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The radiogenic isotope signature of strontium as an environmental tracer of the dynamics of geothermal reservoirs (Podhale Basin, southern Poland)

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The intensive development of geothermal energy in Poland provides new opportunities to study the occurrence and circulation of thermal waters. We have analysed the isotopic variability of thermal waters in the Podhale Basin, using $^{87}Sr/^{86}Sr$ ratios to characterize their hydrodynamic behaviour. Strontium isotopic signatures in the geothermal water samples analysed range from 0.70835 to 0.70877. Extreme $^{87}Sr/^{86}Sr$ values were observed along the western and eastern margins of the Podhale Basin, while other chemical parameters showed extreme values in the southern and northern parts of the area. Contrary to expectations based on recharge and circulation patterns and the negative Spearman correlation, a clear northwards decrease in $^{87}Sr/^{86}Sr$ values was not confirmed. Waters from the Chochołów and Bukowina Tatrzańska wells were found to differ from the other samples, consistent with previous observations that classify these wells as containing mixed waters, recharged during the Holocene and pre-Holocene. The $^{87}Sr/^{86}Sr$ values in Phanerozoic carbonate rocks and the Tatra crystalline core indicate that both lithological units may contribute strontium to the geothermal waters. These results highlight the need for further quantitative assessment of strontium mixing, for example using a two-component mixing model, along with a broader geological interpretation.

Key words: isotopes, strontium, geothermal waters, Podhale Basin, Tatra Mountains.

INTRODUCTION

The first documentation of geothermal waters in Podhale dates back to the mid-19th century. The spring in Jaszczurówka, discovered by Zejszner (1844), was characterized by a water temperature of 20.4°C. However, it was not until the second half of the 20th century and the early 21st century that geothermal potential in the Podhale region and in other parts of the country attracted broader interest (Ney and Sokołowski, 1987; Górecki, 1990, 2011; Biedrzycki et al., 1995; Sokołowski, 1995; Małecki, 1995; Kępińska, 1997; Chowaniec et al., 2001; Bujakowski and Barbacki, 2004; Dowgiałło, 2007; Górecki and Sowiżdżał, 2012). Due to favourable parameters – including high water temperatures, low mineralization, high well productivity, and resource renewability – the Podhale region offers the best conditions in Poland for geothermal water use. Temperatures range from ~20 to nearly 90°C, with total dissolved solids 3.5 g/dmł. The waters are dominated by HCO_3^-, HCO_4^{2-}, Cl^-, Na^+, Ca^{2+} and Mg^{2+} ions (Chowaniec, 2009, 2012). According to the classification proposed by Sokołowski (1995), Podhale is part of the Carpathian Geothermal Province on the Polish side and simultaneously belongs to the Polish-Slovak transboundary geothermal system, which also includes the Slovak basins of Levoča (southern and western parts), Liptov, and Skorušina (Franko et al., 1995). On both the Polish and Slovak sides, this area has experienced strong growth in the use of geothermal waters for district heating, balneotherapy and recreation (Kasagranda and Gurňák, 2017; Kępińska and Hajto, 2023). In this context, determining both the origin and circulation of the geothermal waters is crucial for maintaining and potentially expanding the geothermal potential of the region.

Our study has investigated the isotopic variability of thermal waters in the Podhale Basin based on the determination of the $^{87}Sr/^{86}Sr$ isotopic ratio, in order to provide a more comprehensive characterization of the nature and hydrodynamics of the thermal waters.

The rubidium-strontium method was used in this work, which uses the change in the content of the radiogenic isotope ^{87}Sr in the samples and being based on the $^{87}Sr/^{86}Sr$ isotope ratio. Strontium has four naturally occurring types of stable isotope: ^{84}Sr, ^{86}Sr, ^{87}Sr, ^{88}Sr. Their abundance is 0.56, 9.86, 7.02 and 82.56%, respectively. However, the radiogenic isotope ^{87}Sr also occurs in the environment as a result of the radioactive transformation of ^{87}Rb. Therefore, the content of the isotope ^{87}Sr will have a variable value, which depends on the content of ^{87}Rb in rocks and minerals and over time. Variation in the $^{87}Sr/^{86}Sr$ isotope ratio in various rocks and minerals causes groundwater to have an isotopic composition characteristic of a given geographical region and geological conditions. Therefore, radiogenic ^{87}Sr has become important in geological research. This method provides valuable information concerning

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petrogenetic indicators, and also plays an important role in monitoring geological processes such as erosion, crystallization of minerals or chemical exchange between groundwater and rocks. The use of this method in hydrogeological research allows us to understand the origin of groundwater, its circulation, and its interaction with various types of rocks and minerals. The current $^{87}Sr/^{86}Sr$ ratio depends on its value at the moment of inception of the system, and increases over time. The growth rate depends on the content of radioactive rubidium, i.e. the higher its content, the faster the $^{87}Sr/^{86}Sr$ growth rate (Burchat and Karl, 2015). As demonstrated by Krogulec et al. (2015), the rubidium–strontium method has been successfully applied to identify groundwater circulation conditions in multi-aquifer systems. These authors estimated the percentage contribution of upland components to the waters of the Piaśnica River based on the $^{87}Sr/^{86}Sr$ ratio and strontium concentrations in water samples.

GEOLOGICAL SETTING

The Podhale Basin is located within the Inner Carpathians (Żelaźniewicz et al., 2011; Stupicka, 2013). It is bordered to the north by the Pieniny Klippen Belt (PKB) and to the south by the Tatra Mountains (Fig. 1). The contact between the Podhale Basin and the PKB is tectonic in nature, whereas its contact with the Tatras is a stratigraphic transition. The basin is filled to a depth of ~3,000 m with a sandstone-shale sequence of the Podhale Flysch, which acts as an insulating layer overlying the carbonate formations that form the geothermal aquifer (Chowaniec and Kępińska, 2003). The geothermal reservoir itself is composed mainly of carbonate deposits, which are in sedimentary contact with the formations bordering the crystalline core of the Inner Carpathians (Roniewicz, 1969; Małecka and Roniewicz, 1997). Directly beneath the Podhale Flysch lies a thin layer of Middle Eocene carbonate deposits, known as the Nummulitic Eocene. Below these occurs a thick Mesozoic succession (Triassic to Cretaceous), represented mainly by limestones and dolomites, as well as marls, and subordinately by conglomerates, sandstones and claystones. South of the Podhale Basin lies the highest part of the Inner Carpathians, the Tatra Mountains, which consist of two structural zones: the High Tatra Zone and the Reglowa (Sub-Tatric) Zone. The High Tatra Zone is composed of Paleozoic igneous and metamorphic rocks forming the crystalline core. The Sub-Tatric zone is of Mesozoic age (Triassic–Cretaceous) and is represented by limestones, dolomites, marls, marly shales, sandstones and conglomerates. The folded deposits of the Sub-Tatric succession are arranged into a system of nappes and tectonic slices, partially covering the crystalline core (Sokołowski, 1959).

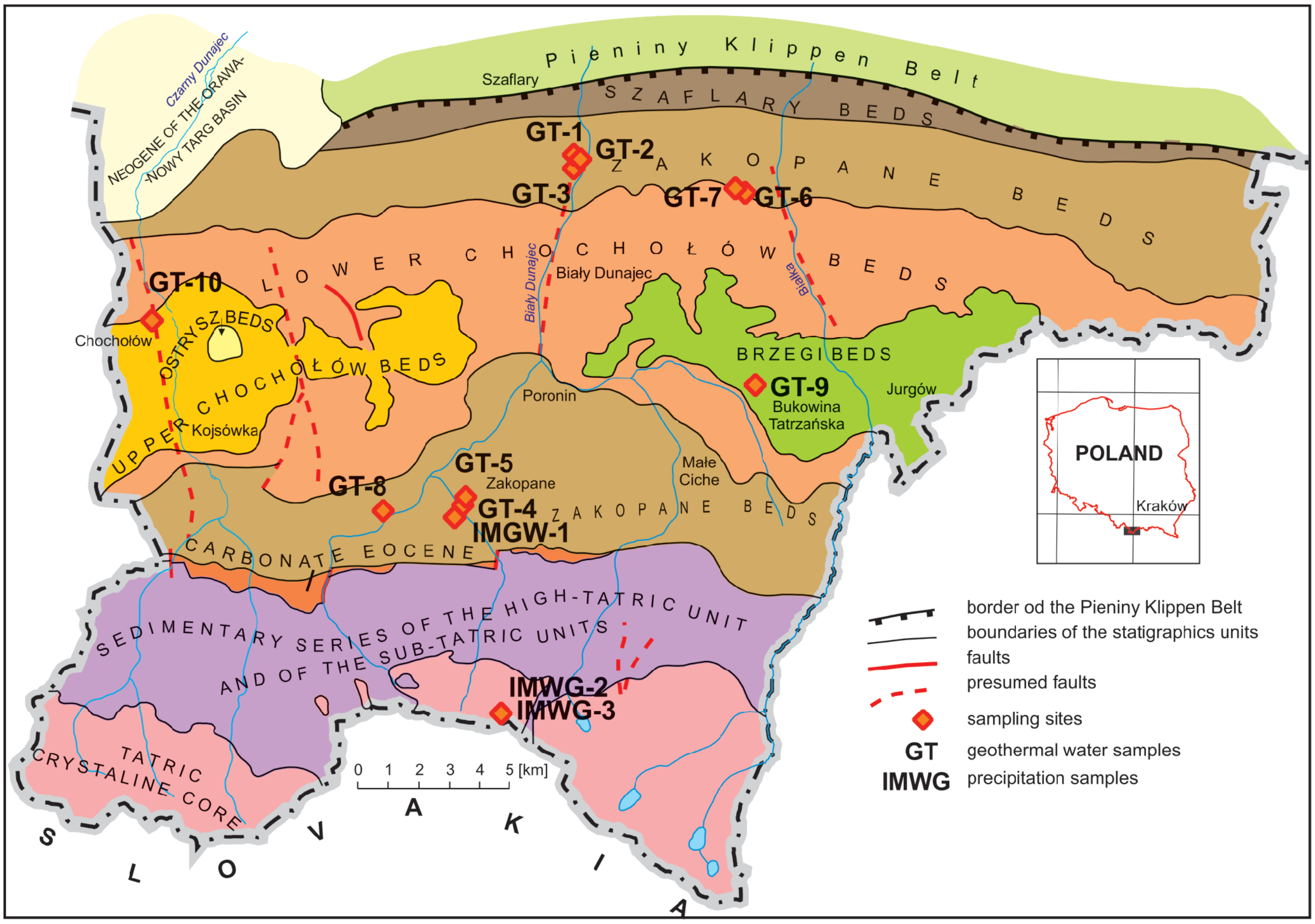

Fig. 1. Geological map of Podhale without Quaternary formations (according to Chowaniec, 2003, 2009) with sampling sites

METHODOLOGY

The study focused on samples of meteoric and thermal waters. Precipitation samples were collected on June 4, 2024, whereas thermal water samples were collected between May and July 2024. A total of 13 samples were collected for the study of strontium isotopic composition, including 10 thermal water samples and 3 precipitation samples (2 rainwater samples – IMGW-1, IMGW-2 and 1 snow sample – IMGW-3). Thermal water samples were obtained from boreholes located in Zakopane (GT-4, GT-5, GT-8), Bukowina Tatrzańska (GT-9), Chochołów (GT-10), Białka Tatrzańska (GT-6, GT-7) and Bańska Niżna (GT-1, GT-2, GT-3). Precipitation samples were collected at the Institute of Meteorology and Water Management (IMWM) stations in Zakopane and Kasprowy Wierch.

In this study, the values of TDS, Sr and Ca were correlated with the $^{87}Sr/^{86}Sr$ ratios obtained in order to identify possible relationships between these parameters. The data on TDS, Sr and Ca were obtained from values published by other authors. The isotopic data from 2024 were compared with long-term average values of TDS, Ca and Sr, often derived from decades of observations. Operacz et al. (2024) demonstrated the stability of the physicochemical parameters of the thermal waters using the Chochołów PIG 1 well as an example. Low coefficients of variation for Ca^{2+} (6%) and EC (1%) indicate that correlating data from different periods is methodologically justified.

Rainwater was collected using a foil sheet to channel it into a container, while the snow sample was gathered in a metal container (rain gauge) where it subsequently melted. Samples of 500 ml were collected in PET plastic containers. The snow sample was collected after the end of the winter season. The snow cover remaining on Kasprowy Wierch was exposed to rainfall. Due to the timing of collection and prevailing weather conditions, the snow sample can be considered as representing an averaged strontium isotopic composition of meteoric waters for the winter-spring season. The results of isotopic analyses are summarized in Table 1, and the locations of the sampling points are shown in Figure 1.

Measurements of Sr isotope ratios in the water were carried out at the Laboratory of Radiogenic Isotopes of the Czech Geological Survey in Prague. Measurements were carried out using a *Thermo-Fisher Scientific Triton Plus TIMS* thermal ionization mass spectrometer. A standard value of 0.1194 was used to correct for mass fractionation during the analysis of $^{86}Sr/^{88}Sr$ isotope ratios. The detailed analytical methodology, sample preparation and separation of strontium was discussed by Erban Kochergina et al. (2022).

The water sample was filtered and then acidified with nitric acid and then evaporated until completely dry. The resulting precipitate was dissolved in a mixture of concentrated H_2O_2–HNO_3, evaporated until completely dry and redissolved in HCl. Separation of strontium from other elements was carried out with ion exchange columns using *Bio-Rad AG50W-X8* and *Eichrom Sr-spec* cation exchange resins. Due to the complicated process of strontium separation, calibration of the columns and the reagents used, including acids, is extremely important for the quality of the separation. Laboratory glassware made of perfluoroalkoxyteflon (PFA) were used. This is a material commonly used in isotope laboratories due to its resistance to acid, temperature etc. (Erban Kochergina et al., 2022).

The notion of amplitude was used in a similar way as for climatic or meteorological data, i.e. for the description of phenomena without a defined equilibrium state. It was applied to the difference between the maximum and minimum measured values.

Statistical analysis was based on the arithmetic mean and standard deviation, with the coefficient of variation [CV = (std/mean) × 100%] applied as a relative measure of data dispersion. A CV of <15% was considered to indicate low variability (high dataset stability). The Spearman's correlation test was used to assess the correlations.

Table 1

Summary of laboratory analysis results

Sample no.	Date of collection	$^{87}Sr/^{86}Sr$	TDS* [mg/dm^3]	Sr* [mg/dm^3]	Ca* [mg/dm^3]	Ca/Sr
GT-1	08.05.2024	0.70840	3120.0	6.330	202.00	31.91
GT-2	08.05.2024	0.70841	2510.0	6.420	203.00	31.62
GT-3	08.05.2024	0.70841	2690.0	6.410	204.00	31.83
GT-4	05.06.2024	0.70859	367.8	1.052	44.58	42.38
GT-5	05.06.2024	0.70860	335.0	0.482	45.23	93.84
GT-6	05.06.2024	0.70844	3364.0	9.000	310.00	34.44
GT-7	05.06.2024	0.70844	1835.5	6.060	180.10	29.72
GT-8	02.07.2024	0.70856	330.0	0.300	38.13	127.10
GT-9	02.07.2024	0.70877	1651.0	5.200	197.11	37.91
GT-10	02.07.2024	0.70835	1092.9	4.680	181.10	38.70
IMGW-1	04.06.2024	0.70892	82.0**	0.04**	16.40**	420.51
IMGW-2	04.06.2024	0.70887	7.0**	0.001**	0.30**	300.00
IMGW-3	04.06.2024	0.70910	7.0**	0.001**	0.10**	100.00

* – averaged results of archival physicochemical analyses (according to Chowaniec, 2009; Sekuła et al., 2020; www.pgi.gov.pl, except for points IMGW-1, IMGW-2 IMGW-3); ** – according to Jarosz et al. (2025); TDS – total dissolved solids

RESULTS

The analyses provided the values of the $^{87}Sr/^{86}Sr$ isotopic ratio for 13 water samples. The highest values $^{87}Sr/^{86}Sr$ were recorded in a snow sample (IMGW-3; 0.70910), which fell on the summit of Kasprowy Wierch. The lowest value was measured in a sample of thermal waters GT-10 (0.70835; Table 1). An amplitude of 0.00075 was calculated. However, taking into account only the results of the $^{87}Sr/^{86}Sr$ ratio determinations for thermal waters, the maximum value was recorded in sample GT-9 and amounted to 0.70877. The amplitude of the $^{87}Sr/^{86}$ ratio value for thermal waters was therefore 0.00042.

Basic statistical calculations were carried out for the values obtained of the $^{87}Sr/^{86}Sr$ ratio. The results are shown in Table 2 below and Figures 2 and 3.

The parameter values analysed were considered with reference to two closed intervals, namely:

$$[x_{ave} - 2s_x;\ x_{ave} + 2s_x] \qquad [1]$$

$$[x_{ave} - 3s_x;\ x_{ave} + 3s_x] \text{ – considered a gross error} \qquad [2]$$

Among all the samples analysed, only IMGW-3 slightly exceeds interval [1] (Fig. 2). In the case of the thermal water samples, only GT-9 falls outside interval [1] (Fig. 3). This provides grounds to consider these results as values distinct from the rest of the dataset. Based on the calculations performed, none of the $^{87}Sr/^{86}Sr$ ratios obtained can be classified as gross errors. Although statistically the GT-10 sample does not raise concerns, it represents an extreme value and can therefore also be regarded as distinctive within the dataset of thermal waters analysed.

The variability of the parameters discussed was characterized using the coefficient of variation (CV; Table 3). Only the strontium isotopic ratio $^{87}Sr/^{86}Sr$ is characterized by a very low coefficient of variation (CV = 0.018%), which may suggest stable conditions for the formation of the strontium isotope composition in the Podhale Basin. The highest variability is observed in the precipitation samples, with CV values exceeding 100% for all parameters except the $^{87}Sr/^{86}Sr$ ratio.

The remaining parameters exhibit high variability. CV values exceeding 100% indicate that the standard deviation is larger than the mean, reflecting extremely high variability of the parameter in the dataset. The CV should be interpreted with caution.

The statistical analysis indicates strong to very strong relationships among the parameters studied (Table 4). The $^{87}Sr/^{86}Sr$ ratio shows a negative correlation with the other parameters, whereas Ca, Sr, and TDS show positive correlations.

Figure 4 shows the distribution image of the $^{87}Sr/^{86}Sr$ ratio, depending on the TDS. Samples GT-4, GT-5 and GT-8 display

Table 2

Basic statistical parameters of the samples analysed

Parameter		x_{ave}	s_x	$x_{ave} - 2s_x$	$x_{ave} + 2s_x$	$x_{ave} - 3s_x$	$x_{ave} + 3s_x$
$^{87}Sr/^{86}Sr$	thermal waters	0.70850	0.00013	0.70824	0.70876	0.70811	0.70888
	thermal waters and meteoric waters	0.70860	0.00024	0.70813	0.70908	0.70789	0.70932

X_{ave} – average value of the parameter studied, s_x – standard deviation

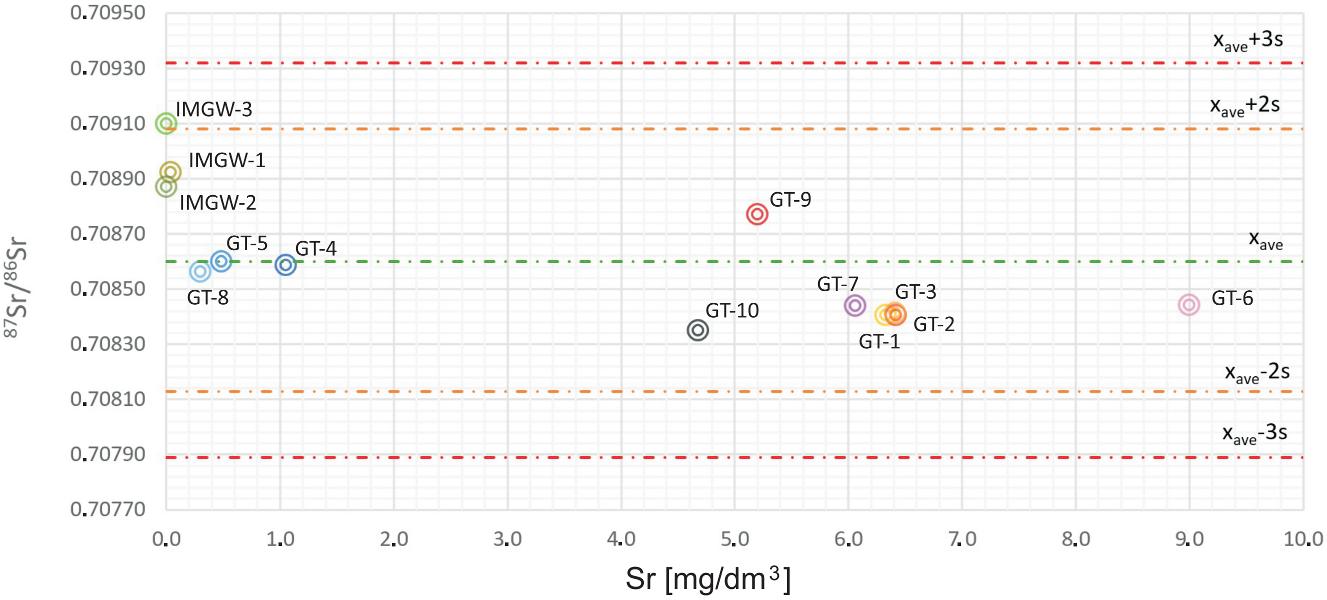

Fig. 2. Distribution of $^{87}Sr/^{86}Sr$ values on a background of characteristic statistical values

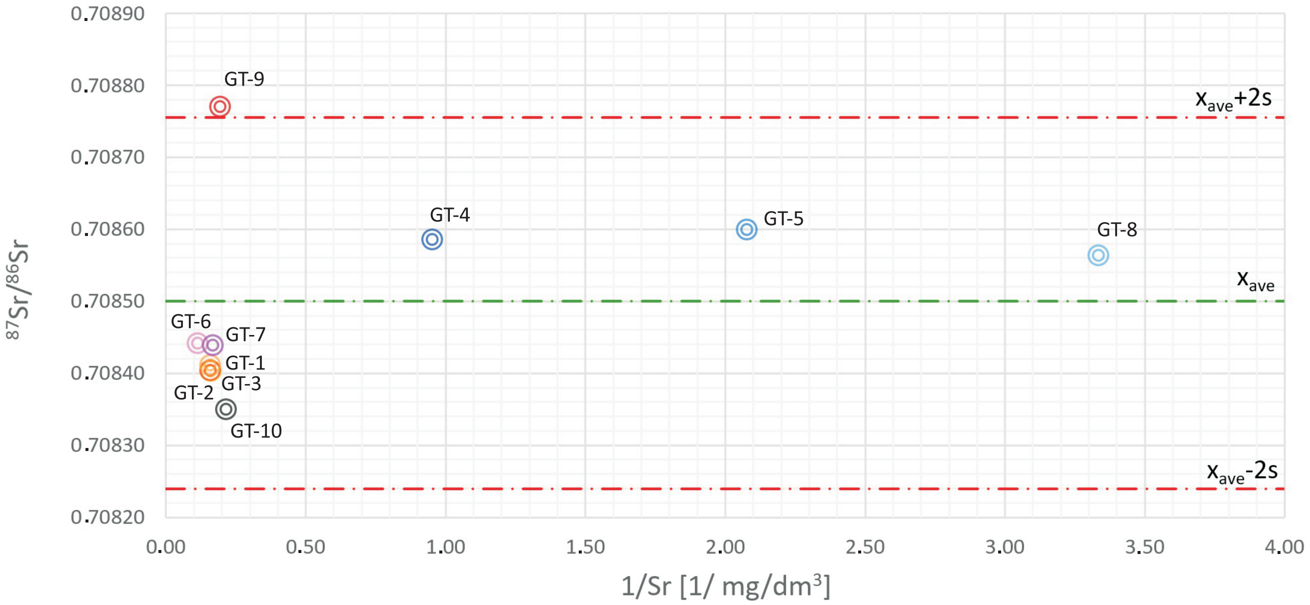

Fig. 3. Distribution of $^{87}Sr/^{86}Sr$ values on a background of characteristic statistical values for the thermal waters

Table 3

Coefficient of variation (CV)

	Parameter	$^{87}Sr/^{86}Sr$	TDS	Sr	Ca
CV [%]	thermal waters and meteoric waters	0.034	90.23	88.68	79.27
	thermal waters	0.018	64.1	61.37	52.72
	meteoric waters	0.017	110.49	131.07	136.38

Table 4

Spearman's rank correlation

Variable	Spearman's rank correlation (statistical data) BD removed pairwise Correlation coefficients are significant with p <0.05000			
	$^{87}Sr/^{86}Sr$	Sr [mg/dm^3]	Ca [mg/dm^3]	TDS [mg/dm^3]
$^{87}Sr/^{86}Sr$	1.000000	–0.737277	–0.725275	–0.748281
Sr [mg/dm^3]	–0.737277	1.000000	0.971115	0.977961
Ca [mg/dm^3]	–0.725275	0.971115	1.000000	0.960111
TDS [mg/dm^3]	–0.748281	0.977961	0.960111	1.000000

Statistically significant values are marked in red

similar TDS values (CV = 6%), whereas GT-7, GT-6, GT-1, GT-2 and GT-3 show comparable $^{87}Sr/^{86}Sr$ ratios (amplitude 0.00004) but a wide TDS range (1835.5–3350.0 mg/L; CV = 21.8%; Fig. 4).

The distribution of $^{87}Sr/^{86}Sr$ ratio values in the water samples analysed is also shown in relation to Ca content (Fig. 5). It can be observed that in Figure 5 the points representing geothermal waters are more clustered than in Figure 4. The coefficient of variation (CV) for Ca is 52.7%, compared to 64.1% for TDS. Samples GT-1, GT-2 and GT-3 show much higher clustering (CV = 0.4%) than in Figure 4 (CV = 9.23%), although still within the range of low variability. The opposite situation, i.e., higher variability of Ca content (CV = 136.38%) compared to TDS (CV = 110.49%), was observed in the rainwater samples (Table 3). The precipitation sample collected at the IMGW station in Zakopane (IMGW-1) shows several tens of times higher Ca content than the two precipitation samples from Kasprowy Wierch (IMGW-2 and IMGW-3).

The analysis of the strontium content in the thermal water samples showed that the lowest values were recorded in the area of Zakopane and Polana Szymoszkowa, i.e. in samples GT-4, GT-5 and GT-8, and these values were 1.052 mg/dm^3; 0.482 mg/dm^3 and 0.300 mg/dm^3 respectively (Fig. 6 and Table 1). The precipitation samples (IMGW-2, IMGW-3) from Kasprowy Wierch contain ~0.001 mg/dm^3 of strontium, while

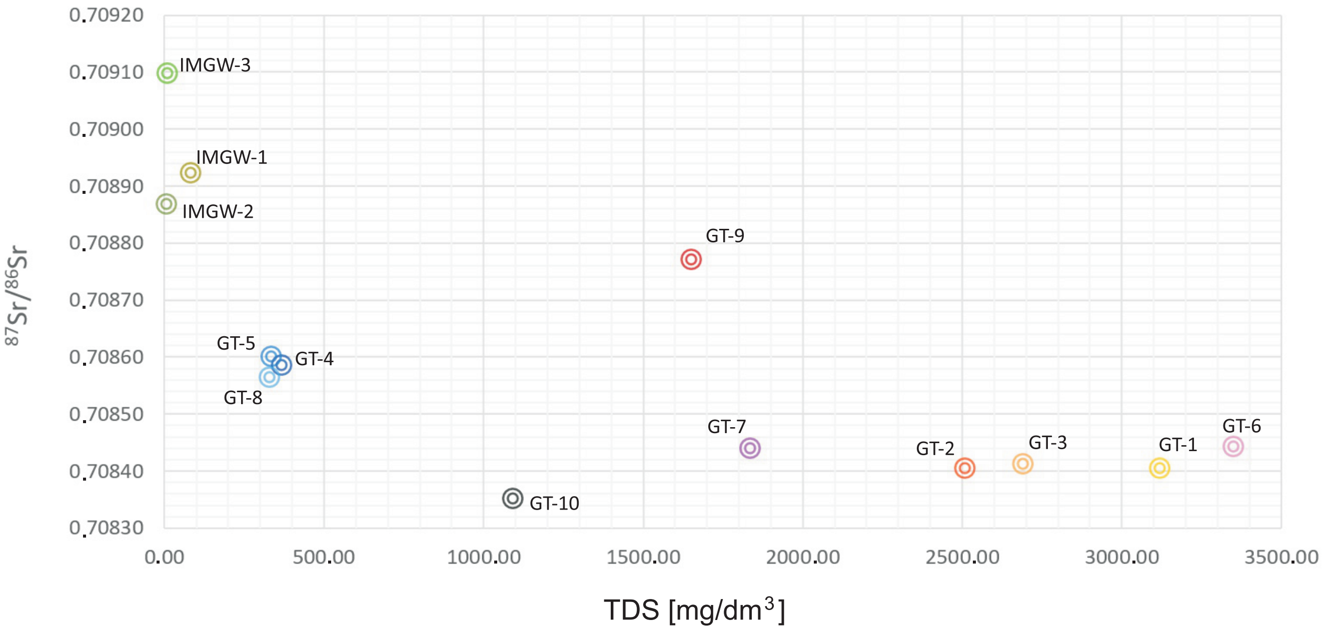

Fig. 4. $^{87}Sr/^{86}Sr$ **distribution relative to total dissolved solids**

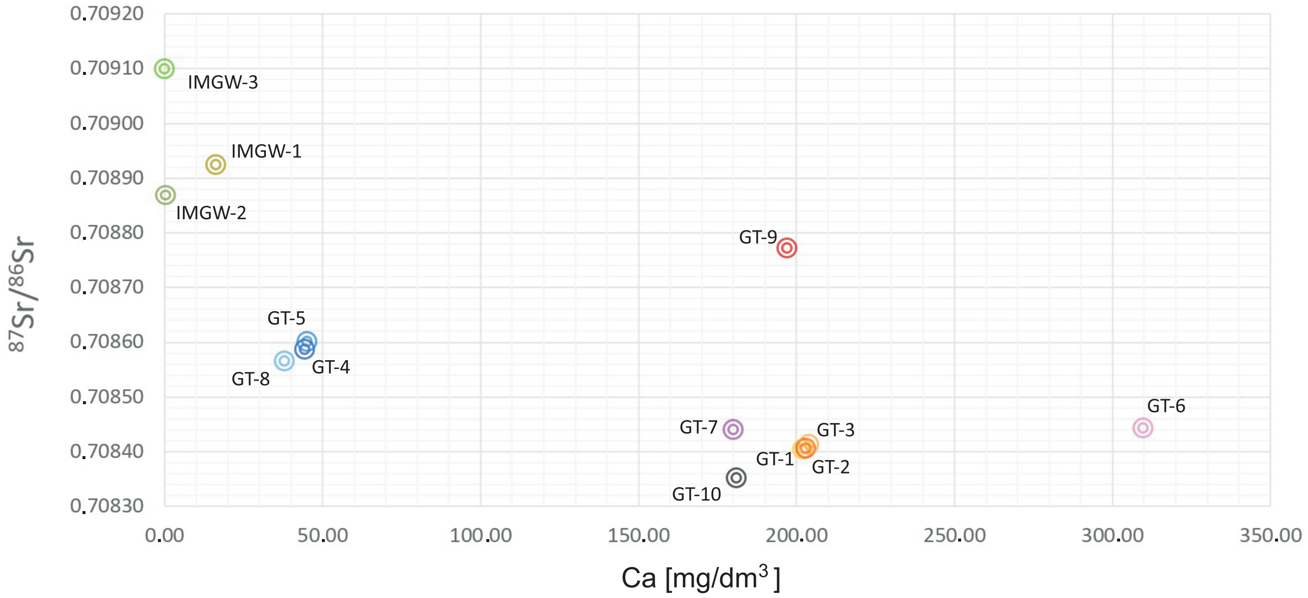

Fig. 5. $^{87}Sr/^{86}Sr$ **distribution relative to Ca content**

the sample from the IMWM station in Zakopane (IMGW-1) contains ~0.039 mg/dm^3. The pattern shown in Figure 6 is generally similar to the distribution seen in the $^{87}Sr/^{86}Sr$ graph relative to the Ca content (Fig. 5). However, there are differences in the location of points representing samples from boreholes GT-9 and GT-10 in relation to the sampling points GT-1, GT-2, GT-3 and GT-7. As can be seen in Figure 6, there was a clear split resulting from differences in Sr content in the samples analysed.

As shown in Figures 4–6, samples GT-9 and GT-10, with extreme values of the $^{87}Sr/^{86}Sr$ ratio in the thermal waters studied is approximately in the area of average contents of TDS, Ca and Sr.

DISCUSSION

Early research identified the Tatra Mountains as the main recharge area of the geothermal reservoir. Subsequent studies have refined this understanding, confirming that recharge occurs on outcrops of Mesozoic and Eocene carbonate rocks, generally in the elevation range of 1000–1600 m a.s.l. (Chowaniec et al., 2009). General mineralization analyses support this, indicating that in the recharge zone (Tatras), dissolved components are largely derived from infiltrating precipitation. This process and the groundwater flow within the Tatra massif

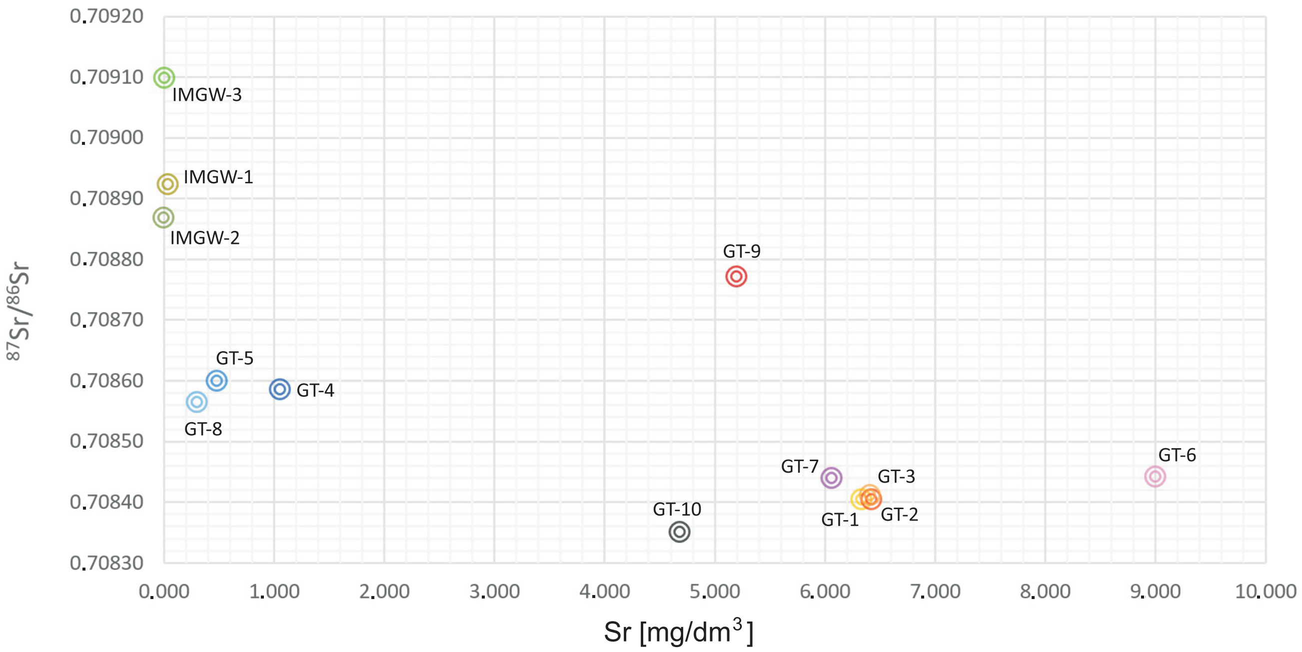

Fig. 6. $^{87}Sr/^{86}Sr$ distribution relative to the content of Sr

have been described by Małecka (1989), Barczyk et al. (1999), Barczyk (2013) and others.

Zuber et al. (2008) and Chowaniec (2009) presented a general groundwater flow model showing that recharge occurs in the northern massif of the Tatra Mountains, after which waters flow northwards towards the boundary between Podhale and the Pieniny Klippen Belt. This boundary acts as a hydraulic barrier, forcing a split of the flow into western and eastern branches that continue towards the Polish-Slovak border. Along this flow path, total mineralization increases due to the significant contribution of the strongly karstified Eocene carbonate formations (Małecka, 1996). Physicochemical studies additionally indicate both vertical and lateral zonation of water mineralization within the Podhale Basin.

Another key factor in understanding and managing the intensive use of transboundary geothermal waters is their age, which serves as an indicator of resource renewability. Isotopic studies on water age began in 1969 with tritium measurements (Nowicki and Sołtyk, 1973). Continued research showed that in the Zakopane IG 1 well area, the age of the exploited waters is ~19 years. Issues concerning the origin and age of geothermal waters were later investigated by Zuber (1986), Małoszewski and Zuber (1997), Małecka and Nowicki (2002), Zuber et al. (2008), and Chowaniec et al. (2009).

As demonstrated by Małecka and Nowicki (2002), waters of the sub-flysch aquifer of the Podhale Basin are of exclusively infiltration origin. In the southern part of the basin, these waters are younger than 50 years, whereas in the central and northern parts they are likely Holocene and even pre-Holocene. A comprehensive summary of isotopic studies conducted in the Tatra Mountains and Podhale Basin was provided by Zuber et al. (2008). These authors pointed out that hydraulic conductivity values derived from pumping tests vary significantly, indicating the presence of hydraulic barriers within the basin. These values are higher than those estimated from tritium ages, which reflect relatively minor regional variations in hydraulic properties across the basin.

A joint interpretation of multiple isotopic and geochemical data – including ^{14}C, ^{13}C, stable isotopes of oxygen and hydrogen, tritium, and noble gases – allows for increasingly precise conclusions. According to Chowaniec et al. (2009), aquifers tapped by the Szymoszkowa GT-1 and Poronin PAN-1 wells are recharged at low elevations. This suggests that outcrops of Mesozoic and Eocene carbonate rocks in lower parts of the Tatra Mountains constitute the main recharge areas for the geothermal waters. Based on this interpretation, observed H values can be attributed to:

- recharge during a colder climate prevailing before the Holocene (Białka GT-1, Bańska IG 1, Bańska PGP-1);
- altitude effect (Zakopane IG 1);
- mixed recharge from colder climatic periods (Chochołów PIG 1, Bukowina Tatrzańska PIG/PNiG-1).

Using the helium dating method, and assuming a linear increase of He concentration with age, Chowaniec et al. (2009) concluded that water tapped by the Białka GT-1, Bańska IG 1 and Bańska PGP-1 wells is much older than the Holocene waters near the Tatra foothills, with an estimated age of over 10,000 years.

Therefore, within the Podhale Basin, the northeastern sector likely contains waters older than 10,000 years, significantly older than those in the northwestern and southern parts (Chowaniec, 2012). In contrast, waters tapped by the Chochołów PIG 1 and Bukowina Tatrzańska PIG/PNiG-1 wells, located on the western and eastern sides of the basin, represent mixed waters containing a component of pre-Holocene origin.

It was observed that, in general, the values of the $^{87}Sr/^{86}Sr$ ratio in the samples analysed decreases with an increase in TDS as well as Ca and Sr contents. Two exceptions to this rule were observed and these are samples GT-9 and GT-10. As mentioned earlier, water samples GT-9 (Bukowina Tatrzańska) and GT-10 (Chochołów) stand out from the rest of the sample series, representing geothermal waters of the Podhale Basin. They represent two extreme values of the ^{87}Sr/^{86}Sr ratio. The geothermal water reservoir is fed by recharge in the Tatra Mountains, where meteoric waters infiltrate deep into the rock mass. The value of the ^{87}Sr/^{86}Sr ratio determined in sample GT-9 is the highest among the geothermal water samples studied and at the same time is closest to the values determined for meteoric water samples. However, it differs significantly from atmospheric precipitation in the content of other components. Therefore, it can be concluded that the GT-9 sample represents waters in which the radiogenic ^{87}Sr dominates. In sample GT-10 the ^{87}Sr/^{86}Sr ratio is the lowest among those found for geothermal water samples. This may indicate the dominance of the isotopic component with a lower content of the radiogenic ^{87}Sr isotope.

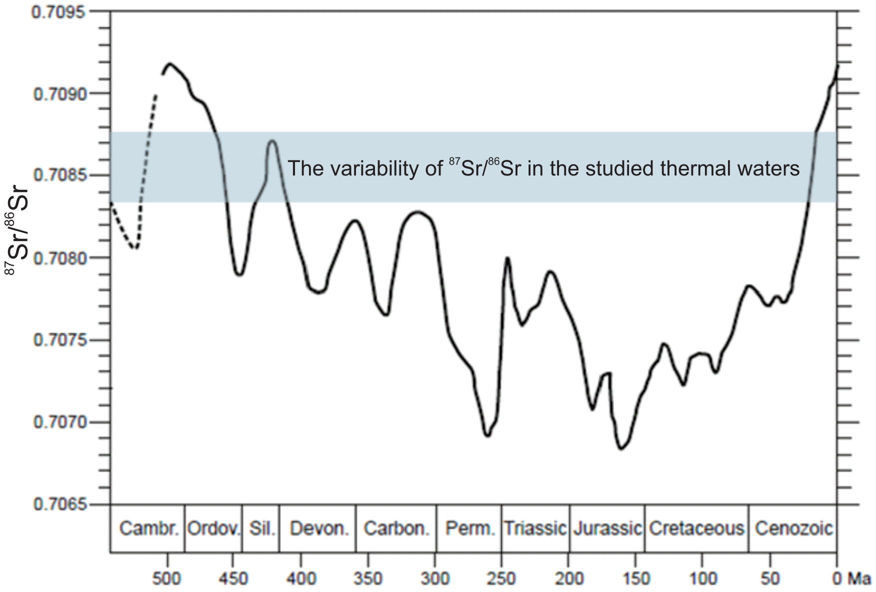

Fig. 7. Graph of variability over time of the ^{87}Sr/^{86}Sr ratio in marine waters of the Phanerozoic (after McArthur et al., 2012, modified by Wierzbowski, 2013)

A significantly different contribution of the radiogenic component was also found in the shallow circulation system of the Podhale Basin. As described by Gągulski (2024), values of the ^{87}Sr/^{86}Sr isotopic ratio in water samples from outcrops (karst springs) and other springs in the Tatra Mts. ranged from 0.708157 to 0.709853. The amplitude was 0.001696, which indicates a much higher dispersion of data than in the case of the geothermal waters. The maximum value obtained, of 0.709853, is much higher than 0.70896, the average value determined for meteoric waters recharging this circulation system (Table 1).

According to Faure (1982 *fide* Kráľ et al., 1995), marine carbonates from the Phanerozoic Eon are characterized by an average ^{87}Sr/^{86}Sr ratio value of 0.708. To be more precise, the value of the ^{87}Sr/^{86}Sr ratio for Triassic to Cretaceous carbonate rocks oscillates between 0.70750 and 0.70782 (Table 5). However, Eocene Series strata are characterized by variability of the value of the ^{87}Sr/^{86}Sr ratio in a small range from 0.70770 to 0.70779 (Table 5).

The above data was read from a graph (Fig. 7), compiled from analyses of a number of isotopic determinations made on samples of marine carbonate rocks (Burke et al., 1982; Wierzbowski, 2013).

Table 5

Values of the ^{87}Sr/^{86}Sr ratio for selected geological intervals (according to McArthur et al., 2012, modified by Wierzbowski, 2013)

Period	Ratio ^{87}Sr/^{86}Sr	
	minimum	maximum
Eocene	0.70770	0.70779
Cretaceous	0.70720	0.70782
Jurassic	0.70682	0.70764
Triassic	0.70750	0.70800

The value of the ^{87}Sr/^{86}Sr ratio obtained for all the geothermal waters studied are higher than the values typical for Mesozoic marine carbonates and at the same time lower than the values obtained for meteoric waters.

Poller et al. (2001) demonstrated that the ^{87}Sr/^{86}Sr isotopic ratio in the crystalline basement rocks of the Western and High Tatras (Slovak side) shows considerable variability. The measured ^{87}Sr/^{86}Sr values ranged from 0.763669 in the Western Tatra orthogneisses to 0.705037 in the High Tatra diorites. Therefore, contribution of this strontium source to the thermal waters of the Podhale Basin cannot be excluded. High values of the ^{87}Sr/^{86}Sr ratio can be supplied, by clay minerals in which rubidium accumulates. This is the source of the radiogenic isotope ^{87}Sr and could come from rubidium-rich mica, which forms clay minerals during the weathering process. Since marine carbonate sediments contain a clay fraction, the waters circulating in such a rock may be enriched with strontium with an isotopic signature that takes into account the inflow of the radiogenic ^{87}Sr isotope (Burchart and Pieńkowski, 1995; Burchart and Kral, 2015).

Pękala and Pytel (2019) examined the leachability of strontium from the Strzegom granite, chalk of the Lublin region, Carpathian sandstones and bricks. They found that in granite, strontium is very strongly bound to the rock matrix and no strontium was found to be released into water from granite. Carpathian sandstone also showed very low susceptibility to Sr leaching. Of the rocks studied, the highest leachability of elements was recorded in the case of chalk. It can be concluded that much higher loads of strontium will be released from the silica-carbonate component deposited in an aquatic environment than from igneous rocks. As shown by Khaska et al. (2015), the ^{87}Sr/^{86}Sr ratio in eluates obtained from the extraction of, for instance, Triassic marls depends on temperature. A rapid increase in the ^{87}Sr/^{86}Sr ratio was observed, which correlates with a temperature rise from approximately 25 to 150°C. The ^{87}Sr/^{86}Sr ratio changed from 0.70822 to 0.70922. However, no changes in the ^{87}Sr/^{86}Sr ratio were observed when the experiment was conducted at a temperature of ~25°C. The marl sample was collected from Triassic rock exposures on the Mediterranean coast, at the northeastern end of the Corbières thrust, north of Narbonne, France. The content of strontium in Mesozoic carbonate rocks decreases with age. The highest average values were found for Maastrichtian Cretaceous formations, while lower average values were found for Jurassic limestones. It was also found that light (decalcified) Cretaceous chalk strata were characterized by a higher content of strontium than, for example, undecalcified chalk or marls (Pękala et al., 2024).The laboratory studies cited, while not fully replicating geochemical processes in the water–rock system, demonstrate the susceptibility of various rocks to elemental leaching and highlight a potential mechanism controlling the $^{87}Sr/^{86}Sr$ isotopic ratio in thermal waters.

As shown by Hissler et al. (2024), the chemical composition of the streams studied is controlled by the two main lithologies of the catchment: silicate and carbonate rocks. An increase in the content of elements such as Sr and Ca was observed along the gradient from the mountainous parts of the catchment in the Western Tatras, composed of crystalline rocks, towards the Liptov Basin, where carbonate deposits dominate. The Sr concentration increased along this gradient from 0.0164 to 0.1499 mg/dm^3. Carbonate rocks appear more susceptible to strontium leaching than silicates, with reported values remaining well below those observed in thermal waters.

CONCLUSIONS

1. Extreme values of the $^{87}Sr/^{86}Sr$ isotopic ratio occur mainly along the western and eastern margins of the Podhale Basin, while the remaining chemical parameters reach their extreme values primarily in the northern and southern parts of the basin, reflecting the complex hydrogeochemical structure of the region.

2. The negative Spearman's rank correlations obtained between the $^{87}Sr/^{86}Sr$ ratio and TDS, Ca and Sr indicate an opposing relationship between the parameters analysed. Despite this statistical relationship and despite expectations based on established recharge and circulation models, the anticipated northward decrease in the $^{87}Sr/^{86}Sr$ ratio is not clearly confirmed by the spatial distribution of the values measured.

3. Thermal waters from the Chochołów and Bukowina Tatrzańska wells differ markedly from other samples, which is consistent with earlier interpretations suggesting mixed Holocene and pre-Holocene recharge.

4. The $^{87}Sr/^{86}Sr$ ratios measured in Phanerozoic carbonate rocks and in the crystalline core of the Tatra Mountains indicate that both lithological units may contribute strontium to the geothermal waters of the Podhale Basin.

5. Further work is needed to quantitatively evaluate the mixing proportions of strontium derived from different lithological sources. Application of the two-component mixing model proposed by Faure and Mensing (2005), together with a broader geological interpretation of the study area, is recommended to better constrain the evolution and flow paths of the thermal waters.

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