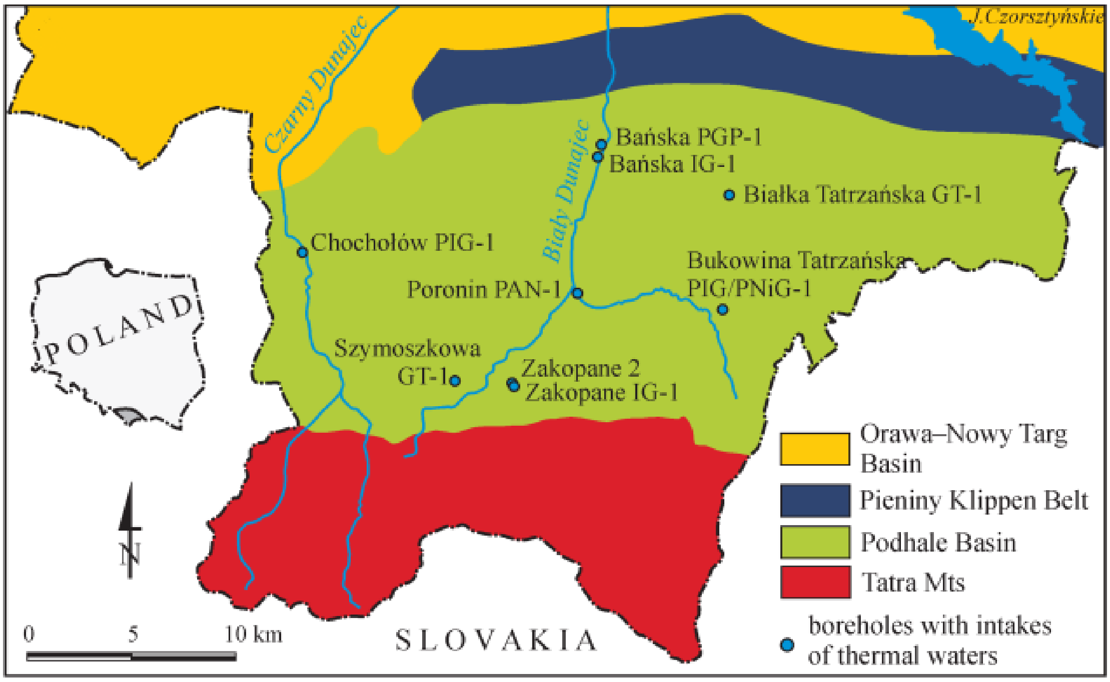

Figure 2. Location of the selected Polish geothermal systems (after Nowak et al., 2016, modified).

2.1.1. Lithology

Considering the variation in structure and geological history, the Carpathians are divided into: Inner Carpathians and Outer Carpathians (Carpathian flysch). Within Poland, the Inner Carpathians are distinguished by three geological-structural units: The Tatra Mountains, the Podhale Trough and the Pieniny Klippen Belt (which is the boundary zone between the Inner Carpathians and the outer Carpathians). The Tatras are divided into two phreato-tectonic zones: the southern (large spread) and the northern, stretching in a narrow belt along the northern side of the Tatras. The southern zone is made up of a crystalline body covered on the northern side by Triassic-Jurassic-Cretaceous sediments. Among the formations building the Tatra units the most important for the problems of groundwater recharge and flow are the fractured and karst dolomites of the Middle Triassic, limestones of the Triassic and Jurassic and quartzites of the Jurassic (Chowaniec et al., 2001).

The Podhale Trough is built of Palaeogene sandstone and shale formations lying on the Mesozoic Tatra units. The bottom, transgressive Paleogene section consists of carbonate rocks developed in the form of nummulies conglomerates and mudstones. The transgressive series is called the Tatra Eocene or Carbonate Eocene. The flysch complex with a maximum thickness of up to 3000 m, age of the Middle Eocene-Poligocene, was divided as following: the Szaflary strata (occurring only in the northern wing of the Podhale Trough), the Zakopane strata (occurring in the northern and southern wings), the Chochołowskie strata (filling the central part) and the Ostryan strata (occurring only in the western part of the Podhale Trough) (Chowaniec et al., 2001).

The Pieniny Klippen Belt, separated from the Podhale basin by a dyked zone, is built from carbonate rocks of Jurassic-Cretaceous-Tertiary age (in the area of Poland). It is possible to distinguish a number of separate tectonic-structural units which can be traced along the whole rock belt (Chowaniec et al., 2001).

Geological map of the Podhale Trough and the Tatra Mountains is shown in *Figure 3.*

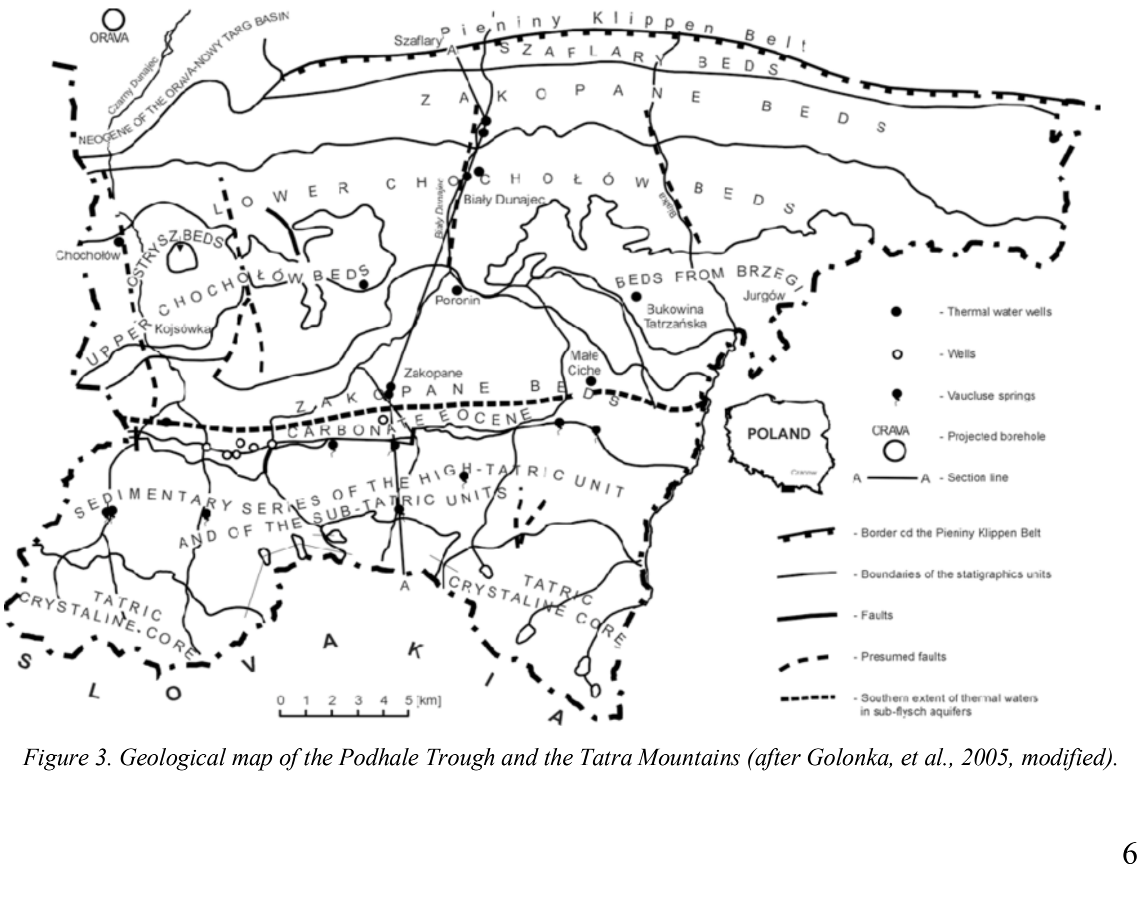

Figure 3. Geological map of the Podhale Trough and the Tatra Mountains (after Golonka, et al., 2005, modified).

2.1.2. Geothermal waters and hydrogeology

As a hydrogeological region, the Carpathians are geologically heterogeneous. In the Tatra region, water-bearing rocks are fractured and karstic carbonate rocks of the Mesozoic and Tatra Mountains' Eocene. In the Podhale region, the Podhale flysch formations (similar to those of the Outer Carpathian Flysch) are water-bearing only in the near-surface zone (mostly to approximately 80 m below ground level). The differentiation in capacity is due to varying permeability of the aquifer and their different thickness. In the area of the Pieniny Klippen Belt, despite the presence of carbonate rocks, there are no high occurrence of karst phenomena, and the tight fissures do not promote water circulation. This area, considering the possibility of water supply, is not prospective (Chowaniec, 2001).

According to geological studies, the Polish region with the highest potential in terms of its geothermal resources is the Podhale Trough, where the thermal water appears in the Eocene-Mesozoic strata. Geothermal energy is ideally suited to this area due to its well developed infrastructure for heating, balneotherapy, and recreation. Depending on the region, the origin and conditions of the thermal water's chemical composition vary due to the impact of infiltrating water on chemical compounds in nearby thermal intakes, the chemical processes that concentrate major elements, and residence time (Sekuła et al., 2020).

2.1.3. Chochołów PIG-1

Nowadays, Chochołów PIG-1 single artesian well is used for the needs of the "Chochołowskie Termy" leisure and recreation complex. The Chochołów PIG-1 borehole was drilled in 1989-1990 as part of a project which planned to drill nine deep boreholes for thermal water within the Podhale Trough in southern Poland, but only six boreholes were completed, including the Chochołów PIG-1 borehole. The Chochołów PIG-1 borehole is located in the northern part of the Witów village, district tatrzański, małopolskie voivodship. The Chochołów PIG-1 borehole reached a depth of 3572 m. The type of extracted water is 0.11% Ca-Mg-Na-SO_4. Mineralization of the water varies from 1.05 g/dm^3 to 1.30 g/dm^3, temperature at the outflow is 82.0°C, where flow is equal 160 m^3/h. Chochołów PIG-1 thermal water borehole is drilled into an aquifer that is known for its tight water table and artesian pressures. Due to favourable hydrodynamic conditions, the exploitation of the Chochołów PIG-1 intake is conducted under conditions of self-flow, without the use of any mechanical equipment. At depths of 3183-3572 m dolomites, dolomitic crumbstone and dolomitised limestone (Middle Triassic) were found (Bielec et al, 2018).

Simplified litostratygraphical profile of the Chochołów PIG-1 geothermal well is presented in *Figure 4.*

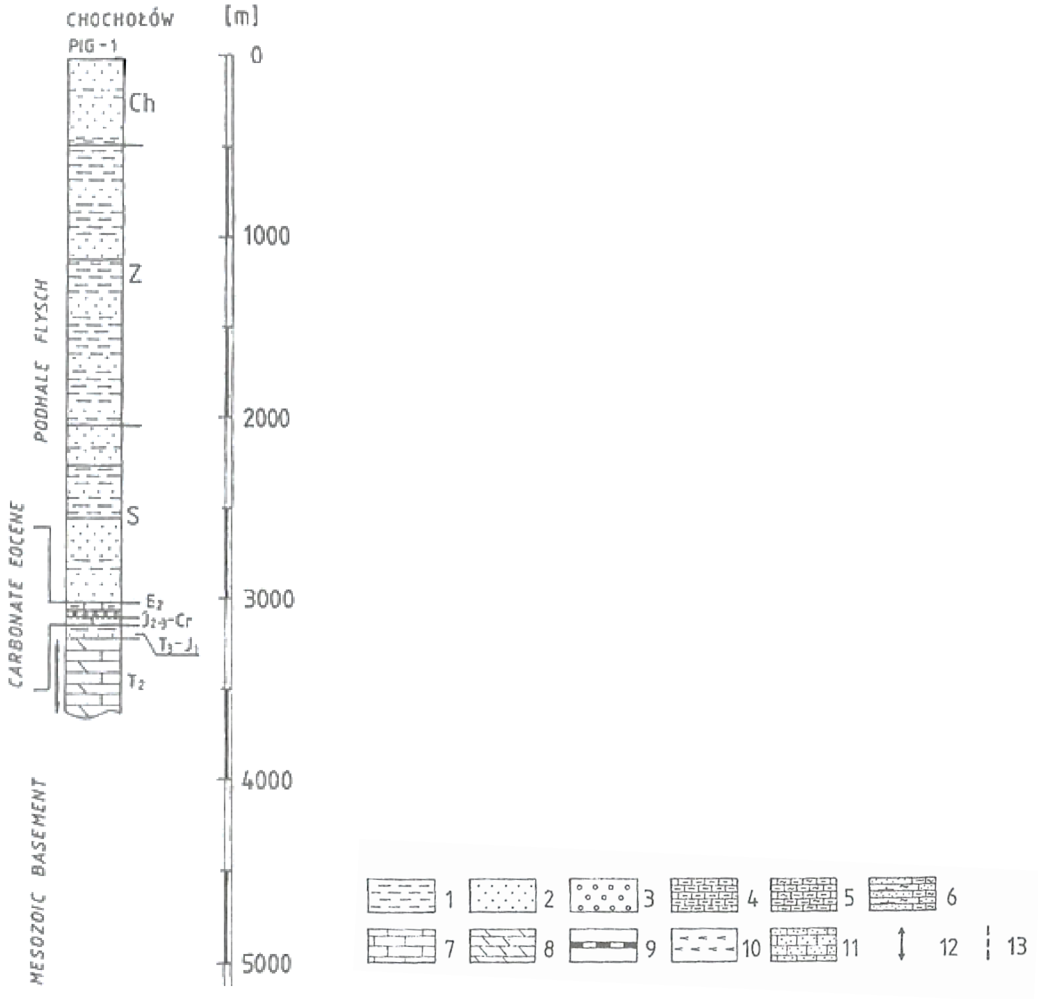

Figure 4. Simplified litostratygraphical profile of the Chochołów PIG-1 geothermal well. Paleogene: 1- shales and sandstone, 2- sandstones and shales, 3- carbonate conglomerates. Mesozoic: 4- narly limestones, 5- marls, 6-serie of clayey marls, marly clays with intercalations of sandstones and mud-stones, 7-limestones,8-dolomites,9-intercalations of radiolarities, 10-anhydrite intercalations, 11- quartzitic sandstone, 12-location of the main geothermal aquifer, 13- location of the other geothermal aquifers (after Kępińska 2006, modified).

2.1.4. Białka Tatrzańska GT-1

Białka Tatrzańska GT-1, single artesian well, is used for the needs of the "Terma Bania" leisure and recreation complex, and is located in the western part of Białka Tatrzańska village, district tatrzański, małopolskie voivodship. The Białka Tatrzańska GT-1 borehole reached a depth of 2500 m. The type of extracted water is Na-Ca-Cl- SO_4, temperature at the outflow is equal 77.0°C, mineralization of the water: 2.0 g/dm^3. At depths of 2330-2472 m dolomites and limestones (Middle Triassic) were found. The concession for thermal water extraction from the Białka mining area is held by Park Wodny Bania S.A (Felter et al, 2022). In the vicinity of Białka Tatrzańska GT-1 well, is located another new borehole Białka Tatrzańska GT-2, which was drilled in 2022 and reached a depth of 2930 m, characterised with the same lithology as the first one and has also been drilled for the use of "Terma Bania" recreation complex (PIG, PIB, 2022).

2.1.5. Szymoszkowa GT-1

Szymoszkowa GT-1, single artesian well, located in Zakopane, district tatrzański, małopolskie voivodship, was drilled in 2006 and reached a depth at 1737 m. The occurrence of thermal waters has been documented in Paleogene, Jurassic and Triassic carbonate formations. The concession for the extraction of thermal waters from the Szymoszkowa mining area was granted to the Dorado Sp. z o.o. company. The intake is exploited seasonally, from May to September, in order to supply water to two outdoor swimming pools located on Polana Szymoszkowa. The water must be heated before being injected into the pools, because temperature at the outflow is equal 27.0°C. Type of extracted water is Ca-Mg-Na-HCO_3-Cl, mineralization of the water: 0.4 g/dm^3 (Felter et al, 2022).

2.2. The Austrian systems

Mostly depth of the thermal waters in Austria is up to several thousand meters, particularly in large basins outside of the Alps. In other way, geothermal waters can reach the earth's surface heated by geological-tectonic fracture systems that exist in alpine massifs. The general use of thermal water in Austria has therefore often become an important industry, at least on a regional scale (Bundesministerium Land- und Forstwirtschaft Regionen und Wasserwirtschaft, 2023). In Austria, thermal waters are primarily found in the large Neogene basins and their subsoils, which contain extensive thermal water deposits, namely in the Molasse basin (North Alpine foreland basin) and in the Vienna and Styrian basins and their transition to the Pannonian basin to the east (Elster et al., 2016).

Overview of thermal water deposits in Austria with regard to the type of thermal water intakes is presented in *Figure 5.* Distinction was made as to whether they originally emerged naturally, or whether they were first encountered through artificial exploration.

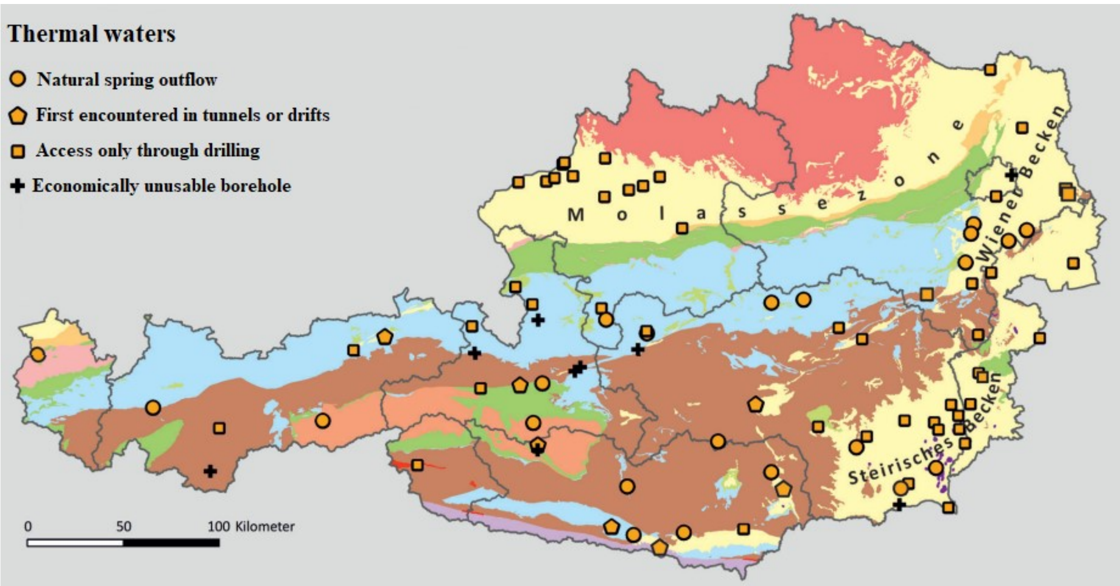

Figure 5. The occurrence of thermal waters in Austria (Elster et at., 2016, modified).

The location of the selected Austrian geothermal systems is presented in *Figure 6.*

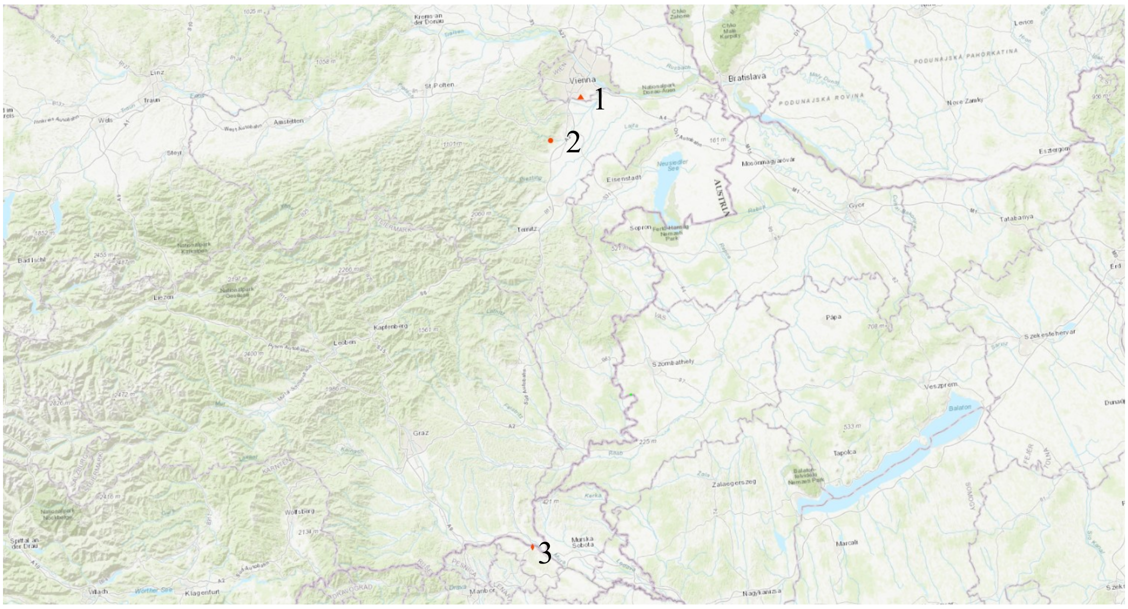

Figure 6. The location of the selected Austrian geothermal systems: 1- Oberlaa Thermal 1, 2- Marienquelle, Baden, 3- Bad Radkersburg II (https://geoera.eu/projects/hover8/hover-map-viewer/, 2023, modified).

2.2.1. Oberlaa Thermal 1

Oberlaa Thermal 1 single artesian well, located at the western edge of the southern Vienna Basin, in Oberlaa city, is used for the needs of the “Therme Wien” leisure and recreation complex. The type of extracted thermal water in Oberlaa is Na-Ca-SO_4-Cl, with a total mineralisation of approximately 3.6 g/dm^3 and outlet temperature equal to 47.6°C (date of the temperature measurement: 22.04.2009). In the vicinity of Oberlaa Thermal 1, is located another single artesian well Oberlaa Thermal 2, which is up to 933 m deep and the temperature at the outflow equal to 46.8°C. The thermal water aquifer consists locally of the Rothneusiedl Formation (Badenian), the Anninger limestone (Rhaetian) and Main dolomite (Norian). At the Oberlaa Thermal 1 well, which is up to 418.5 m deep, the most productive water inflows come from the Rothneusiedl Formation. This has varying porosities, but does not contain any damming layers. In Oberlaa reduction of sulphate to sulphide may be related to the degradation of organic material from hydrocarbon-bearing Triassic and Jurassic sediments. As for the origin of the sulphate, the Sulphur-34 signature of 27.7 ‰ indicates saline waters of the higher Lower Triassic. Worth mentioning is the high content of silicic acid (> 40 mg/dm^3), which can be explained by a deep thermal water circulation (Elster et al., 2016).

Geological profile of Oberlaa is presented in *Figure 7*.

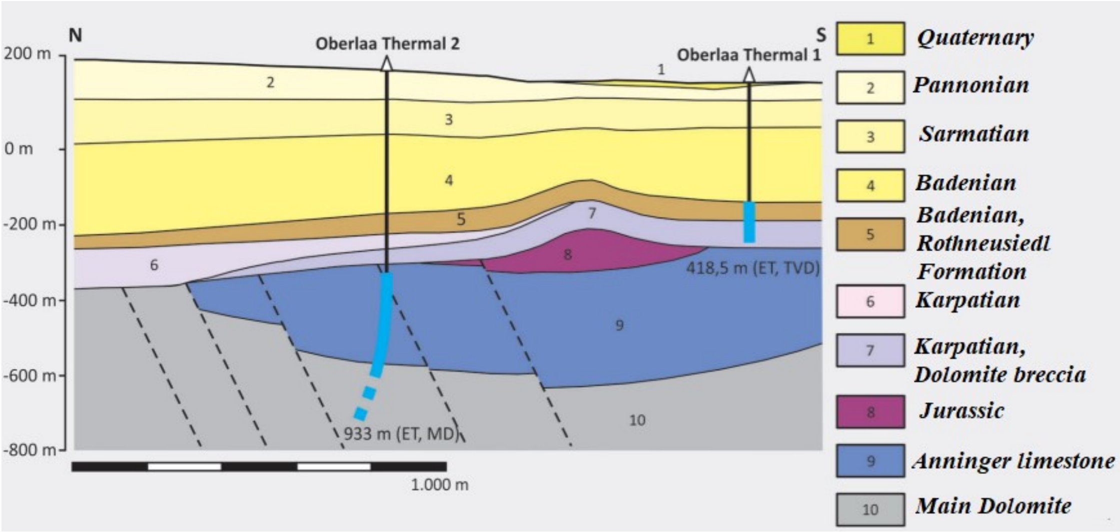

Figure 7. Geological profile of Oberlaa (Elster et al., 2016, modified).

2.2.2. Marienquelle, Baden

The thermal springs of Baden are located on the western edge of the southern Vienna Basin. This is the place where the middle section of the thermal aquifer of the Göller cover (Tyrolean-Norse cover system of the Northern Limestone Alps) dips below the Neogene basin fill (Elser et al., 2016). In Baden are located three main springs: Josefsquelle Borehole 1, Marienquelle and Römerquelle, and through its history with the Kaisers of the House of Habsburg, is also known as the "Spa of Emperors" (https://historicthermaltowns.eu/, 2023). The type of extracted thermal water in Baden is Ca-Na-Mg-SO_4-Cl (with H_2S) with a total mineralisation of approximately 1.7 g/dm^3. In addition, high content of hydrogen sulphide (>5.0 mg/dm^3) in this thermal water shows similarity to water from the Oberlaa. According to Hacker & Zötl (1993), possible causes of this are the effect of thermal water on sulphate deposits, the effect of associated petroleum waters and the reduction of microbacteria. In the case of influence of the petroleum waters, some trace substances such as iodides and bromides would be expected, but these only occur in very low concentrations (Götzl et al., 2012).

Based on the Sulphur-34 signature (23.2 to 25.5 ‰), Götzl et al. (2012) assume for the origin of the evaporites from the Upper Lower Triassic to Middle Triassic.

Comparing the thermal waters of Baden with the others of the Western High Plateau of the southern Vienna basin, it is noticeable that its residence time is comparatively low in relation to the temperature reached (Elser et al., 2016). This could be due to a shortened convection time compared to Oberlaa. In addition, it should be noted that the freely gases consist for the most part (approximately 95%) of nitrogen (Götzl et al., 2012).

Marienquelle is a single captured spring, which is up to 450 m deep and the temperature at the outflow is equal to 34.2°C (date of the temperature measurement: 16.02.2010) (Elser et al., 2016). The catchment chamber of the Marienquelle is located about 10 m below the riverbed of the Schwechat river, directly on the rock (Kaiser, 2000).

Geological profile of Baden is presented in *Figure 8*.

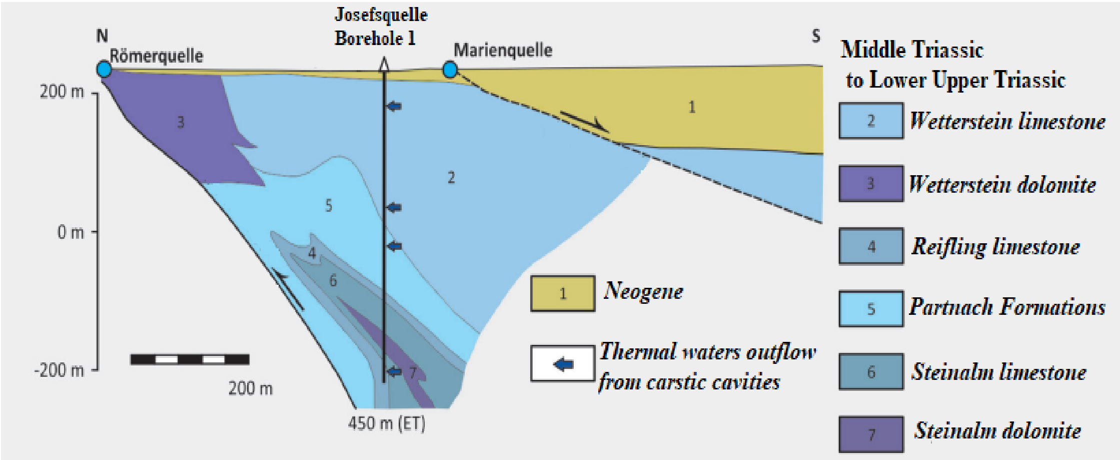

Figure 8. Geological profile of Baden (Elster et al., 2016, modified).

2.2.3. Bad Radkersburg II

The Bad Radkersburg - Hodoš pilot area is located along the borders of Slovenia, Hungary and Austria. Thermal waters are produces by three main aquifers: Upper Miocene (Szentgotthard in Hungary), Middle Miocene (Radenci in Slovenia and Loipersdorf, Bad Radkersburg in Austria), Pre-Neogene Basement (Bad Radkersburg in Austria and Benedikt, Korovci in Slovenia). The thermal water deposits of Bad Radkersburg are located at the western end of the Radgona-Vas-Graben (Radgona-Vas tectonic half-trench) (Lapanje, et al., 2012). The main geological structure in the Bad Radkersburg - Hodoš pilot area are the Pre-Neogene basement rocks (built from the Mesozoic carbonate rocks and the prevalent Paleozoic metamorphic rocks) and the Neogene sedimentary rocks. These rocks in the Raba fault zone are fractured and fissured which enable thermal water to flow and therefore create mentioned geothermal aquifer (geothermal waters are abstracted from this aquifer e.g., in Bad Radkersburg) (Rman & Lapanje, 2013).

Geological structure of the Bad Radkersburg - Hodoš pilot area is presented in *Figure 9.*

Figure 9. Geological structure of the Bad Radkersburg-Hodoš pilot area (after http://transenergy-eu.geologie.ac.at, 2023, modified).

Thermal waters of Bad Radkersburg (two single artesian wells: Bad Radkersburg II and IIa) are used for bathing and balneology, e.g., supply baths in leisure and recreation complex. The type of extracted thermal water in Bad Radkersburg is Na-HCO_3 with a total mineralisation of approximately 8.0 g/dm^3. Due to the values of oxygen and deuterium, a meteoric origin can be assumed. Increased proportions of free carbon dioxide are according to Miocene and Pliocene volcanism. Consequently, the free-floating gases consist almost exclusively of CO_2 (Elster et al., 2016).

Bad Radkersburg II is up to 1932 m deep and the temperature at the outflow is equal to 76.3°C (date of the temperature measurement: 09.11.1990) (Elster et al., 2016).

Geological profile of Bad Radkersburg is presented in the *Figure 10*.

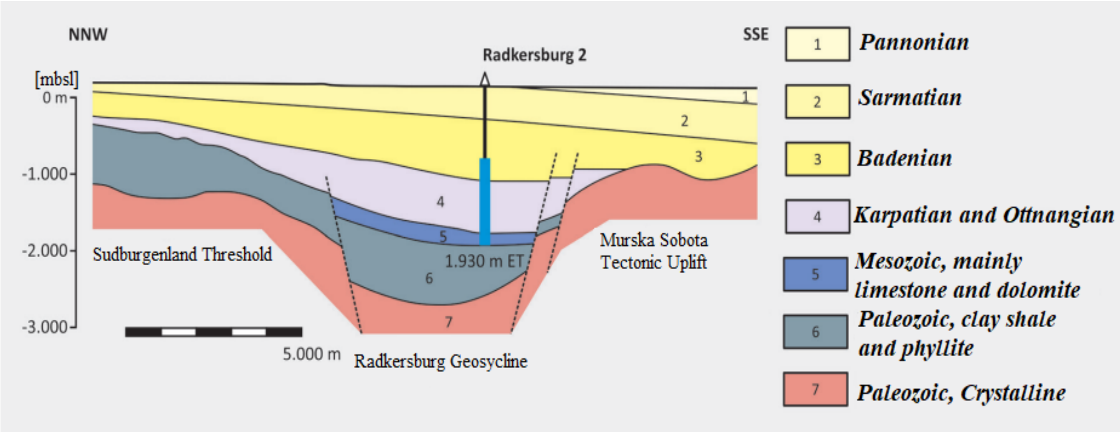

Figure 10. Geological profile of Bad Radkersburg (Elster et al., 2016, modified).

3. Geothermal systems and geothermal energy

The geothermal systems are quite different from petroleum and groundwater systems. They are characterised by higher complex, are dynamic and less defined. In addition, in order to determine the type and extent of the geothermal systems, exploration drilling and well testing have to be conducted (Zarrouk et al., 2019). Geothermal systems include the following elements: rock formations with defined lithology, tectonics and reservoir properties, geothermal fluids with specific chemical composition, physical characteristics, origins and age, depth temperatures and pressures (Kępińska, 2006). Generally, geothermal systems can be classified in terms of: the manner of heat transport (conductive and convective systems), mobility of the components (systems with and without mobile components), nature of the components (thermal water systems, hot dry rock systems, magmatic systems), state of the components (solid components systems, magmatic melts systems with or without gases and vapour, low or high enthalpy systems), hydraulic closure of the components (closed and open systems) (Albu et al., 1997).

There are several factors that affect the occurrence, renewability, resources and physicochemical properties of thermal water. Among them can be distinguished: hydrogeological conditions (particularly porosity and permeability of the aquifer rocks), aquifuges, localization of alimentation area, conditions for water circulation in the geothermal aquifer (Sekuła et al., 2020). Geology, like all other sub-surface resources, is fundamental to the formation of geothermal reservoirs (Benti et al., 2023).

Hot springs and fumaroles indicate the presence of geothermal reservoirs. However, exploration has revealed that there are also hidden reservoirs. In some cases, there is a correlation between the distribution and intensity of surface geothermal activities within a particular area and the extent and capacity of underlying geothermal reservoirs (Arnórsson, 2000).

Geothermal resources, which refers to reservoirs of hot water occurring naturally or man-made at different temperatures and depths under the Earth's surface, can be classified based on the natural fluid temperature (outlet temperature) into (Geothermal Technologies Office, 2023): high-enthalpy (temperature higher than 150°C), medium-enthalpy (temperature between 90°C and 150°C) and low-enthalpy (temperature lower than 90°C). Resources characterised by high and medium enthalpy occur only in geological zones (principally volcanic) featuring by high heat fluxes, are used mainly for power generation and for the cascading direct usage of exhausted fluid. The direct usage of low-enthalpy resources can be seen practically anywhere, e.g., geothermal heat pumps, greenhouse heating, space and district heating, aquaculture, balneotherapy, bathing and swimming, industrial and agricultural applications. The potential use of geothermal resources represents energy savings and significantly increased economic benefits (Carapezza et al., 2022). Therefore, as a clean energy source (e.g., low greenhouse gas emissions) and continuous power generation, geothermal energy is commonly used for electricity generation, heating or cooling buildings and other industrial applications (Benti et al., 2023).

Geothermal exploration is conducted in order to locate geothermal areas that are potentially suitable for development and to identify drilling sites within them. Geophysical surveys, geological mapping, and geochemical surveys are all part of this exploration. Geochemical surveys are conducted primarily to predict subsurface temperatures, to determine the origin of geothermal fluids and to understand the direction of subsurface flow. In the geochemical prospecting of geothermal resources, there is a fundamental belief that the concentration of many components in the geothermal fluid, i.e. natural aqueous solutions and gaseous steam, are reflective of the thermal conditions at depth. Research has shown that the equilibrium with minerals in the aquifer rock is responsible for the aqueous concentrations of certain chemical and isotopic components in borehole discharges (Arnórsson, 2000).

In contrast, the aqueous concentration of other components are controlled by theirs supply to the geothermal fluid. Temperature affects the equilibrium between the solution and the minerals in such a way that the concentrations, or ratios ofconcentrations, of the aqueous constituents change with temperature. For that reason, the temperature of the geothermal fluid is reflected by the aqueous concentrations of the chemical and isotopic components equilibrated with the minerals in geothermal systems (Arnórsson, 2000).

Geochemistry is an important aspect of geothermal exploration drillings and later geothermal reservoir development. It is used to determine information about the chemical properties of discharged fluids, the level and temperature of aquifers at the bottom of wells, and the steam to water ratio in reservoirs. As a result, it furthers understanding of geothermal reservoir production characteristics (Arnórsson, 2000).

Geothermal waters in Poland are defined as those waters which are considered to have a temperature of not less than 20°C at the outflow of the intake. In other countries, e.g. Slovakia, another division can be distinguished. The value of 20°C is purely conventional and was adopted at the Congress of Balneologists and Chemists in Nauheim in 1911. Since Polish thermal water deposits cover around 80% of the country's area, Poland is an European thermal water potentate (Kruczek, 2016). Polish geothermal resources are classified as low-enthalpy. So far, they have been best recognized in the Mesozoic formations of Polish Lowlands (Hajto & Górecki, 2010). In Austria, according to the laws on healing and health resorts of the Austrian federal provinces, groundwater from 20°C at the outflow of the intake are considered to be thermal waters (Elster et al., 2016).

4. Hydrogeochemistry of studied thermal waters

Sustainable exploitation of geothermal resources requires an understanding of the geochemistry of geothermal fluids and their impact on the environment (Guo, 2012).

Studied thermal waters occurs within carbonate sedimentary rock (minimum fifty percent of the primary and recrystallized constituents are composed of one, or more, of the carbonate minerals, such as: dolomite, aragonite, calcite, magnesite), especially the dolomite, which is a pure carbonate sedimentary rock, with the ratio of magnesium carbonate to calcite larger than 1 to 1 (https://geoera.eu/projects/hover8/hover-map-viewer, 2023). All the studied systems have lithology in common, which determines the mineral composition of the water.

Diagrams and graphs presented in *Figures 11., 12., 13., 14.,* were created on the basis of an "AquaChem" Water Quality Data Analysis and reporting Software. This software is used for plotting graphic representation of the chemical characteristics of water, which enables further interpretation of the analysed water data (https://www.waterloohydrogeologic.com, 2023).

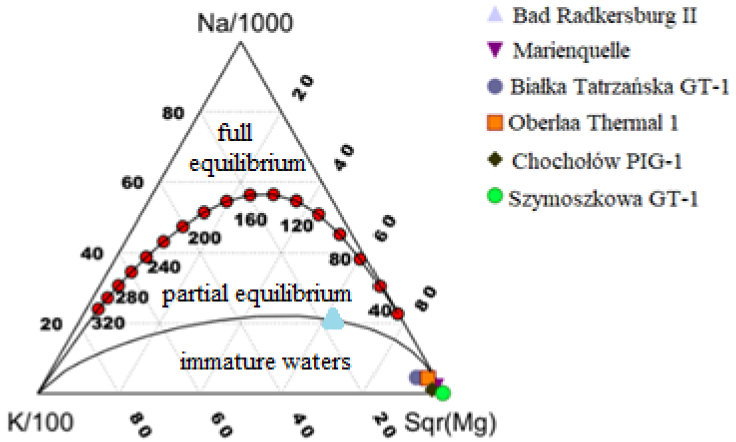

Figure 11. Giggenbach diagram of the studied geothermal waters.

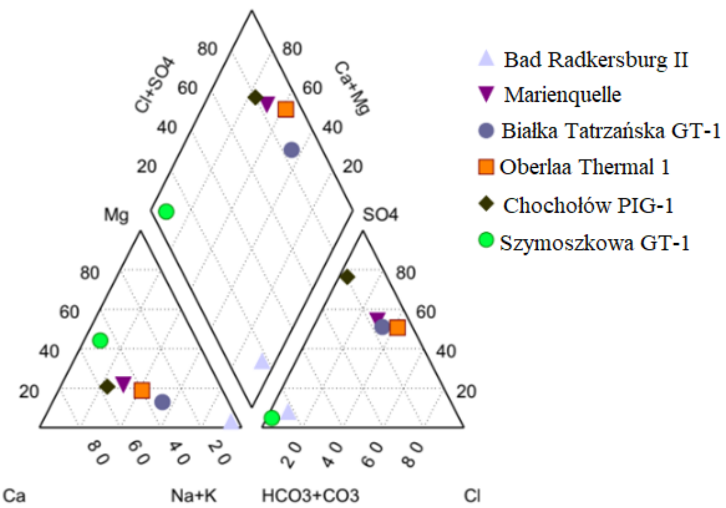

Figure 12. Piper diagram with chemical characteristics of the studied geothermal waters.

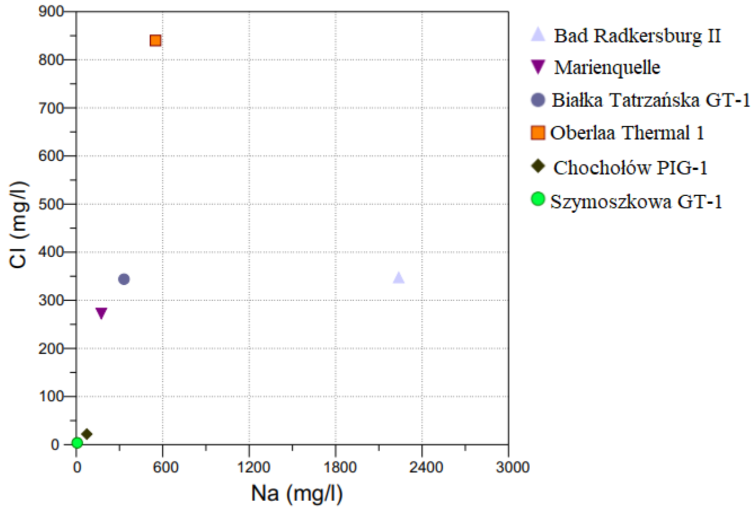

Figure 13. Na-Cl diagram of the studied geothermal waters.

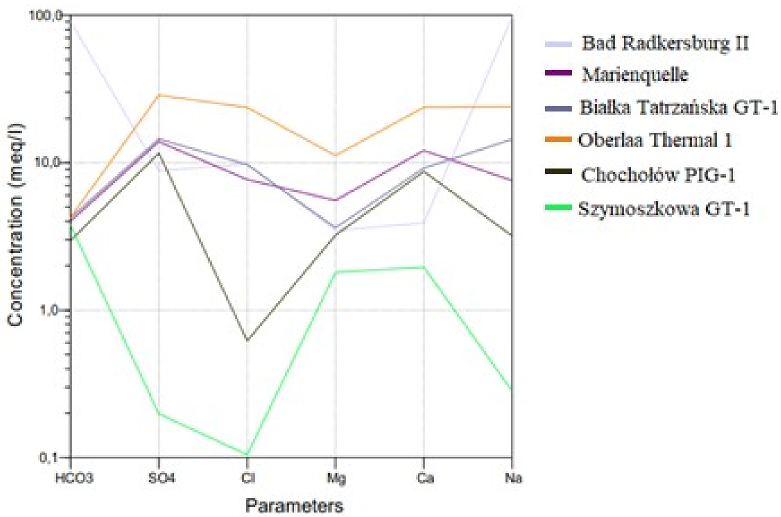

Figure 14. Concentration of the chemical components of the studied geothermal waters.

The Giggenbach diagram (*Figure 11.*) was used to determine which of the selected geothermal waters had reached complete equilibrium or partial equilibrium with a rock medium. In addition, this diagram is used to obtain the estimated reservoir temperatures. Five points, which reflective five systems: Marienquelle, Oberlaa Thermal 1, Chochołów PIG-1, Szymoszkowa GT-1, Białka Tatrzańska GT-1, are located in the diagram in the field of immature waters, which provides the lack of thermodynamic equilibrium in these systems. Therefore, it should be taken into account that the temperatures obtained by estimation using classic chemical geothermometers for immature waters do not provide actual temperatures values. The point of Bad Radkersburg II is located on the border between partial equilibrium and immature waters which suggest that water from this system has a longer residence time in the rock medium and longer reaction time between water and rock medium than from the other systems. However, estimated reservoir temperature obtained from classical chemical geothermometers should be interpreted with reserve. Based on the Giggenbach diagram, by drawing an equilibrium line from Sqr(Mg) corner, it is possible to estimate the reservoir temperature for Bad Radkersburg II, which is equal to 190°C. This value is also inaccurate, since the point representing this system is not located in the full equilibrium area or on the border between it and partial equilibrium, where the most reliable values of temperatures can be obtained.

The Piper diagram *(Figure 12.)* was used to present chemical characteristics of the studied geothermal waters. Diagram showed that the type of the water from Bad Radkersburg II is $Na-HCO_3$, from Szymoszkowa GT-1 is $Ca-Mg-HCO_3$, and the other systems are $Ca-Cl-SO_4$ with an increasing proportion of magnesium.

Na-Cl diagram (*Figure 13.)* showed that geothermal water in Oberlaa Thermal 1 is characterised by a high Cl- content (the highest of all systems). In addition, the content of Cl- in Białka Tatrzańska GT-1 is similar to the Bad Radkersburg II, but this Austrian system has a much higher content of Na^+ (the highest of all systems). The diagram also showed that Cl- and Na^+ content in Marienquelle does not differ much from the Białka Tatrzańska GT-1 and both in Szymoszkowa GT-1 and Chochołów PIG-1 content of these chemical components are low (the lowest in Szymoszkowa GT-1).

Diagram which presented concentration of the chemical components of the studied geothermal waters (*Figure 14.)* showed that water from Szymoszkowa GT-1 almost does not contain Cl- and the content of the other dissolved components is low (low mineralization). Waters of Bad Radkersburg II contain a high concentration of HCO_3- and Na^+. The chemical composition of geothermal water from Białka Tatrzańka GT-1 is similar to waters from Marienquelle and Oberlaa Thermal 1, but they vary in the degree of mineralization (Oberlaa Thermal 1 has higher mineralization than these two others).

5. Geothermometers

Knowledge of the groundwater temperature values in the aquifer plays a key and crucial role in the exploration of geothermal water deposits. Despite the fact that measuring the temperature of groundwater directly at the bottom of the borehole gives the results closest to the actual value, this method is very expensive, so geothermometers are used during the exploration phase to reduce costs (Karingithi, 2009).

The exploration and development of geothermal resources would be impossible without chemical and isotope geothermometers, which are also significant during exploitation in monitoring how geothermal reservoirs respond to production loads. Depending on the phase, we can distinguish the following uses of geothermometry:

- exploration phase: estimate subsurface temperature,
- geothermal development and monitoring: interpret the composition of well flows in terms of the location of production horizons in wells,
- chemical analyses: explain the chemical reactions occurring in the decompression zone around the wells as a result of boiling or cooling by adding cold water.

Geothermometers can be divided into three groups: water or solute, steam or gas and isotope geothermometers (Arnórsson, 2000).

5.1. Chemical geothermometers

Chemical geothermometers are collectively referred to as water and steam geothermometers (Arnórsson, 2000). They are sets of equations, based on the results of analyses of the chemical and isotopic composition of geothermal waters and gases, which enable the estimation of the reservoir temperatures. Most common, classic chemical geothermometers, use the concentrations of dissolved silica or the ionic ratios (K-Mg, Na-K, Na-K-Ca). Those equations are based on the assumption that the fluid and the rock medium are in thermodynamic equilibrium or close to it. Furthermore, this equilibrium is assumed to be maintained along the entire path of water flow to drainage zones. Accordingly, the equations are sensitive to the precipitation of secondary minerals, such as calcite or silica, or the presence of CO_2. As a result of the cooling of the primary fluid or its boiling, water–rock–gas systems re-equilibrate. In addition, mixing with shallow circulation waters affects ion ratios, resulting in incorrect temperature estimation

(Kiełczawa, 2023).

Geothermometers do not always provide information on the maximum temperature within a geothermal reservoir. They are capable of indicating the temperature of the source aquifer where equilibrium last occurred. It will not be possible to provide by geothermometers information about deeper and hotter regions of the reservoir if the source aquifer is shallow (Arnórsson, 2000).

5.2. The GeoT application

The GeoT, which is a command-driven application, reads input and writes output "ascii" files. To read the input files this programme needs to have a text editor (e.g., Wordpad), which allows the input files to provide that the problems can be edited and modified to create new input files for other problems (GeoT User's Guide, 2015).

The GeoT App is based on the multicomponent geothermometry method presented by Reed and Spycher (1984). In this method, full chemical analyses of water samples are used to calculate the saturation indices (log(Q/K)) of reservoir minerals within the temperature range, e.g., from 25°C to 300°C. The mineral saturation index is obtained from the calculated ion activity product (Q) and the thermodynamic equilibrium constant (K) for each selected mineral. The most important factor is to enter relevant mineral composition of the studied geothermal waters into the input file and select the minerals with which the solution will reach the equilibrium (by analysing the rock medium it is possible to select appropriate minerals which could equilibrate with selected water type). The reservoir temperature can be obtained from the graph, where saturation indices are plotted as a function of temperature, and a clustering of log(Q/K) curves are close to zero at any given temperature (for a group of selected deposit minerals). The line indicating 0 is considered to be the equilibrium expected to be achieved. When the obtained result is inaccurate, consideration should be given to equilibrate the studied waters with another mineral or/and dilute or concentrate the solution (in addition it is possible to modify the proportion of contained gas). By applying corrections for the effects of dilution or mixing of the analysed fluid composition and adding back any gases that may have exsolved from the deep fluid as it travelled to the surface, the composition of the deep fluid is reconstructed prior to calculating saturation indices (Spycher et al. 2016).

This multi-component approach has advantages over classical geothermometers, because it relies on complete fluid analyses and a thermodynamic equilibrium in contrast to classical geothermometers, which are based on the dilution of a few minerals (Spycher et al. 2016).

In addition, GeoT App enables users to calculate classic chemical geothermometers, moreover, based on the output data (median, mean, standard deviation and mean root square error) it is possible to create graph of standard statistical functions (Spycher et al., 2014).

6. Results

Reservoir temperatures have been estimated with the use of chemical geothermometers, on the basis of available results of physicochemical analyses of water, compiled by GeoERA project and published as HOVER map viewer on the website https://geoera.eu/projects/hover8/hover-map-viewer/.

6.1. Chemical geothermometers calculations

Reservoir temperatures were calculated on the basis of the silica geothermometer (TQ) and the chalcedony geothermometers (TCh_1, TCh_2) in accordance with the following equations:

$$T_Q = \frac{1309}{5.19 - logSiO_{2(aq)}} - 273.15\ [°C],$$

$$T_{Ch1} = \frac{1032}{4.69 - logSiO_{2(aq)}} - 273.15\ [°C],$$

$$T_{Ch2} = \frac{1112}{4.91 - logSiO_{2(aq)}} - 273.15\ [°C],$$

where $SiO_{2(aq)}$ concentrations is given in mg/dm^3 (Kiełczawa et al., 2021). Calculated $SiO_{2(aq)}$ concentrations in mg/dm^3 of the selected thermal waters are shown in *Table 1*. To obtain the value of $SiO_{2(aq)}$, the concentrations of H_2SiO_3 were multiplied by 0.769 (weight conversion).

Table 1. SiO2(aq) concentrations of the selected thermal waters.

Name of the intake	**$SiO_{2(aq)}$ concentrations [mg/dm^3]**
Chochołów PIG-1	51.29
Białka Tatrzańska GT-1	66.29
Szymoszkowa GT-1	8.23
Bad Radkersburg II	45.99
Marienquelle, Baden	22.45
Oberlaa Thermal 1	32.30

The estimated reservoir temperatures for the selected geothermal systems using classic chemical geothermometers are shown in *Table 2.*

Table 2. Estimated reservoir temperatures for the selected geothermal systems with the use of classic chemical geothermometers.

Name of the intake	**Outlet temperature [°C]**	**Q [°C]**	**Ch_1 [°C]**	**Ch_2 [°C]**
Białka Tatrzańska GT-1	77.00	115.44	86.61	86.89
Chochołów PIG-1	82.00	103.00	*73.16*	*74.35*
Szymoszkowa GT-1	27.00	33.08	*0.26*	*5.23*
Bad Radkersburg II	76.30	97.95	*67.74*	*69.28*
Oberlaa Thermal 1	47.60	82.48	51.30	53.83
Marienquelle, Baden	34.20	67.84	35.94	39.32

The estimated reservoir temperatures marked in italics in the *Table 2.* showed not reliable results as the temperature values obtained are lower than the outlet temperature. It is related to the fact that in some cases the usage of chemical geothermometers for the liquid phase requires difficult, broad and complicated interpretation or sometimes they do not work properly.

To obtain better results and more precisely estimate the reservoir temperatures the GeoT application has been used.

6.2. Temperature estimation using the GeoT application

Based on the lithology, which was a key factor for selecting the studied systems, a large complex of rock-forming minerals has been chosen for the simulation. The most important of them are: dolomite, quartz, chalcedony, montmorillonite, calcium and magnesium beidellite, calcite, sodium plagioclase (albite), potassium feldspar (microcline), kaolin, muscovite.

Using GeoT application, two final graphs were obtained for every system. First group of graphs *(Figures 15.,17.,20.,22.,24.,27.)* presents the final saturation index of thermal water for the selected minerals. Second group of graphs (*Figures 16.,18.,2.1,23.,25.,28.*) showed standard statistical functions of thermal water: median (RMED), mean (MEAN), standard deviation (SDEV) and mean root square error (RMSE). Temperature obtained from GeoT "T(C) at minimum RMED" was taken as the estimated reservoir temperature (according to the GeoT user's manual). This is the temperature at which the median of scaled log(Q/K) absolute values (RMED) is minimum. Also, the temperature spread is given, therefore the obtained temperature is specified with error margin.

- **Chochołów PIG-1**

Computed saturation index log(Q/K), of thermal water from Chochołów PIG-1, as a function of temperature, showing clustering near zero close to the temperature 89.5°C is presented in *Figure 15.*

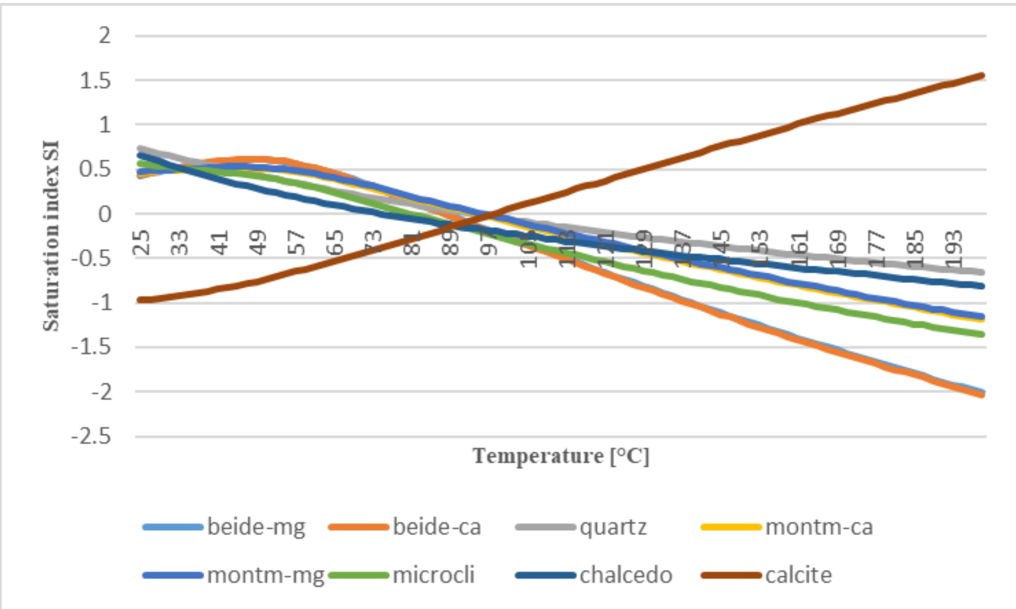

Figure 15. The saturation index of thermal water from Chochołów PIG-1 for the selected minerals.

Standard statistical functions of thermal water from Chochołów PIG-1 are plotted in *Figure 16*.

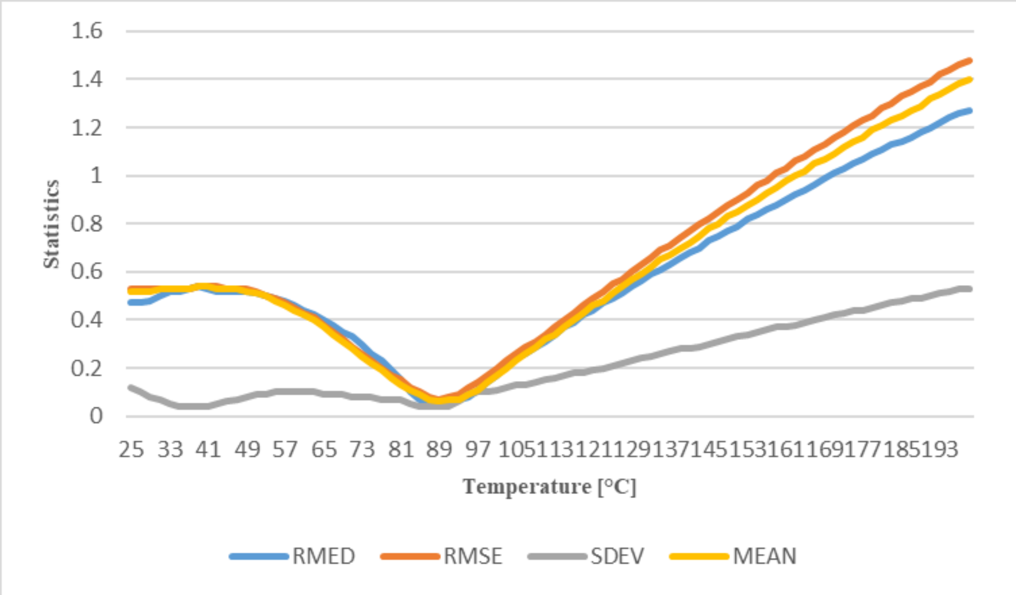

Figure 16. Standard statistical functions of thermal water from Chochołów PIG-1; median (RMED), mean (MEAN), standard deviation (SDEV) and mean root square error (RMSE).

- **Białka Tatrzańska GT-1**

Computed saturation index, log(Q/K), of thermal water from Białka Tatrzańska GT-1, as a function of temperature, showing clustering near zero close to the temperature 106.7°C is presented in *Figure 17*.

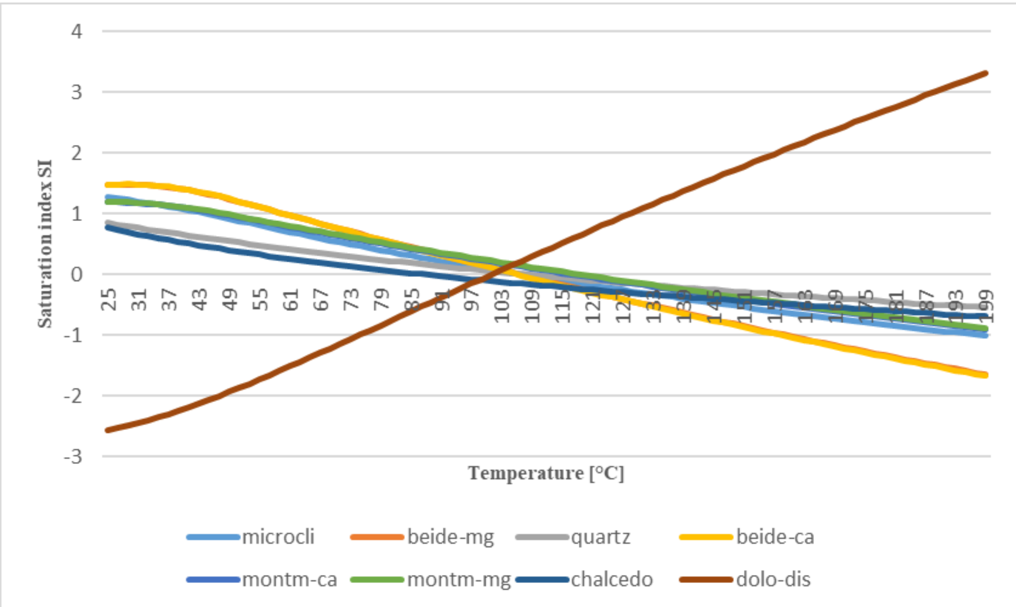

Figure 17. The saturation index of thermal water from Białka Tatrzańska GT-1 for the selected minerals.

Standard statistical functions of thermal water from Białka Tatrzańska GT-1 are plotted in *Figure 18*.

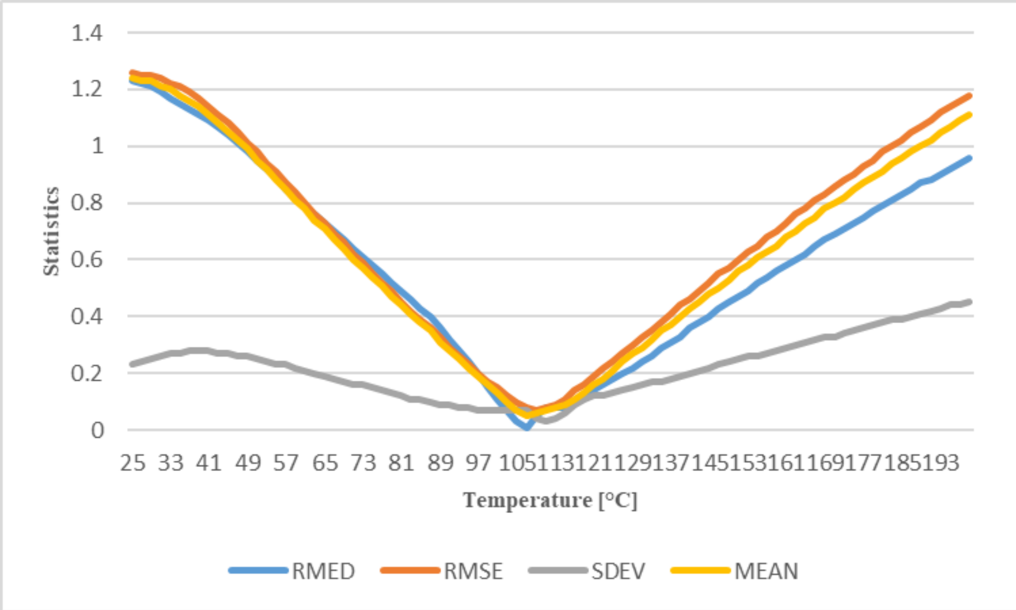

Figure 18. Standard statistical functions of thermal water from Białka Tatrzańska GT-1; median (RMED), mean (MEAN), standard deviation (SDEV) and mean root square error (RMSE).

- **Szymoszkowa GT-1**

To reduce the impact of re-equilibration, concentrations of the ions were stabilized by equilibrating the studied water with calcite. The saturation index of thermal water from Szymoszkowa GT-1 before equilibrating with calcite is presented in *Figure 19*.

The saturation index of thermal water from Szymoszkowa GT-1, after equilibrating the studied water with calcite, as a function of temperature, showing clustering near zero close to the temperature 45.2°C is shown in *Figure 20.*

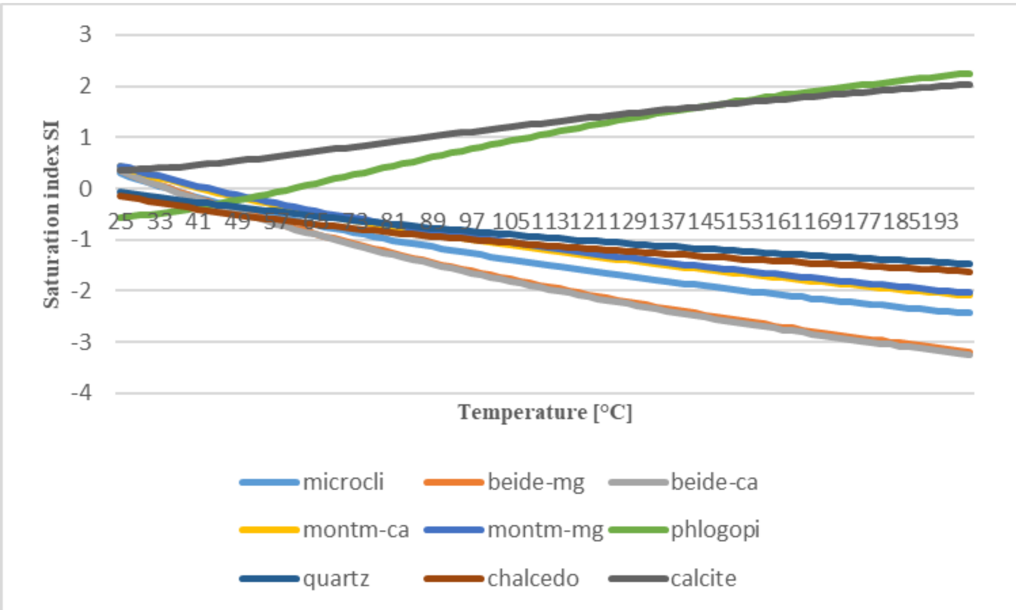

Figure 19. The saturation index of thermal water from Szymoszkowa GT-1 for the selected minerals before equilibrating with calcite.

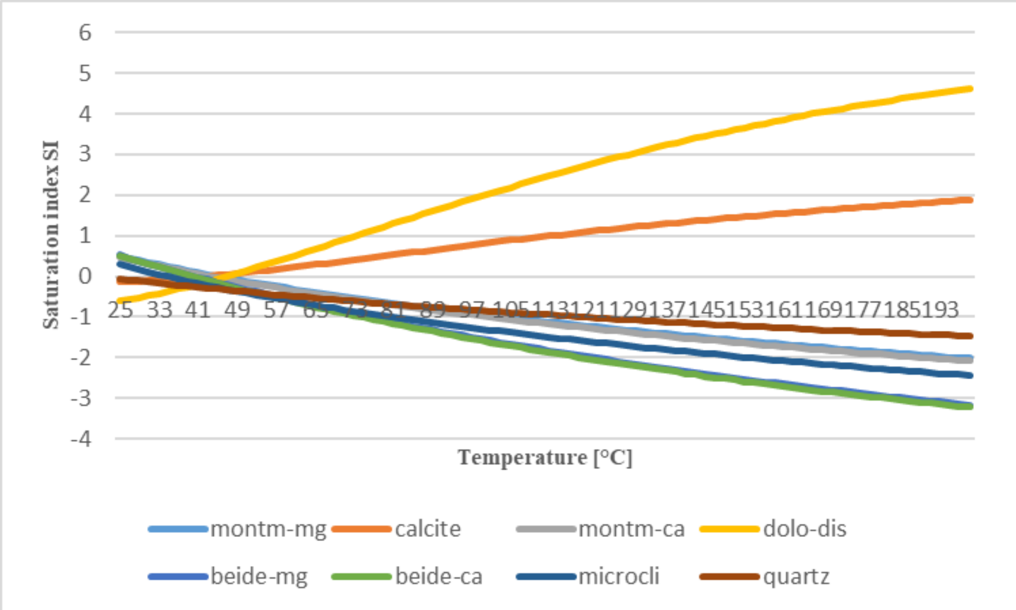

Figure 20. The saturation index of thermal water from Szymoszkowa GT-1 for the selected minerals.

Standard statistical functions of thermal water from Szymoszkowa GT-1 after equilibrating the studied water with calcite are plotted in *Figure 21*.

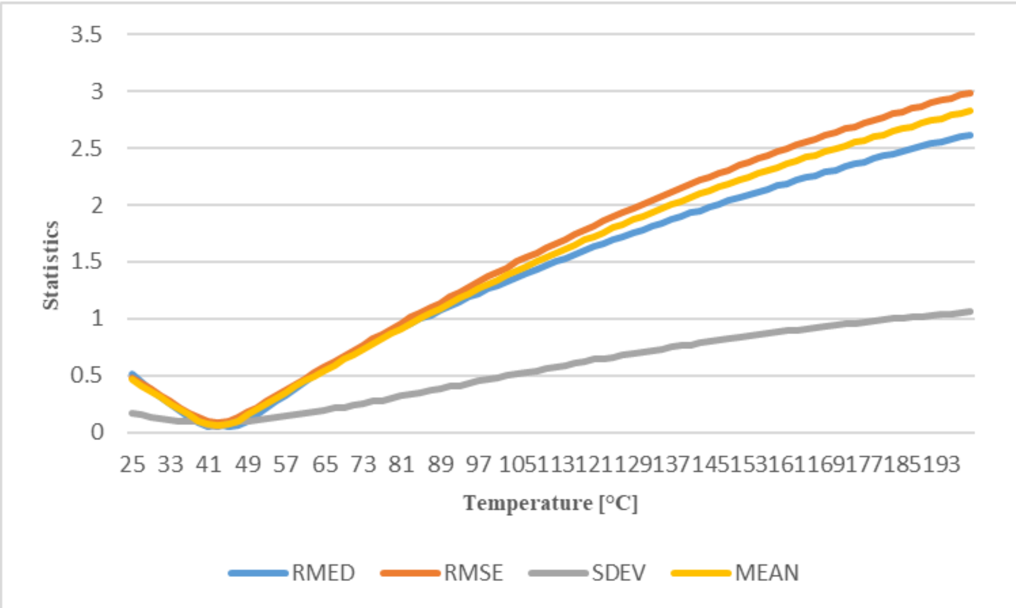

Figure 21. Standard statistical functions of thermal water from Szymoszkowa GT-1; median (RMED), mean (MEAN), standard deviation (SDEV) and mean root square error (RMSE).

- **Oberlaa Thermal 1**

Computed saturation index, log(Q/K), of thermal water from Oberlaa Thermal 1, as a function of temperature, showing clustering near zero close to the temperature 76.3°C is presented in *Figure 22.*

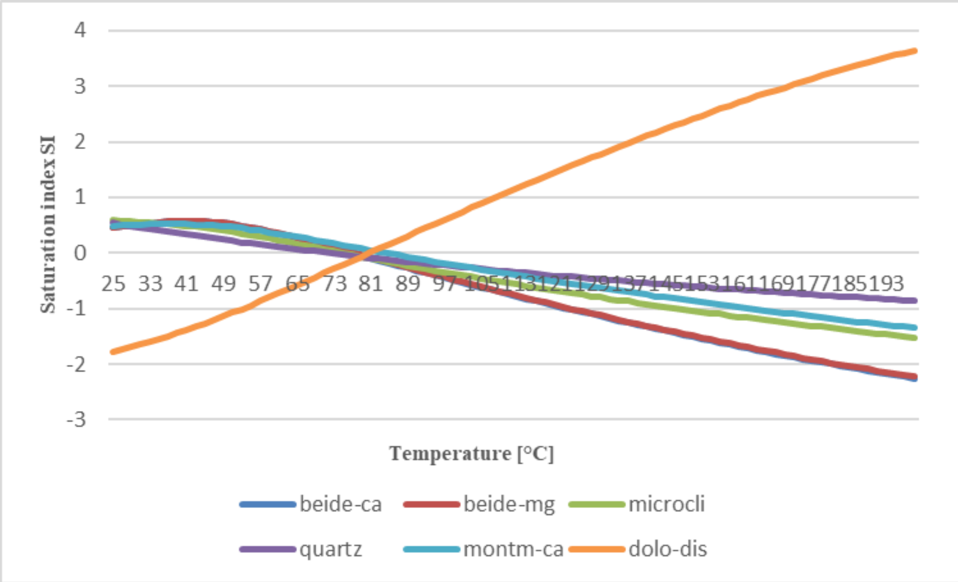

Figure 22. The saturation index of thermal water from Oberlaa Thermal 1 for the selected minerals.

Standard statistical functions of thermal water from Oberlaa Thermal 1 are plotted in *Figure 23.*

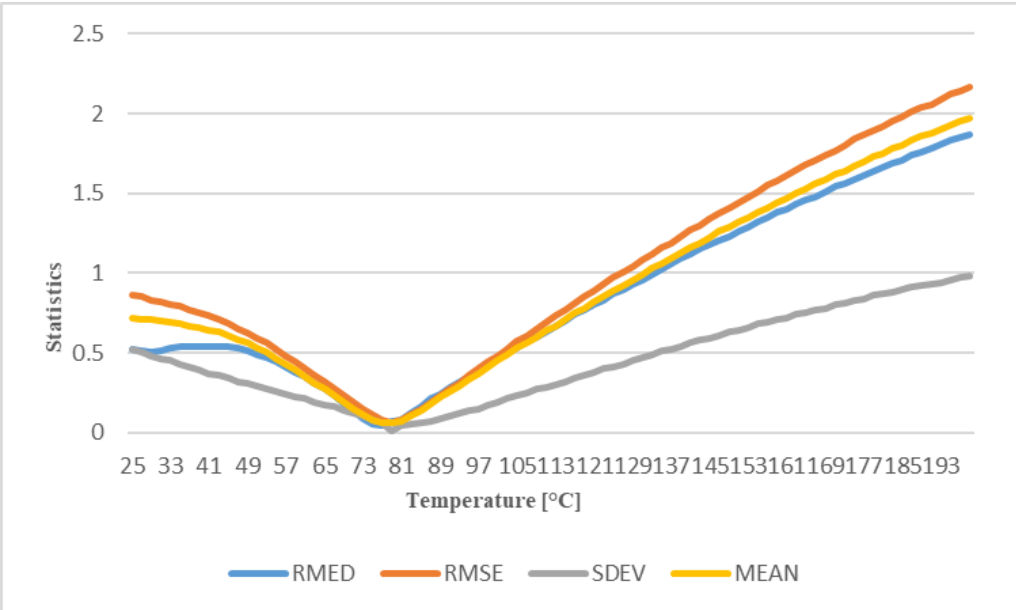

Figure 23. Standard statistical functions of thermal water from Oberlaa Thermal 1; median (RMED), mean (MEAN), standard deviation (SDEV) and mean root square error (RMSE).

- **Marienquelle, Baden**

Computed saturation index, log(Q/K), of thermal water from Marienquelle, as a function of temperature, showing clustering near zero close to the temperature 64.0°C is presented in *Figure 24.*

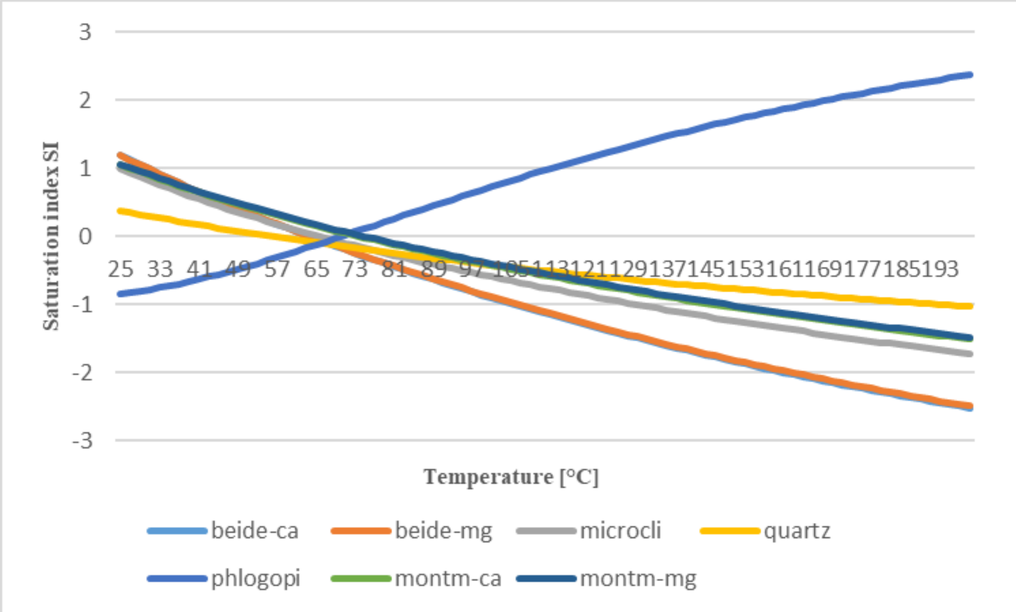

Figure 24. The saturation index of thermal water from Marienquelle for the selected minerals.

Standard statistical functions of thermal water from Marienquelle are plotted in *Figure 25*.

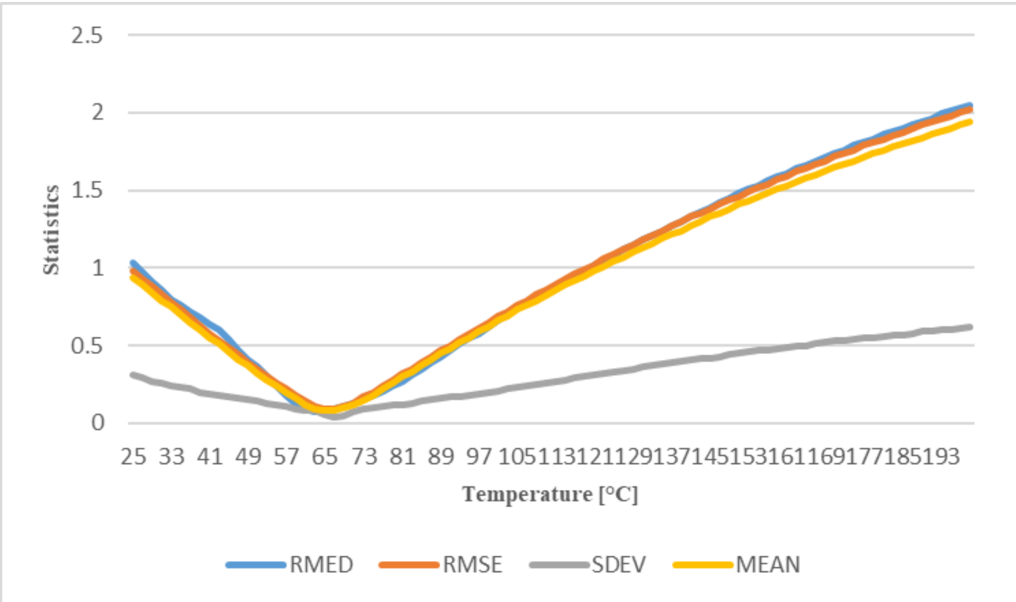

Figure 25. Standard statistical functions of thermal water from Marienquelle; median (RMED), mean (MEAN), standard deviation (SDEV) and mean root square error (RMSE).

- **Bad Radkersburg II**

Since the geothermal water from Bad Radkersburg II is characterised by high mineralization and it is quite concentrated, it was equilibrated with dolomite and the solution was diluted 200g/1kg water. In addition, the gas was added in the amount of 0.05 (weight fraction in total discharge).

The saturation index of thermal water from Bad Radkersburg II before changes in the solution is shown in *Figure 26.*

The saturation index of thermal water from Bad Radkersburg II, after equilibrating the studied water with dolomite, dilution and adding gas, as a function of temperature, showing clustering near zero close to the temperature 118.7°C is shown in *Figure 27*.

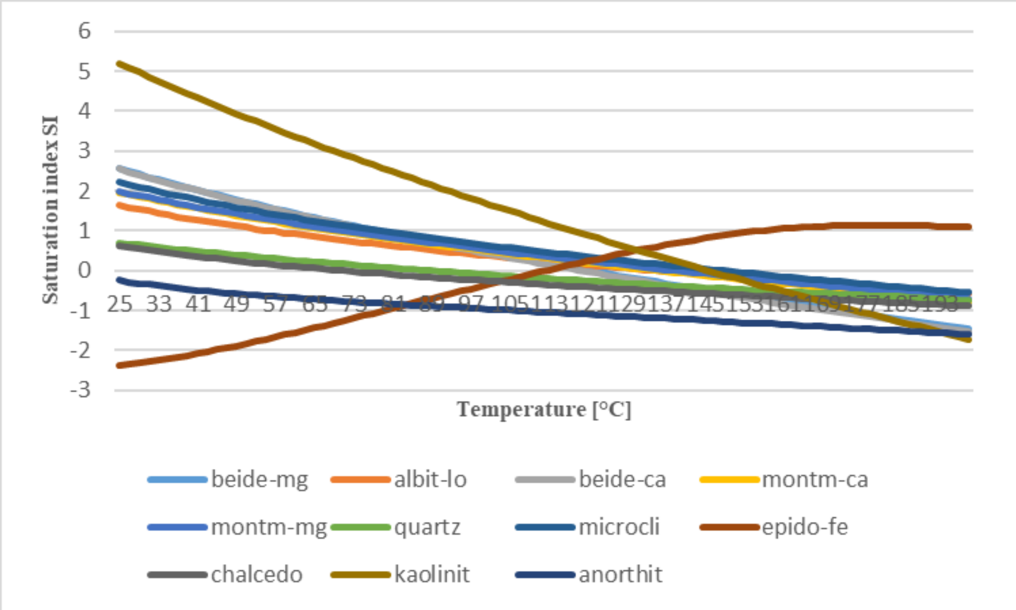

Figure 26. The saturation index of thermal water from Bad Radkersburg II for the selected minerals before changes in the solution.

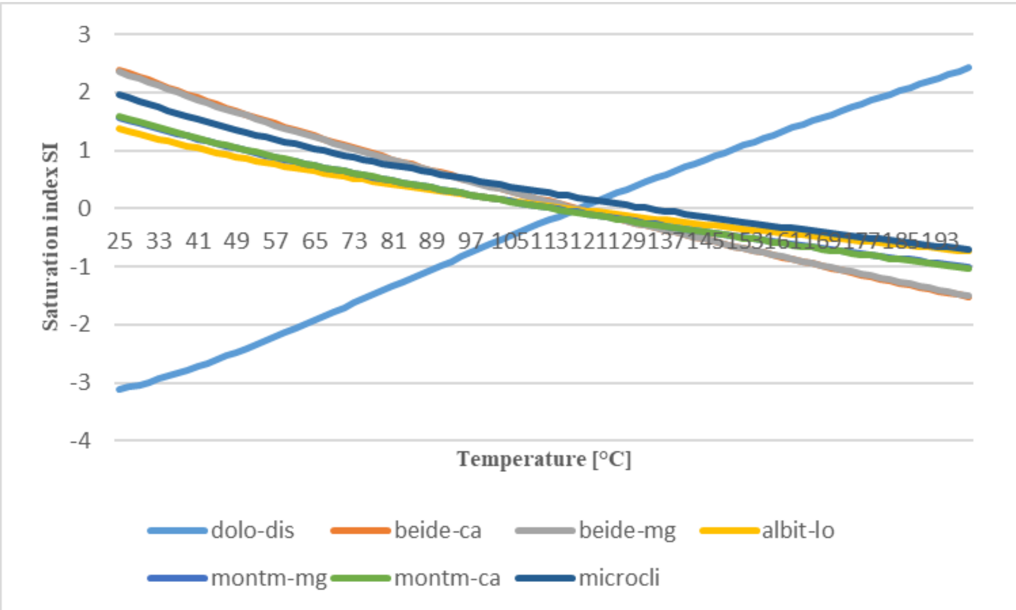

Figure 27. The saturation index of thermal water from Bad Radkersburg II for the selected minerals.

Standard statistical functions of thermal water from Bad Radkersburg II after changes in the solution are plotted in *Figure 28.*

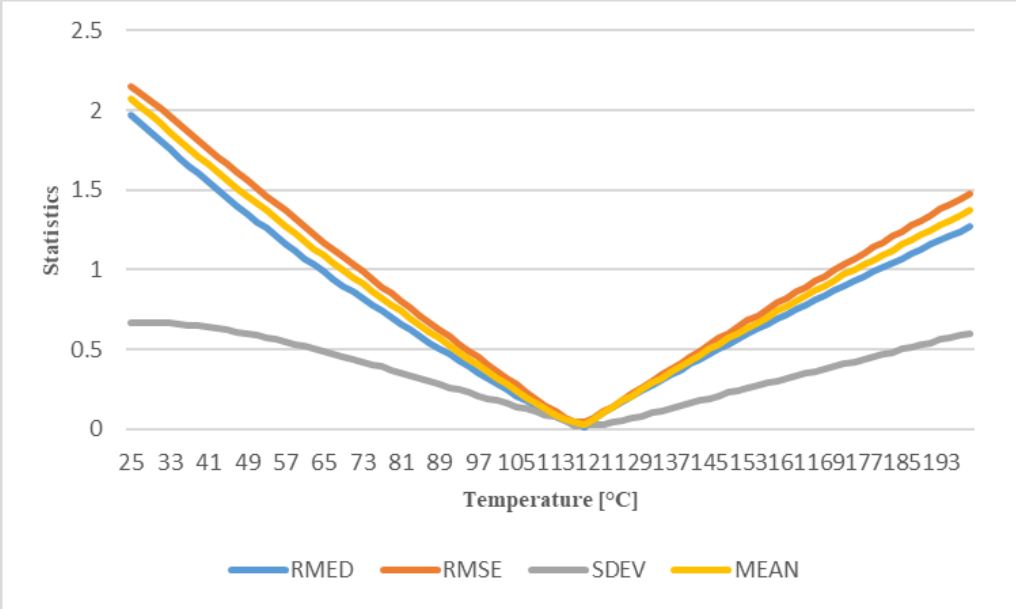

Figure 28. Standard statistical functions of thermal water from Bad Radkersburg II; median (RMED), mean (MEAN), standard deviation (SDEV) and mean root square error (RMSE).

7. Conclusions and discussions

Obtained estimated reservoir temperatures of the selected geothermal systems using classic chemical geothermometers and the GeoT App compared to the outlet temperatures are shown in *Table 3.*

Table 3. Estimated reservoir temperatures of the selected geothermal systems compared to the outlet temperatures.

Name of the intake	Outlet temperature [°C]	Estimated temperature using GeoT App [°C]	Q [°C]	Ch_1 [°C]	Ch_2 [°C]
Białka Tatrzańska GT-1	77.00	106.7 ± 6	115.44	86.61	86.89
Chochołów PIG-1	82.00	89.5 ± 7	103.00	*73.16*	*74.35*
Szymoszkowa GT-1	27.00	45.2 ± 3	33.08	*0.26*	*5.23*
Bad Radkersburg II	76.30	118.7 ± 2	97.95	*67.74*	*69.28*
Oberlaa Thermal 1	47.60	76.3 ± 6	82.48	51.30	53.83
Marienquelle, Baden	34.20	64.0 ± 9	67.84	35.94	39.32

The highest estimated temperature using the GeoT App was found in the Bad Radkersburg II (118.7°C ± 2) and the lowest in the Szymoszkowa GT-1 (45.2°C ± 3), temperatures from the other systems were equal, as following: Białka Tarzańska GT-1: 106.7°C ± 6, Chochołów PIG-1: 89.5°C ± 7, Oberlaa Thermal 1: 76.3°C ± 6, Marienquelle, Baden: 64.0°C ± 9.

Despite the fact that, the obtained, by using silica geothermometers, temperatures are not lower than the outlet temperatures measured in the studied intake, calculated classic chemical geothermometers showed not reliable results and differ from those calculated by using much more accurate method – multicomponent geothermometry (the GeoT application). In the case of chalcedony geothermometers most of the obtained temperature values are lower than the outlet temperature (marked in italics). It has not been working properly and in some cases involves complicated and broad interpretation. This is due to the fact that waters in selected geothermal spring and wells rarely flow out directly from reservoirs without re-equilibration, steam loss, dilution, or mixing with waters of shallower systems. The example of system where mixing with waters of shallower systems was found is Szymoszkowa GT-1. Based on the Giggenbach diagram, it can be observed that water from this system is classified as immature waters, which results in lack of the thermodynamic equilibrium and it suggest that the water from Szymoszkowa GT-1 has shallow water inflow. Based on the Piper diagram and the diagram of the concentration of the chemical components, it should be noticed that Chochołów PIG-1 and Szymoszkowa GT-1 have similar chemical composition, but different degrees of mineralisation, which is caused by shallow water inflow (mixed water systems, dilution) in the case of Szymoszkowa GT-1. Also, in the Szymoszkowa GT-1 could be observed low chlorine content, which means that the minerals of the gypsum-salt series do not dissolve there, thus dolomites and limestones are the key rock medium there.

Therefore, it should be taken into account that the temperatures obtained by estimation using classic chemical geothermometers for immature waters do not provide actual temperatures values and they cannot be read from the Giggenbach diagram too. The point of Bad Radkersburg II, which is located on the border between partial equilibrium and immature waters suggest that estimated reservoir temperature obtained from classical chemical geothermometers should be interpreted with reserve, since it is not located in the full equilibrium area or on the border between it and partial equilibrium, where obtained results are more reliable. Based on the Giggenbach diagram, by drawing an equilibrium line from Sqr(Mg) corner, it is possible to estimate the reservoir temperature for Bad Radkersburg II, which is equal to 190°C. This value is also not reliable, which is caused, not only by type of the water from this system (location on the diagram), but also longer residence time in the rock medium and longer reaction time between water and rock medium and several other factors.

While estimating the reservoir temperatures using the GeoT App, for two of six geothermal systems, changes into the primary solution was done. Since the Szymoszkowa GT-1 is characterised by low mineralization, to reduce the impact of re-equilibration, concentrations of the ions were stabilized by equilibrating the studied water with calcite. In the example of Bad Radkersburg, characterised by high mineralization, it was equilibrated with dolomite and the solution was diluted 200g/1kg water. In addition, as the solution showed supersaturation with respect to the mineral composition, for obtaining the equilibrium (to compensate for outgassing during water flow in the system), the contribution of the gas phase was analysed and adopted in the model in the amount of 0.05 (weight fraction in total discharge). Also, it should be noticed that in the case of Bad Radkersburg II concentration of sodium increases at a much faster rate than the concentration of chlorine, so the sources of sodium in these waters are aluminosilicate minerals; inflow from the deep subsoil is also possible. Waters from Bad Radkerburg II were found to be meteoric origin (Elster et al., 2016), so their systems are formed as a result of the infiltration of precipitation, heating at considerable depths, and also the ascent along faults and fissures, which could suggest the inflow from crystallin basement. This origin and geology define the thermal water with high temperature and high content of HCO_3- and Na^+ , which were obtained for Bad Radkersburg II from the calculations and diagrams. In the case of Chochołów PIG-1 obtained estimated temperature was not significantly different than the outflow temperature, therefore it can be assumed that the rock medium deposit is isolated (closed structure). Consequently, additional care should be taken during exploration in order not to disturb the hydrodynamic conditions and overexploit. In addition, it is recommended to drill another injection borehole which will ensure the security of resources (a system of two wells: the first one used to bring water to the surface and second one through which the cooled water will be reinjected back into the aquifer should be considered.

In the systems, where significant difference between outflow and estimated temperature is observed, it may be inferred that geological structure is characterised by nappe (thrust sheet), therefore it is difficult to determine whether water flows long and far from the supply area to the drainage area and whether or not it is a relict deposit.

Furthermore, it may be stated that the water from Białka Tatrzańska GT-1 has a similar chemical composition to the waters for Marienquelle and Oberlaa Thermal 1. Both in the case of Oberlaa Thermal 1 and Marienquelle, on the basis of Sulphur-34 isotope studies, it can be concluded that the sulphate ions in the waters originate from Mesozoic gypsum-salt sediments and hydrogen sulphide may originate from the reduction of organic matter (overlaying of organic and bitumen-containing soils and sediments). Also, concentrations of H_2S in Marienquelle may originate from the reduction of bituminous substances in the rock inserts of the gypsum-salt series. In addition, the concentration of sulphates greater than 20 % mval infer the presence of increased mineral forms of nitrogen (NO_3-), which is in accordance with the literature (Elser et al., 2016), (Macioszczyk et al., 2002). Moreover, considering that the area where Białka Tatrzańska GT-1 is located is on the northern slope of the anticline, so signs of bituminous are in the area of tectonic faults (Mastella et al., 1975), it may be concluded that the estimated temperature, with significant difference compare to the outflow temperature, is related to the migration of heat from the rock system. This tectonically involved area, which cause heat inflow from the rock system, may be the reason of high estimated temperatures in Białka Tatrzańska GT-1 (it should be noticed that there is no inflow of additional water because the composition does not indicate mixing with other water).

8. Summary

The estimation of the reservoir temperatures for the selected geothermal systems was a first attempt made to obtain this temperature in those systems. Obtained temperatures by estimation using classic chemical geothermometers were not reliable, therefore the final reservoir temperatures for the selected geothermal systems were calculated by using the GeoT application. The highest estimated temperature was found in the Bad Radkersburg II (118.7°C ± 2) and the lowest in the Szymoszkowa GT-1 (45.2°C ± 3), temperatures from the other systems were equal, as following: Białka Tarzańska GT-1: 106.7°C ± 6, Chochołów PIG-1: 89.5°C ± 7, Oberlaa Thermal 1: 76.3°C ± 6, Marienquelle, Baden: 64.0°C ± 9.

Since the interest in using geothermal energy is growing year by year, estimation of geothermal reservoir temperatures has a future-proof application. Therefore, obtained estimated temperature values can be used for further analysis and research in the sustainable exploitation of those deposit, what this entails, for the use of geothermal heat pumps, greenhouse heating, space and district heating, aquaculture, balneotherapy, recreation, aquaculture, industrial and agricultural applications. Based on the estimated temperatures, it can be concluded that for geothermal systems with low outflow temperature, energy efficiency can be increased by drilling a deeper borehole.

The chemical compositions diagrams confirm the information contained in the literature. The type of the water from Bad Radkersburg II is Na-HCO_3, from Szymoszkowa GT-1 is Ca-Mg-HCO_3, and the other systems are Ca-Cl- SO_4 with an increasing proportion of magnesium. The analysis concluded that the lithology, which determines the mineral composition of the aquifer, is a key factor in the estimation of reservoir temperature in the selected geothermal systems.

Further analyses can be extended to test scenarios with different CO_2 contents by using other than GeoT software.

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10. List of tables and figures