GEOCHEMISTRY OF GERMANIUM IN THERMAL WATERS OF THE JELENIA GÓRA GEOTHERMAL SYSTEM (SUDETES, POLAND): SOLUTE RELATIONSHIPS AND AQUIFER MINERALOGY

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Abstract: A long-term (2004–2021) study of the chemical composition of thermal waters in the Jelenia Góra geothermal system provided information on a wide set of components. The subject of the present study is the geochemistry of germanium (Ge), which occurs in concentrations ranging from 2.7 to 6.3 µg/L in the waters studied. Interpretation of a set of 46 chemical analyses identified relationships between germanium and other elements in thermal waters from individual intakes. In the old thermal waters of Cieplice and Karpniki of deep circulation, germanium is derived from silicates and its concentration is controlled by the solubility of Ge-bearing quartz with an average Ge content of 1.5 µg/g. The source of germanium in the deep old thermal water at Staniszów is mainly sulphides, most likely arsenopyrite, but the secondary contribution of Ge from silicates (biotites, amphiboles) should not be ignored. The mineral phase, responsible for controlling Ge activity in this water, cannot yet be identified. The shallow thermal waters at Cieplice, which are a mixture of old thermal waters and modern waters, differ from the deep waters. Germanium in shallow waters probably is derived from silicates, but owing to mixing, there are no chemical equilibrium conditions; the concentration of Ge is determined by the dynamic equilibrium of the mixed water components. The modern water of intake no. 2 (Cieplice) differs from other shallow waters and also shows similarities to the Staniszów water. The germanium in the no. 2 water probably comes mainly from ferromagnesian minerals (biotite, amphiboles), although the influence of sulphides cannot be excluded. The relationships of germanium to other elements, including the Ge/Si ratio, appear to be effective indicators of hydrogeochemical conditions. Thermal waters from the different locations show both similarities and differences in chemical composition, especially of minor and trace components. At the present, still weak stage of recognition, the Jelenia Góra geothermal system can be treated as an area of occurrence of local systems responsible for the quantity and quality of thermal waters in individual intakes.

Key words: Germanium, groundwater geochemistry, geothermal water, granite geochemistry, Karkonosze granite, Jelenia Góra geothermal system.

INTRODUCTION

The history of germanium (Ge) research in geochemistry dates back just over 100 years, to when this element was discovered in 1885 (Winkler, 1886). The earliest data on Ge in various minerals were given by Krüss (1888), Chrustschoff (1892), Lincio (1904) and Urbain (1909), whereas in waters by Bardet (1914) in mineral water of Vichy, France, and by Müller (1924) in mine waters from a smithsonite mine in Kentucky, USA. Interest in this element increased after World War II, owing to its practical applications. At present, germanium is one of the elements critical to modern technologies. It is used, i.a., in fibre optics, electronics and the manufacture of catalysts. It has evoked also interest in medicine, especially in Japan and the Republic of Korea. In the field of geological sciences, attention is paid to germanium in economic geology and there is growing interest in this element in other branches of the geological sciences.

In Poland, as far as groundwater is concerned to date, germanium is documented only in the therapeutic waters of the Sudetes Mountains (Dobrzyński *et al.*, 2017, 2018) and selected fresh, mineral and therapeutic waters of the Carpathians (Dobrzyński *et al.*, 2011; Skwarczyńska-Wojsa *et al.*, 2021). Relationships between germanium and other elements in the therapeutic waters of the Sudetes indicated the possibility of using Ge data to describe hydrochemical conditions on local and regional scales (Dobrzyński *et al.*, 2017, 2018). A much broader set of analytical chemical data on the geothermal waters of the Jelenia Góra geothermal system (JGS), the Western Sudetes, has been collected now, allowing an in-depth analysis of the geochemical conditions in this system. The objectives of this work are: (1) to determine the relationship between Ge and other elements, particularly those, to which it has a strong affinity, such as Si, Zn, As, and Fe, and (2) to find processes to control Ge concentrations in JGS geothermal waters.

GERMANIUM HYDROGEOCHEMISTRY

The average germanium abundance in the upper continental crust is estimated at 1.4 µg/g (Rudnick and Gao, 2014). Germanium commonly demonstrates silicon-like geochemistry and owing to the substitution of Ge for Si, most of the germanium in the Earth's crust is scattered in silicate minerals. The element is used as a tracer in petrogenetic processes, leading to the (re)crystallisation of rocks in mantle, metamorphic, and volcanic-plutonic environments.

As a trace element, germanium rarely forms its own minerals, which are mostly sulphides, like argyrodite (Ag_8GeS_6), renierite (($Cu,Zn)_{11}(Ge,As)_2Fe_4S_{16}$), and germanite ($Cu_3(Ge,Ga,Fe)S_4$). The chalcophile properties cause Ge to show affinity for Zn, Cu, Sn, Ag, As, and Fe and to accumulate in sulphides, mainly in sphalerite (ZnS), chalcopyrite ($CuFeS_2$), arsenopyrite (FeAsS), and pyrite (FeS_2). Amongst oxides, the highest germanium concentrations are found in rutile (TiO_2), magnetite ($Fe^{2+}Fe^{3+}_2O_4$) and cassiterite (SnO_2), whereas among silicates, usually in topaz ($Al_2SiO_4F_2$), epidote ($Ca_2(Al_2Fe^{3+})[Si_2O_7][SiO_4]O(OH)$),

garnet and tourmaline (Ivanov, 1996). Germanium also shows a biophile (organophile) preference to concentrate in organic matter, particularly in lignites (e.g., Bernstein, 1985; Höll *et al.*, 2007). Germanium is most often extracted from sphalerite ores and from lignite and hard coals (Frenzel *et al.*, 2014).

In fresh groundwater (i.e., waters of total dissolved solids, TDS, below 1 g/L), germanium belongs to trace components, i.e. substances, which usually occur at concentrations below 0.1 mg/L. Generally, an increased germanium level mainly occurs in geothermal and/or mineral (TDS above 1 g/L) waters, in waters with either low or high pH, and sometimes in saline waters (Rosenberg, 2009). For instance, elevated concentrations of germanium were found in CO_2-rich thermal waters, waters containing methane, nitrogen-rich waters, acid thermal water in the oxidation zone of sulphide deposits, and alkaline sodium-dominated thermal waters (Ivanov, 1996). Germanium concentrations in geothermal waters vary widely, from very low levels (below detection limits) to almost 300 µg/L, but it rarely exceeds 50 µg/L (Dobrzyński *et al.*, 2018). Increased germanium content is often found in alkaline and/or thermal groundwater, especially in active volcanic zones and/or in bedrock, composed of reactive silicate minerals, as in young volcanic rocks. According to Pentcheva (1975), the highest concentrations of Ge occur in alkaline, thermal groundwater with TDS below 800 mg/L. The reaction of thermal alkali-rich waters with organic-rich sedimentary rocks might also favour high germanium concentrations (Bernstein, 1985).

Germanic acid ($Ge(OH)_4$) and Ge-fluoride complexes at high fluoride concentrations are the most important inorganic species of germanium in aqueous solutions (Wood and Samson, 2006). Of the organic species, the most important are probably methylgermanium species. Monomethylgermanium and dimethylgermanium have been found in surface waters (Lewis *et al.*, 1988). The high solubility of tetramethylgermanium was proposed as being responsible for high germanium concentrations in mineral waters, occurring in carbonaceous sedimentary rocks (Ivanov, 1996).

The most important factors affecting germanium concentrations in natural waters appear to be temperature, pH, redox, as well as the geochemistry and mineralogy of the reservoir rocks. As with the other elements, the concentration of germanium in groundwater is the result of processes supplying Ge to the water (dissolution, desorption) and processes removing it from the water (precipitation, adsorption).

The decomposition of Ge-source solid phases, especially silicates, is favoured by increasing temperature and pH, which in turn promote an increase in Ge concentration, due to the dissociation of germanic acid. Immobilisation of the element in/onto solid sink phases depends on changes in the solution chemistry (pH, E_H) and temperature, which, for example, occur when geothermal water gradually rises towards the surface or mixes with shallower groundwater of a contrasting composition and/or temperature.

MATERIALS AND METHODS

The subject of this research is geothermal waters, occurring in the geothermal system of Jelenia Góra Valley (Jelenia Góra geothermal system – JGS). Thermal waters from all nine operated water intakes were studied (intakes bearing the symbols: C-1, C-2, 1, 2, 4, 5 and 6 at Cieplice; KT-1 at Karpniki; ST-1 at Staniszów; Fig. 1). The study is based on the 46 chemical analyses of thermal waters, performed in the years 2004–2021 by authors. The number of analyses of water from each intake is given in Table 1. Water samples were filtered in the field by membrane filters of 0.45 µm pore size, preserved with ultra-pure nitric acid, and stored in LDPE bottles. Physicochemical analyses covered field measurements (pH, E_H and T), and lab determinations of major, minor and trace elements (by Inductively Coupled Plasma Mass Spectrometry ICP-MS, spectrophotometric, volumetric methods). Chemical analyses of the waters sampled in this study were carried out using the same methods in the same laboratories. Hydrogencarbonates and chlorides were analysed volumetrically, while spectrophotometrically: sulphates, fluorides, nitrates, phosphates, ammonium nitrogen and sulphides. Other components, including trace elements, were determined by ICP-MS (ACME, Canada). Germanium determination in minerals and rocks was carried out in the Analytical Chemistry Expert Centre (Biological and Chemical Research Centre, University of Warsaw). For the determination of Ge total content in rocks and mineral, the samples were powdered. The dissolution and extraction of Ge samples were followed by an in-house procedure (Karasiński *et al.*, 2021). All samples were decomposed in a closed-vessel microwave-assisted decomposition system (Millipore, Ethos Up). The acid composition as well as the pressure and temperature conditions were selected individually for the sample type. Total Ge analysis was performed on NexION 300D (PerkinElmer, USA) using external calibration with internal standard (Rh) correction. Archival results on the germanium in rocks and minerals (research by ES) come from analyses carried out at the University of Göttingen, using ICP-MS and LA-ICP-MS methods, respectively. Statistical analyses of hydrochemical data were performed using Statistica (ver. 7.1) programme. Geochemical modelling of waters was performed using the PHREEQC (ver.3.7.3) programme (Parkhurst and Appelo, 2013), with the thermoddem database. The saturation status of the waters in relation to the mineral phases was assessed on the basis of calculated saturation indices (SI).

OUTLINE OF GEOLOGICAL SETTING AND HYDROGEOLOGICAL CONDITIONS

The basement of the Jelenia Góra Valley consists of igneous rocks (mainly granites), which are covered by a thin and discontinuous cover of Quaternary sedimentary deposits, consisting of granite regoliths, pre-glacial gravels, varved clays, glacial tills, fluvio-glacial sands and gravels, peats and alluvial (muds, sands, gravels) sediments.

The sedimentary cover is usually between 5 and 20 m thick. Two main aquifers occur in the area. The first, usually unconfined shallow cold fresh groundwater horizon occurs in the sedimentary cover and the fractured roof part of the granite bedrock. The second aquifer consists of geothermal waters in the deeper parts of the granite (Fistek and Dowgiałło, 2003; Marszałek, 2007a, 2010). The occurrence of thermal waters is determined by the presence of permeable fractures and zones of tectonic relaxation in igneous rocks. In the Cieplice area of thermal water ascension, its mixing with fresh waters of the shallow aquifer occurs, resulting in hydrochemical anomalies (Ciężkowski and Mroczkowska, 1985; Fistek and Dowgiałło, 2003). The groundwater of both aquifers is characterised by the presence of radon, which is a common feature in the area of occurrence of the Karkonosze granite (Przylibski *et al.*, 2020).

The geothermal waters of JGS occur in Hercynian Karkonosze pluton igneous rocks consisting of equigranular and porphyritic granites, hybrid quartz diorites and granodiorites, microgranular magmatic enclaves, and composite and lamprophyre dykes (Słaby and Martin, 2008). These rocks form most of the basement of the Jelenia Góra Valley, the Karkonosze (Giant Mountains) range, and part of the Rudawy Janowickie Mountains (Fig. 1). The Karkonosze Mountains and Rudawy Janowickie Mountains are among the mountain ranges of the Western Sudetes. In the Jelenia Góra Valley, thermal waters are known in three places: the Cieplice health resort (thermal station), Karpniki and Staniszów. The thermal waters of Cieplice have been known since at least the 12th century and were used for centuries in balneotherapy. The geothermal waters of Karpniki and Staniszów, discovered in 2013, so far are used for central heating and recreation.

The regional drainage base for groundwater, including thermal waters, in the Jelenia Góra Valley is the Bóbr River (e.g., Marszałek, 2007a). The geothermal waters at Cieplice are rendered accessible by eight intakes, six of which are shallow ones, namely casing springs and drilled wells with depths of 5.2 to 52.3 m) and two deep boreholes, C-1 and C-2, with depths of 2,002.5 and 750 m, respectively (Fistek and Dowgiałło, 2003). Seven of the Cieplice intakes were available for water sampling. Geothermal water boreholes at Karpniki (KT-1 well) and Staniszów (ST-1 well) have 1,997 and 1,501 m deep, respectively (Łukaczyński and Polaczek, 2014a, b). Geothermal waters in the C-1, C-2, KT-1 and ST-1 wells represent deep circulation waters probably of Late Glacial/Early Holocene age, whereas thermal waters in the shallower intakes at Cieplice are a mixture of old geothermal waters and tritium-bearing modern waters (Ciężkowski *et al.*, 1992; Łukaczyński and Polaczek, 2014a, b). The recharge (alimentation) area of Cieplice deep-circulation thermal waters was proposed as to being in the Rudawy Janowickie mountain range (Ciężkowski *et al.*, 1996), along the eastern rim of the Jelenia Góra Valley. The recharge zone for intake KT-1 (Karpniki) likewise was suggested as being in the Rudawy Janowickie range (Łukaczyński and Polaczek, 2014a). The proposed location of the deposit mining area of ST-1 (Staniszów) thermal water (Łukaczyński and Polaczek, 2014b) indicates a recharge area situated, south-east of the intake. Given the assumed Late Glacial/
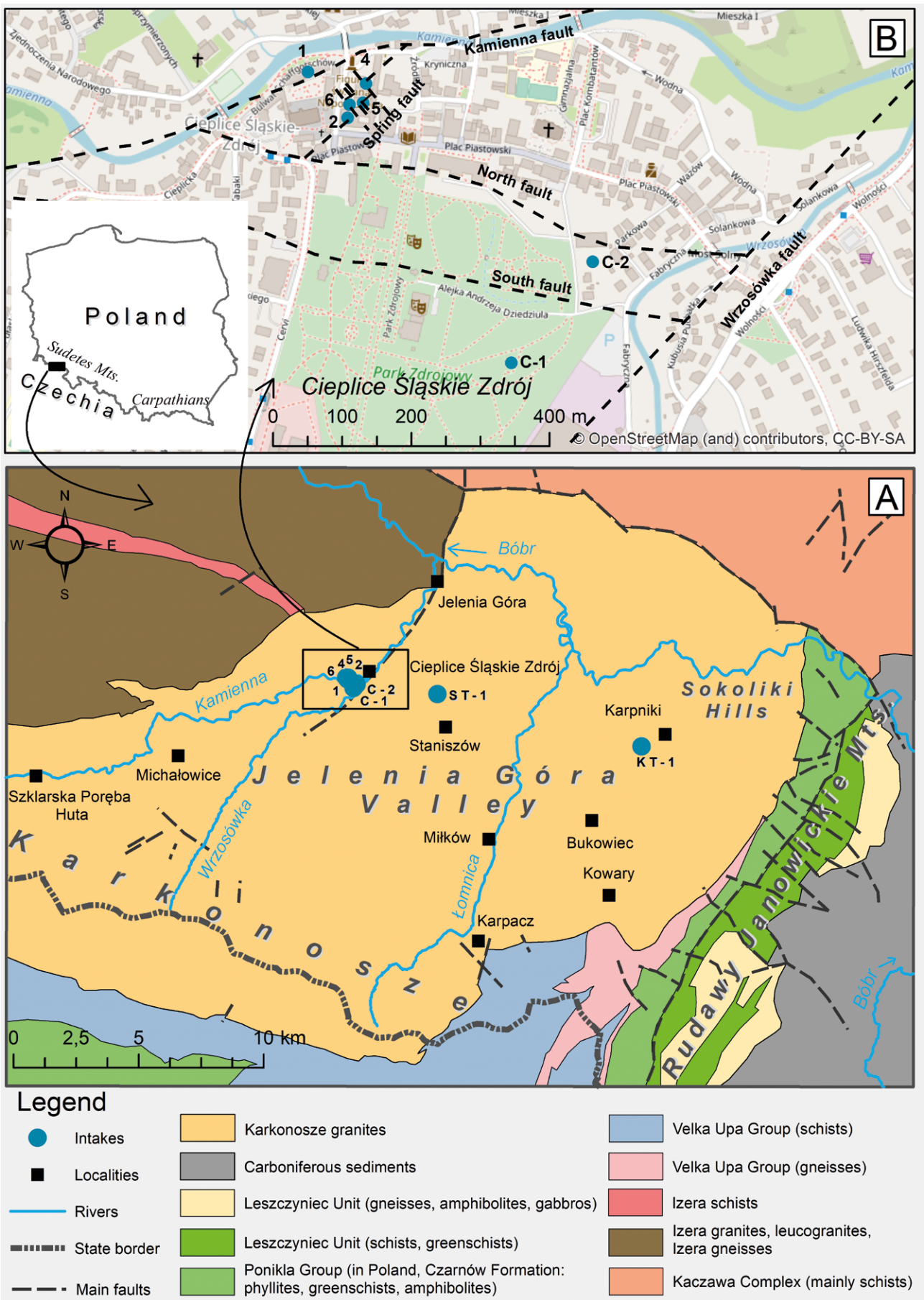
Fig. 1. Geological map of Jelenia Góra Valley (after Sawicki, 1995) with the location of geothermal water intakes (**A**). Structural sketch of the thermal water occurrence at Cieplice (**B**) after Fistek and Dowgiałło (2003).

Early Holocene age of this water ($^{14}C = 5.5 \pm 1.0$ pmC; Tab. 1) and its oxygen and hydrogen stable isotopes composition (lighter than the waters of modern infiltration in the study area), the ST-1 water recharge zone might be in the Karpacz-Kowary-Miłków area, possibly at higher altitudes than the intake. It should be understood that the age and location of recharge areas of the investigated thermal waters are still open questions and require further detailed research.

The JGS thermal waters from the deep wells (C-1, C-2, KT-1, ST-1) are isolated from surface influences and naturally protected against anthropic activities. The thermal waters from the shallow intakes, containing a component of modern waters, are potentially subject to contamination.

A broad characterisation of the hydrogeological conditions of the Jelenia Góra Basin is given by Marszałek (1996, 2007a, b, 2010) and Fistek and Dowgiałło (2003), while the general hydrogeochemical characteristics of the thermal waters can be found in the works of Fistek and Dowgiałło (2003), Ciężkowski et al. (2011), and Liber-Makowska and Kiełczawa (2020).

MINERALOGY AND GEOCHEMISTRY OF AQUIFER ROCKS

The Jelenia Góra geothermal system (JGS) is located in the eastern part of the Karkonosze granite pluton. This pluton, together with its metamorphic envelope, is located in the north-eastern part of the Bohemian Massif, in the Western Sudetes (Aleksandrowski et al., 2019). This intrusion was formed in several stages during the Hercynian (Variscan) orogeny and is dated at 328–304 million years (Duthou et al., 1991; Kröner et al., 1994; Mazur et al., 2007). As a result of tectonic events taking place during the Alpine orogeny between 16–2.6 Ma (Ziegler and Dèzes, 2007), a set of tectonic blocks was uplifted, which today form the Karkonosze Mountains, visible in surface morphology (Aleksandrowski et al., 2019).

Different types of rocks were released within the pluton, depending on the texture, the proportion of minerals, and the way they grew (Słaby and Martin, 2008), which are related to the stages of formation of the batholith. Contemporary studies on determining the genesis of pluton have shown that during its formation, there was a mixing of two magmas – mafic and felsic, which are characterised by differences in chemical composition (Słaby and Martin, 2008; Aleksandrowski et al., 2019). Mixing occurred several times during pluton formation, and as a result, the granite rocks formed after solidification show diversity.

The following rock types are distinguished in the Karkonosze pluton: porphyritic granite called 'central granite' or 'Liberec and Jizera', equigranular granite called 'ridge', 'crestal' or 'Harrachov', and granophyric granites (Borkowska, 1966; Žák and Klomínský, 2007; Słaby and Martin, 2008). Granites forming the pluton are crossed by numerous veined rocks which formed in magmatic and post-magmatic processes. Hybrid rocks formed in magmatic processes, including hybrid quartz diorites and granodiorites, microgranular magmatic enclaves, composite and

lamprophyre dykes represent zones of incomplete mixing of magma (Słaby and Martin, 2008).

Porphyritic granites are the most common variety distinguished within the pluton. In the studied system, they are the dominant rocks occurring in the areas of recharge and transition zones and intake locations of the thermal waters. Typical for this type of granite are anhedral–subhedral, elongated, 4–5 cm long, sometimes twinned megacrystals of alkali feldspars ($KAlSi_3O_8$) with a pale pink colour, characterised by zonality of growth (Borkowska, 1966; Słaby and Martin, 2008). In that facies of granite, typical are alkali feldspars surrounded by a white rim of plagioclase ($NaAlSi_3O_8$–$CaAl_2Si_2O_8$) with a width of 3–4 mm (rapakivi texture; Borkowska, 1966). Also present are grey, anhedral quartz (SiO_2) crystals, and unevenly distributed biotite crystals ($K(Mg,Fe)_3AlSi_3O_{10}(OH)_2$), sometimes occurring next to calcic amphiboles, which together with feldspars form a medium- or coarse-grained matrix (Słaby and Martin, 2008). Such accessory minerals as zircon ($ZrSiO_4$), apatite ($Ca_5(PO_4)_3(F,Cl,OH)$), epidotes (allanite, clinozoisite/zoisite), titanite ($CaTiSiO_5$), magnetite, ilmenite ($FeTiO_3$), monazite ($REE(PO_4)$) and secondary sericite and chlorite are present in this variety of granite. In the eastern and north-eastern parts of the porphyritic granite, fine growths of fluorite (CaF_2) and pyrite are found.

Equigranular granites occur as dispersed, small bodies within the porphyritic granites (Słaby and Martin, 2008). They are characterised by uniform size of minerals, similar in texture to the matrix of porphyritic granites (Borkowska, 1966; Słaby and Martin, 2008). Minerals assemblages are similar to those of the porphyritic facies. Next to the lighter alkali feldspars in the porphyritic granite, plagioclases only occasionally form rims (Borkowska, 1966). The equigranular granites are characterised by the absence of amphiboles and a lower proportion of biotite. Small amounts of muscovite ($(KAl_2(AlSi_3O_{10})(OH)_2$) are present in the equigranular facies. Accessory minerals include zircon, apatite, epidotes (allanite), magnetite, ilmenite, titanite, and monazite, occasionally fluorite, and secondary sericite and chlorite (Borkowska, 1966; Słaby and Martin, 2008).

Granophyric granites form the least common facies, occurring in the form of pockets within the equigranular granite (Słaby and Martin, 2008). Micro-pegmatite structures, identified microscopically in this variety presumably may indicate that this granite represents a transitional link between magmatic and post-magmatic vein formation (Borkowska, 1966).

Hybrid rocks, including hybrid quartz diorites and granodiorites, microgranular magmatic enclaves, and composite and lamprophyre dykes, occur in the form of veins crossing the pluton. They are characterised by similarity in trend, high inclination, minor thickness (2–3 m) and high extension (several dozen metres; Borkowska, 1966). Hybrid quartz diorites and granodiorites, owing to the high content of biotite and calcic amphiboles are characterised by a dark colour. They have a texture between porphyritic and equigranular. In the mineral composition of the rock, in addition to quartz, feldspars, plagioclases, and the previously mentioned biotite and amphiboles, there are, as in

Table 1

Selected physicochemical and isotopic parameters of geothermal waters in Jelenia Góra geothermal system (JGS)[a].
Concentrations in mg/L, unless otherwise indicated.

Location	Water intake								
	Cieplice	Cieplice	Karpniki	Staniszów	Cieplice	Cieplice	Cieplice	Cieplice	Cieplice
Name of intake (number of analyses)[b]	C-1 (4)	C-2 (4)	KT-1 (9)	ST-1 (9)	1 (5)	2 (5)	4 (5)	5 (4)	6 (1)
Intake depth [m]	2002.5 (artesian flow)	750	1997 (artesian flow)	1501	52.3	6.1	37.5	5.2	5.2
pH	7.95–8.65	8.08–8.37	8.24–8.51	7.72–8.80	7.73–8.52	6.63–7.12	7.59–8.21	8.25–8.81	8.12
T [°C]	73.0–79.4	56.5–58.8	46.8–51.2	25.1–38.4	18.6–21.6	21.0–23.3	26.9–31.0	31.6–37.9	35.7
E_H, SHE-corrected [mV]	-157 – -76	-133 – -38	-210 – -61	-151 – -61	+310 – +558	+352 – +550	+213 – +515	-86 – +80	16
IS [mmol/kg of H_2O]	19.07–21.84	18.98–22.40	14.55–16.64	14.49–17.51	19.12–23.41	25.68–27.39	19.19–21.76	19.05–21.89	18.97
Ca	7.97–8.78	8.40–10.16	5.29–5.95	7.81–11.02	9.26–27.40	95.45–163.27	10.69–27.84	9.54–10.70	10.25
Mg	<0.05–0.13	<0.05–0.06	<0.05–0.19	<0.05–0.14	0.08–0.87	12.44–21.00	0.27–1.43	0.05–0.14	0.15
Na	148.43–170.95	148.06–188.64	109.43–127.16	97.53–134.59	143.26–187.88	117.26–210.59	144.61–169.32	149.76–172.04	168.49
K	4.05–4.80	4.08–5.44	2.73–3.16	0.97–1.53	4.11–7.15	46.51–63.24	3.49–7.07	3.98–4.43	3.84
HCO_3^-	142.9–150.7	151.6–171.14	139.6–153.9	112.3–151.6	145.0–232.5	229.7–294.7	143.4–187.7	143.1–159.2	140.9
SO_4^{2-}	136.0–180.0	120.0–174.0	76.0–104.0	80.0–138.0	110.0–174.0	70.0–174.5	120.0–162.0	132.0–177.0	134.0
Cl^-	44.50–49.40	43.61–46.90	27.30–31.70	33.00–35.45	41.12–110.40	24.90–64.88	41.83–78.90	43.50–50.90	43.30
F	10.6–12.7	9.2–12.5	11.5–13.4	8.5–10.5	9.2–12.0	2.3–3.5	7.2–11.3	8.2–11.3	10.9
Br [µg/L]	227–245	237–291	124–147	111–195	184–289	116–1297	190–266	226–246	238
S^{-2}	0.02–0.17	0.07–0.66	0.04–0.15	0.33–5.30	<0.01–0.01	<0.01–0.02	<0.01–0.01	0.06–0.09	0.01
B [µg/L]	225–285	241–279	224–293	134–273	192–286	105–161	190–253	235–282	231
Si	38.08–50.00	32.95–44.51	24.16–30.33	14.05–16.48	27.85–44.46	18.55–26.77	26.02–40.94	30.49–43.94	35.17
Ge [µg/L]	5.1–5.9	4.9–6.3	4.0–5.7	2.7–6.0	3.5–5.8	3.5–5.0	3.3–5.1	4.9–5.8	5.5
As [µg/L]	43.1–46.9	40.8–87.6	54.0–64.8	23.8–37.5	39.2–50.7	23.4–28.7	40.1–47.1	43.0–45.6	44.7
Fe [µg/L]	<10–10	<10–30	<10–15	<10–26	<10–121	<10–278	<10–30	<10–142	<10
Zn [µg/L]	0.8–59.3	<0.5–64.2	1.3–61.1	<0.5–102.5	7.3–106.8	12.6–88.9	15.8–145.7	1.3–53.2	16.7
V [µg/L]	<0.2–0.8	<0.2–0.7	<0.2–0.6	<0.2–0.9	<0.2–1.6	1.8–8.3	0.2–1.7	<0.2–0.9	0.2
Mo [µg/L]	15.9–18.2	15.8–19.7	24.6–31.1	13.2–17.6	12.8–18.0	4.1–7.6	13.5–17.4	16.5–18.7	16.3
W [µg/L]	57.6–67.9	57.6–72.2	64.7–83.1	43.8–63.9	37.6–68.4	2.4–7.1	40.1–61.9	57.4–67.9	59.1
Ge/Si [µM/M]	45.5–53.0	52.7–57.5	61.1–73.5	72.1–151.3	45.7–58.4	57.8–97.0	46.5–61.1	51.2–62.4	64.3
Cl/Br [M/M]	438–465	338–446	423–555	399–700	321–1352	113–661	354–936	434–475	410
F/Cl [mM/M]	400–499	393–513	744–895	460–563	155–545	72–217	170–480	301–459	470
$\delta^{18}O$ ₍VSMOW₎ [‰]	-10.3b	-10.3c	-10.52 (±0.1) – - 10.55 (±0.1)d	-10.43 (±0.1)e	-10.4 – -10.2c	-9.8 – -9.7c	-10.3 – -10.2c	-10.3c	-10.4 – -10.3c

Location	Water intake								
	Cieplice	Cieplice	Karpniki	Staniszów	Cieplice	Cieplice	Cieplice	Cieplice	Cieplice
δ^2H_{VSMOW} [‰]	-74 – -72c	-71c	-75.7 (±1) d	-74.1 (±1)e	-72c	-69 – -68c	-74 – -72c	-74 – -72c	-73 – -72c
Tritium [TU]	0.0 (±1.5)f	1.3 (±1.5)f	0.0 (±0.3) d	0.0 (±0.3)e	0.3 (±1.5)f	49.3 (±2.3)f	1.7 (±1.5)f	1.6 (±1.5)f	0.0 (±1.5)f
^{14}C [pmC]	3.3 (±1.0)f	1.1 (±1.0)f	0.0 (±1.0) d	5.5 (±1.0)e	7.0 (±1.0)f	101 (±1.0) f	8.6 (±1.0)f	2.4 (±1.0)f	4.5 (±1.0)f
$\delta^{13}C_{VPDB}$ [‰]	-8.2 (±0.2) f	-8.1 (±0.2) f	-8.3 (±0.2) d	-10.5 (±0.2)e	-8.4 (±0.2) f	-17.4 (±0.2)f	-9.2 (±0.2) f	-8.0 (±0.2) f	-8.3 (±0.2) f
^{222}Rn [Bq/L]	23g	9.4–20.0h	5.9 (±0.3) – 290.1 (±1.6)d; 245 (±2)i	116.4 (±0.6) – 174 (±1)e	8.8–14.5h	125–163h	42.1– 54.1h	36.5– 57.8h	40.7– 45.0h
PCC	Na-SO$_4$-HCO$_3$	Na-SO$_4$-HCO$_3$	Na-HCO$_3$-SO$_4$	Na-HCO$_3$-SO$_4$	Na-SO$_4$-HCO$_3$-(Cl)	Na-Ca-HCO$_3$-Cl-SO$_4$	Na-SO$_4$-HCO$_3$-(Cl)	Na-SO$_4$-HCO$_3$	Na-SO$_4$-HCO$_3$

a – based on results of authors' research, unless otherwise indicated; b – number of in-house chemical analyses; c – Zuber *et al*., 1989; d – Łukaczyński and Polaczek, 2014a; e – Łukaczyński and Polaczek, 2014b; f – Ciężkowski *et al*., 1985; g – Ciężkowski *et al*., 1992; h – Ciężkowski *et al*., 2016; i – Przylibski *et al*., 2018. IS – ionic strength (calculated by PHREEQC program), PCC – prevalent chemical character (hydrochemical type is based on ions with > 20% gram equivalents).

other varieties, accessory minerals such as zircon, apatite, magnetite, titanite, and ilmenite (Słaby and Martin, 2008). Composite dykes are mafic vein rocks that, as a result of subsequent uplift movements, have been strongly deformed. They are characterised by a high proportion of accessory minerals, which include zircon, apatite, ilmenite and epidotes. As in the case of porphyritic granites, rapakivi and anti-rapakivi textures are quite common. In addition to feldspars, there are subhedral biotite and amphibole crystals in the rock, as well as anhedral quartz crystals. Lamprophyres, like quartz diorites and granodiorites, form a system of veins crossing mainly the porphyritic granites. They contain, in addition to euhedral amphiboles, plagioclase, magnetite, and biotite, small amounts of alkali feldspar and quartz. Apatite, titanite, pyroxene and olivine are also rare. Microgranular magmatic enclaves form rounded or oval bodies within the granites. They have a dark colour and fine-grained texture, and are remnants of pre-existing, unmixed mafic magma. They consist primarily of biotite and amphibole with accessory zircon, apatite, ilmenite and magnetite (Borkowska, 1966).

It is worth emphasising that in addition to the granites of the Karkonosze pluton, metamorphic envelope rocks, including mica schists, gneisses, amphibolites and marbles, are also present in the recharge area of the investigated thermal waters proposed in the Rudawy Janowickie Mountains. From the point of view of the research conducted, not only the presence of rock-forming and accessory minerals is important, but also the occurrence of ore mineralisation in the border of the pluton as well as in the rocks in direct contact with it (Mochnacka *et al*., 2015; Kozłowski *et al*., 2016). Diffuse and nest mineralisation, associated with post-magmatic pegmatite formation can be identified in the entire pluton. However, pegmatites are more abundant in the eastern part than in the central or western parts of the pluton (Aleksandrowski *et al*., 2019). This is particularly important,

owing to the location of the thermal water recharge and transit areas in the eastern part of the pluton. Furthermore, in Rudawy Janowickie, in the eastern metamorphic envelope of the Karkonosze pluton, there are various phases of mineralisation associated with the interaction of granite intrusion containing, i.a., sphalerite, pyrite, arsenopyrite, chalcopyrite and bornite (Cu_5FeS_4) (Mochnacka, 1982). From the vicinity of Kowary and Wołowa Góra, uranium-polymetallic mineralisation was described (Mochnacka, 1966; Mochnacka *et al*., 2015; Domańska-Siuda, 2012), in which there are such minerals as arsenopyrite, pyrite, marcasite (FeS_2), galena (PbS), sphalerite, chalcopyrite, bornite, enargite (Cu_3AsS_4), and brannerite ($(U,Ca,Th,Y)(Ti,Fe)_2O_6$). Mineralisation of pyrrhotite (FeS), chalcopyrite, pyrite, arsenopyrite, sphalerite, galena, and marcasite was found in Sowia Dolina (Owl Valley), near Karpacz (Mochnacka *et al*., 2007). Another example of interesting mineralisation is the association of ore minerals in granite in the area of Szklarska Poręba Huta, including chalcopyrite, pyrite, marcasite, wolframite ($(Fe,Mn)[WO_4]$), and sphalerite, among others (Kozłowski *et al*., 2002; Mochnacka *et al*., 2015).

GENERAL GEOCHEMICAL CHARACTERISTICS OF THE JGS THERMAL WATERS

The thermal waters of JGS are characterised by low mineralisation (ionic strength 14.5–27.4 mmol/kg H_2O), temperatures (at outflow) between 19 °C and 79 °C, slightly alkaline and alkaline pH (7.6–8.8, except water of intake no. 2 which has pH of 6.6–7.1; Tab. 1). The redox potential in deep thermal waters (C-1, C-2, KT-1, ST-1) is reductive (between -210 mV and -40 mV), while in shallow waters it is higher and much more varied (between -90 mV and +560 mV).

The chemical composition of the thermal waters is dominated by hydrogencarbonates, sulphates and sodium ions. The thermal waters from the shallow intakes (at Cieplice) are mixtures of old geothermal waters with modern (tritium-bearing) cold waters, and present compositional diversity in terms of many parameters, including temperature and redox potential. The physicochemical characteristics of geothermal waters studied given in Table 1 are on the studies by the present authors, whereas isotopic data ($\delta^{18}O$, δ^2H, T, ^{14}C, $\delta^{13}C$, ^{222}Rn) are from literature sources.

The stable isotope ($\delta^{18}O$, δ^2H) composition of the JGS geothermal waters is consistent with the isotope pattern of local precipitation and indicates their infiltration origin (e.g., Ciężkowski *et al.*, 1992, 1996). This together with tritium and radiocarbon data, indicates variation in the age of the water and the process of mixing the two aforementioned water components.

RESULTS AND DISCUSSION

Germanium in aquifer rocks and main rock-forming minerals

The published data on Ge in rocks and minerals of Karkonosze pluton are very limited (Waleńczak, 1969; Kozłowski,1973). Germanium in the Izera granites and gneisses which together with the Karkonosze granite comprise the Karkonosze-Izera Crystalline Complex, was studied by Oberc-Dziedzic *et al.* (2005), while Breiter *et al.* (2013a, b) presented data about the Ge content in quartz and selected other granites of the Bohemian Massif. For the purposes of this study, germanium determinations for the rocks and minerals of the Karkonosze pluton were made and unpublished (ES) data were used (Tabs 2, 3).

The Ge concentration in the studied granites shows low variability (1.40–1.89 µg/g; Tab. 2). The equigranular granites have slightly higher concentrations (1.83 µg/g, 1.89 µg/g) than the porphyritic granites (1.40–1.78 µg/g), but still within the limits of uncertainty. The Ge concentration in the hybrid rocks does not differ significantly from those of granites and ranges from 1.34 to 1.73 µg/g.

Samples of porphyritic granite with pronounced alteration and granite showing no sign of change were selected for Ge research from the core material from the KT-1 borehole (Karpniki). Both rock samples exhibit identical textures, macroscopically, the mineralogical composition of both samples is similar, but the altered granite is crumbly. These changes are assumed to have developed under the influence of thermal waters in zones of tectonic relaxation of the rocks. The altered porphyritic granite is depleted in Ge (1.45 µg/g), compared to the unaltered granite (1.78 µg/g).

The Ge results for the rocks of the Karkonosze pluton are consistent with the literature data. The average abundance of Ge in the upper continental crust is estimated at 1.4 µg/g (Rudnick and Gao, 2014), while in granites at 1.3 µg/g (Faure, 1998). Wittmann and Hörmann (1972) and Bernstein (1985) report similar ranges of Ge concentration in granites, from 0.5 µg/g to 4.7 µg/g, and from 0.5 µg/g to 4 µg/g, respectively. Breiter *et al.* (2013b) give the concentration of germanium in Bohemian Massif granites in the range of 1.0–6.2 µg/g. Ge concentrations in the studied rocks of the Karkonosze pluton (1.34–1.89 µg/g) are similar to those found in the neighbouring rocks of the Karkonosze-Izera Crystalline Complex (in Izera granites from 1.3 to 1.7 µg/g, leucogranite – 2.5 µg/g, and Izera gneiss – 3.2 µg/g; Oberc-Dziedzic *et al.*, 2005).

The concentrations of Ge in the studied main rock-forming minerals of the rocks of the Karkonosze pluton (quartz, alkali feldspar, plagioclase, biotite) are presented in Table 3. The samples taken for the tests show a variable degree of differentiation (mixing and fractional crystallisation) of the granite/hybrid melt, i.e., variable enrichment in incompatible chemical elements. The content of mafic melt in granite samples is highest in porphyritic granites and lowest in equigranular granites. Enclaves show a high proportion of a crustal melt in a mixture of mafic and felsite melts (Słaby

Table 2

Germanium concentration in the rocks of the Karkonosze pluton.

Rock type (according to Słaby and Martin, 2008)	Locality	Ge [µg/g]	Source
Primitive porphyritic granite	Miłków, Poland [50°49′N, 15°46′E]	1.396 (±0.209) [a]	This study
Slightly evolved porphyritic granite	Michałowice, Poland [50°50′N, 15°35′E]	1.749	E. Słaby [b]
Evolved porphyritic granite	Szklarska Poręba Huta, Poland [50°50′N, 15°30′E]	1.530 (±0.230) [a]	This study
Porphyritic granite	KT-1 borehole, Karpniki, Poland [50°50′46.43″N, 15°50′53.54″E]	1.780 (±0.267) [a]	This study
Porphyritic granite (altered)	KT-1 borehole, Karpniki, Poland	1.453 (±0.218) [a]	This study
Equigranular granite	Szklarska Poręba Huta, Poland [50°50′N, 15°30′E]	1.887	E. Słaby [b]
Equigranular granite	Hašlerova Chata, Czechia [50°47′N, 15°31′E]	1.826 (±0.274) [a]	This study
Hybrid quartz diorite-granodiorite	Fojtka, Czechia [50°50′N, 15°04′E]	1.341 (±0.201) [a]	This study
Microgranular magmatic enclave	Karpacz (Mały Staw), Poland [50°49′N, 15°46′E]	1.401 (±0.210) [a]	This study
Microgranular magmatic enclave	Rudolfov, Czechia [50°47′N,15°06′E]	1.723	E. Słaby [b]
Composite dyke	Sokoliki Hills, Poland [50°52′N, 15°52′E]	1.726 (±0.259) [a]	This study

a – Uncertainty (expanded) of Ge concentration measurement (U = 15%); b – unpublished ICP-MS data.

Table 3

Germanium concentration in main rock-forming minerals of the Karkonosze pluton.

Host mineral	Rock type	Locality	Ge [µg/g]	Ge/Si [µM/M] [a]	Source
Quartz	Porphyritic granite	KT-1 borehole, Karpniki, Poland	0.779 (±0.117) [b]	0.64	This study
Quartz	Porphyritic granite (altered)	KT-1 borehole, Karpniki, Poland	0.710 (±0.107) [b]	0.59	This study
Alkali feldspar	Porphyritic granite	KT-1 borehole, Karpniki, Poland	1.320 (±0.198) [b]	1.69	This study
Alkali feldspar	Porphyritic granite (altered)	KT-1 borehole, Karpniki, Poland	1.251 (±0.188) [b]	1.60	This study
Alkali feldspar	Equigranular granite	Szklarska Poręba Huta, Poland	1.62 (±0.25) [c] [n = 9]	2.07	E. Słaby [d]
Alkali feldspar	Hybrid quartz diorite-granodiorite	Fojtka, Czechia	1.16 (±0.10) [c] [n = 15]	1.48	E. Słaby [d]
Alkali feldspar	Hybrid quartz diorite-granodiorite	Rudolfov, Czechia	1.21 (±0.29) [c] [n = 14]	1.55	E. Słaby [d]
Plagioclase	Porphyritic granite	KT-1 borehole, Karpniki, Poland	1.222 (±0.183) [b]	1.70	This study
Plagioclase	Porphyritic granite (altered)	KT-1 borehole, Karpniki, Poland	1.142 (±0.171) [b]	1.59	This study
Plagioclase	Equigranular granite	Szklarska Poręba Huta, Poland	1.05 (±0.42) [c] [n = 6]	1.46	E. Słaby [d]
Plagioclase	Hybrid quartz diorite-granodiorite	Fojtka, Czechia	1.12 [n = 1]	1.56	E. Słaby [d]
Plagioclase	Hybrid quartz diorite-granodiorite	Rudolfov, Czechia	1.22 [n = 1]	1.70	E. Słaby [d]
Biotite	Porphyritic granite	KT-1 borehole, Karpniki, Poland	3.917 (±0.588) [b]	9.01	This study
Biotite	Porphyritic granite (altered)	KT-1 borehole, Karpniki, Poland	3.015 (±0.452) [b]	6.94	This study
Biotite	Primitive porphyritic granite	Miłków, Poland	4.22 (±1.76) [c] [n = 12]	9.71	E. Słaby [d]
Biotite	Slightly evolved porphyritic granite	Michałowice, Poland	4.54 (±2.07) [c] [n = 19]	10.44	E. Słaby [d]
Biotite	Less evolved equigranular granite	Hraničná, Czechia [50°50´N 15°55´E]	5.33 (±1.77) [c] [n = 19]	12.26	E. Słaby [d]
Biotite	Microgranular magmatic enclave	Bukowiec, Poland [unknown coordinates]	5.06 (±3.59) [c] [n = 18]	11.64	E. Słaby [d]
Biotite	Microgranular magmatic enclave	Szklarska Poręba Huta, Poland	6.97 (±2.36) [c] [n = 22]	16.03	E. Słaby [d]
Biotite	Microgranular magmatic enclave, moderately dark	Szklarska Poręba Huta, Poland	4.96 (±1.67) [c] [n = 18]	11.41	E. Słaby [d]

Mineral phases	Ge [µg/g]	Ge/Si [µM/M] [a]	Source
Quartzes of granite	0.91; 0.83–0.94 [e] [n = 5]	0.75; 0.69–0.78	Waleńczak (1969)
Alkali feldspars of granite	2.4; 2.3–2.6 [e] [n = 4]	3.07; 2.94–3.32	Waleńczak (1969)
Plagioclases of granite	1.45; 1.2–1.7 [e] [n = 4]	2.02; 1.67–2.37	Waleńczak (1969)
Biotites of granite	4.33; 4.2–4.4 [e] [n = 4]	9.96; 9.66–10.12	Waleńczak (1969)
Quartzes in high-temperature pegmatites	0.95–2.4 [n = 7]	0.79–1.99	Waleńczak (1969)
Quartzes in middle-temperature pegmatites	1.5–5.2 [n = 8]	1.24–4.30	Waleńczak (1969)
Low-temperature quartzes	0.93–1.3 [n = 7]	0.77–1.08	Waleńczak (1969)
Quartzes in hydrothermal quartz veins	0.88; 0.63–1.2 [e] [n = 7]	0.73; 0.52–0.99	Waleńczak (1969)
Druse quartzes	1.11; 0.58–1.7 [e] [n = 5]	0.92; 0,48–1.41	Kozłowski (1973)
Vein quartzes	0.99; 0.61–1.3 [e] [n = 7]	0.82; 0.51–1.08	Kozłowski (1973)

a – Ge/Si [µM/M] ratio was calculated assuming an average composition of plagioclase (after data from Borkowska, 1966) and biotite (calculated after data from Słaby and Martin, 2008) in porphyritic granites; b – uncertainty (expanded) of Ge concentration measurement (U=15%); c – median and standard deviation; d – unpublished LA-ICP-MS data; e – mean and range.

and Martin, 2008). The Ge content of the rock-forming minerals shows variability. Germanium of granite quartz (0.71 and 0.78 µg/g) is lower, compared to alkali feldspars (1.16–1.62 µg/g) and plagioclases (1.05–1.22 µg/g). Ge concentrations for both types of feldspar have similar values, with alkali feldspars appearing slightly more enriched. Higher concentrations of germanium were found in biotites. Ge concentrations in porphyritic granite biotite (from 3.02 to 4.54 µg/g) are lower than in equigranular granite (5.33 µg/g). High variability is also shown by biotites from mafic enclaves, for which the Ge concentrations range are from 4.96 to 6.97 µg/g. Minerals separated from the altered porphyritic granite (KT-1 borehole, Karpniki) are depleted, compared to minerals of the unaltered granite, which is most evident in the case of biotite. The reduction in Ge concentration in quartz and feldspars is relatively smaller and within the measurement uncertainties.

Waleńczak (1969) provided the first, fairly broad insight into the germanium content of quartzes, alkali feldspars, plagioclases and biotites in the Karkonosze granite. The results obtained about Ge in quartzes, plagioclases and biotites in the present study are consistent with Waleńczak's data (Tab. 3). Only in the case of alkali feldspars Waleńczak (1969) reported higher concentrations (2.3–2.6 µg/g) than this study (1.25–1.62 µg/g).

The Ge concentration, encountered in the main rock-forming minerals of the Karkonosze pluton, does not exceed those reported in the literature. The mean Ge concentration in quartzes of other granites in the Bohemian massif varies between 0.40 and 3.0 µg/g, usually below 1.7 µg/g (Breiter *et al.*, 2013a).

Bernstein (1985) gives the range of Ge concentrations in the quartz of igneous rocks as 0.8–3.3 µg/g, which is similar to that of Ivanov (1996), who states the Ge concentration range in magmatic quartzes as 0.1–3.5 µg/g. On the basis of the compiled data (after Wittmann and Hörmann, 1972; Bernstein, 1985; Ivanov, 1996), the range of Ge concentrations in alkali feldspars, plagioclases and biotites of granitic rocks is 1–12 µg/g, 1–9.5 µg/g, and 1–8.5 µg/g, respectively.

Statistical analysis of hydrochemical data

Statistical tests help to identify the relationships of germanium to the elements, with which it is most closely associated geochemically. The studied thermal waters show both similarities and distinct differences in chemical characteristics. A set of 46 chemical analyses, including 40 parameters (variables) were used for statistical analyses. Only five (Li, Na, Si, Ge, and SO_4) of 40 variables meet Shapiro-Wilk normality test requirements.

Cluster analysis confirms the marked chemical distinctiveness of the water from intake no. 2 (in Cieplice) from the other thermal waters (Fig. 2). As for the waters from the other intakes, a bipartite distribution emerges: (1) the group including waters from KT-1 and ST-1 wells, and (2) the group including Cieplice waters from deep (C-1, C-2) and shallow (intakes nos. 1, 4–6) intakes. Both groups also are divided into two parts. The pattern, emerging from the clustering, appears to reflect the hydrogeological and hydrogeochemical conditions well.

Clustering makes it possible to distinguish five groups of cases in the data population, i.e., water samples from: (a) C-1 and C-2 intakes (Cieplice), (b) KT-1 (Karpniki), (c) ST-1 (Staniszów), (d) shallow intake no. 2 (Cieplice), and (e) other shallow intakes (intakes nos. 1, 4–6) at Cieplice. Owing to the lack of a normal distribution, non-parametric statistical tools were used. The non-parametric Kruskal-Wallis test shows that for the majority of the variables considered (physicochemical parameters), significant differences between the aforementioned five groups of cases occur (Supplementary material 1).

The Kendall's Tau test was used to assess the non-parametric rank correlation between the measured quantities (parameters). All correlation coefficients are given in Supplementary material 2. Germanium presents a relatively stronger rank correlation ($|\tau|$ above 0.25) with respect to 11 elements only (Fig. 3), i.e., the strongest positive correlation with Si, B and W, and the strongest negative correlation with V, P, Zn, U, Sb, Mg, NO_3 and Cu.

On the other hand, in the Factor Analysis (Supplementary material 3), Ge is included in factor no. 2 that combines Si, Ge, Na, SO_4 and Be (listed in the order of the factor load value). This group of solutes shows the relationship of Ge in the waters studied to the decay of silicate minerals (Si), probably mainly plagioclases (Na). The waters of alkaline pH studied easily achieve supersaturation with respect to calcite (section "Saturation state of thermal waters"), which effectively limits the activity of the calcium released, presumably mainly from plagioclases. Beryllium occurs in groundwater in very low concentrations; the average concentration in groundwater of the supergene zone is estimated to be 0.19 µg/L (Shvartsev, 2008). In the thermal waters studied, the Be concentration varies between <0.05 µg/L and 0.79 µg/L, mean 0.22 µg/L. Despite being in group 2 of the periodic table (alkaline earth metals), beryllium is a hard cation showing greater proximity to elements that form hydroxo- and oxo-hydroxo- complexes in aqueous solutions, such as Al and Si. In the case of the waters studied, this explains the close affinity of beryllium to silicon and, indirectly, to germanium. Sulphate is the second anion in thermal waters, next to hydrogencarbonates/carbonates. Sulphide sulphur occurs in waters at concentrations much lower than sulphate, usually below 0.7 mg/L (Tab. 1). The genesis of the sulphates in the JGS thermal waters has not been clarified, so far. They are most probably connected to the decomposition of sulphide minerals, which occur in the batholith and its metamorphic cover (Mochnacka *et al.*, 2015). The redox potential in deep thermal waters (C-1, C-2, KT-1, ST-1) is between -210 mV and -38 mV and usually is above the S^{+6}/S^{-2} redox pair equilibrium potential. The association of Ge with sulphates indicates a role in the decomposition of Ge-bearing sulphide minerals in supplying Ge to the waters studied. Relationships similar to those indicated above already have been reported between these elements in thermal waters. For instance, Pentcheva (1967) found the strongest positive correlations between Ge and such elements as Si, Na and W, accompanied by a strong negative correlation between Ge and Ca, in the thermal waters of Bulgaria.
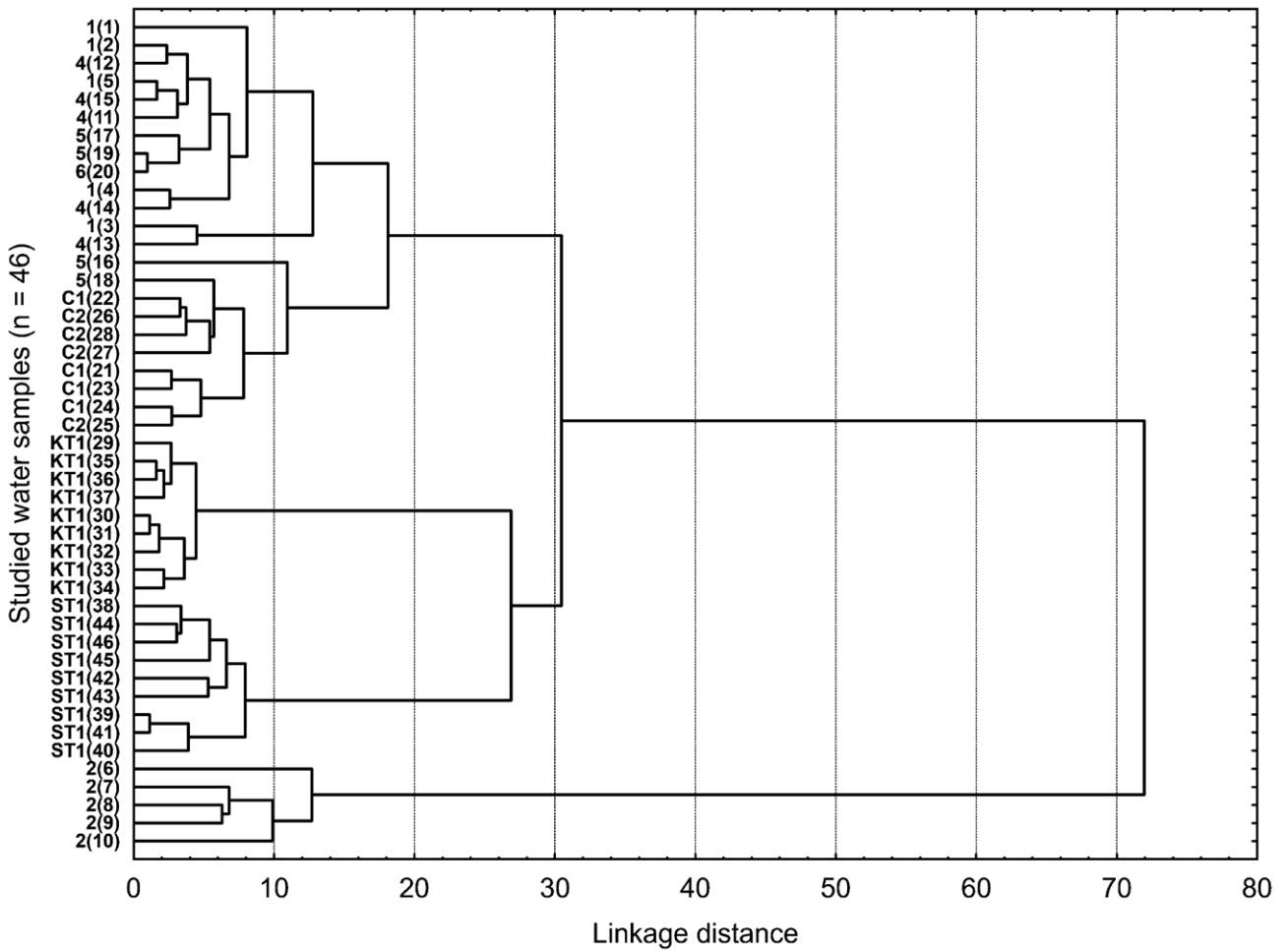
Fig. 2. Hierarchical clustering dendrogram of the thermal waters studied (Ward's linkage and Euclidean distances applied). Explanations: 1, 2, 4, 5, 6, C1, C2, KT1, ST1 – symbols of water intakes. The number in the bracket indicates the numbering of individual water sample.
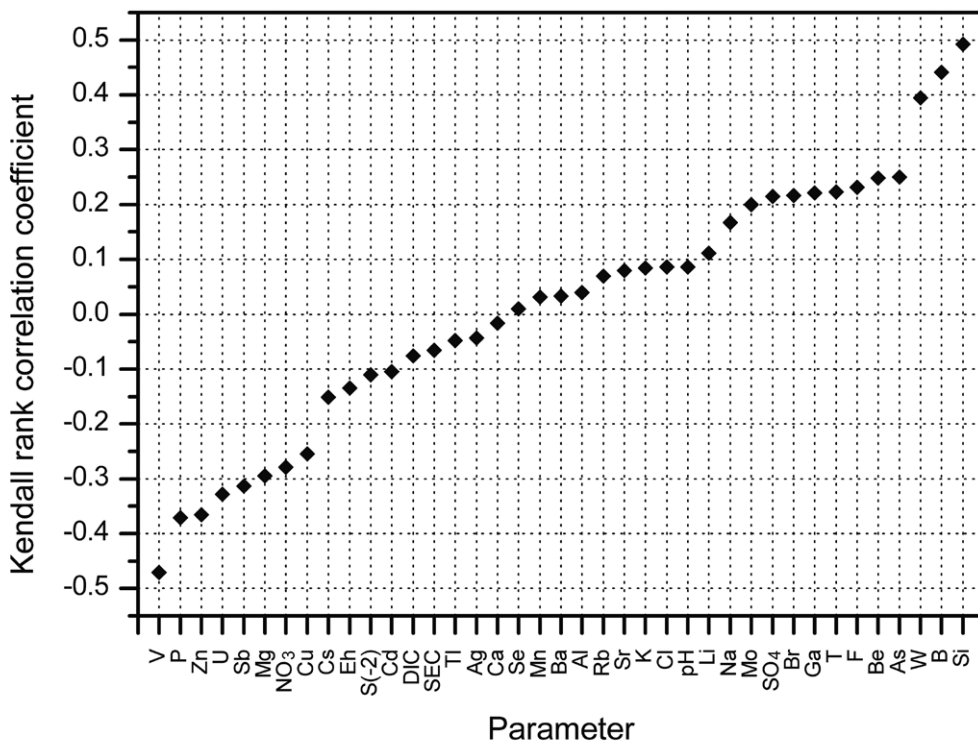

Fig. 3. Kendall rank correlation coefficients between germanium and various parameters.

Hydrochemical relations

The division of the waters studied into five groups (sub-populations) related to individual intakes, as well as other indications from statistical analyses, are confirmed by the relationships between constituents and physicochemical parameters. The search for interrelationships between the components was focused mainly, but not exclusively, on relationships (directly or indirectly) to germanium. Germanium concentrations in the waters studied, between 2.7 µg/L and 6.3 µg/L (Tab. 1), are at a level often noted in thermal waters, but it is not among the high concentrations in such waters. The Ge concentrations of tens to over two hundred µg/L sometimes have been found in mineral and thermal groundwater; a compilation of examples is given in Dobrzyński *et al.* (2018).

In the thermal waters studied, the higher the temperature, the greater the chance of encountering higher concentrations of germanium (Fig. 4). In deep waters at higher temperature (C-1, C-2, KT-1), germanium concentrations are less variable than in the waters at lower temperatures from shallow intakes (intakes nos. 1, 2, 4–6). This is probably due to the expected geochemical equilibrium in deep parts of the geothermal system, unlike that in shallow thermal waters, which are mixtures with modern cold waters and present a chemical non-equilibrium with the aquifer rocks. In the ST-1 water, the variation in Ge concentration is greatest, which is particularly noteworthy, given the depth of the intake (filtered at a depth of 1,360–1,405 m) and the confined nature of the aquifer. There was no apparent relationship between germanium concentration and pH in the waters studied and this is also in the case for redox potential (Supplementary material 4, Figs S1, S2).

It may be noted that studies of redox conditions also can provide information on the depth of groundwater exchange. In the waters studied, oxidizing conditions found only in waters from the shallow intakes (intakes nos. 1, 2, 4; Tab. 1), indicate that in other shallow waters (intakes nos. 5, 6), the share of the modern groundwater component is less. Even early assessment of the proportion of mixing water components (Ciężkowski and Szarszewska, 1978) also indicated that the highest proportion of waters with higher concentrations were in waters from intakes nos. 5 and 6. Redox potential would indicate that the proportion of modern waters in waters (intakes nos. 5, 6) is less than in the others and/or that the cold waters of the deeper circulation system are involved in the mixing.

Associations between germanium and a range of elements, such as V, Mo, W, B, Si, As, F, Cl, and Br, among others, have been found in many thermal waters. The relationship between germanium and silicon reveals the fundamental difference between the hydrogeochemical conditions occurring in the ST-1 water (Staniszów), and the other waters studied (Fig. 5). This indicates the lack of a relationship between Ge and Si source phases in the ST-1 water recharge and transit zones, which is puzzling, given the common geochemical affinity of Ge to Si. In the waters at Cieplice (C-1, C-2, 1, 2, 4, 5, 6) and Karpniki (KT-1), Ge positively correlates with Si. The high variability of the Si concentration in the Cieplice waters is due to the dilution of the thermal waters in varying proportions with cold fresh groundwater. The lowest Si concentrations in the no. 2 water may be caused by the fact that it is probably (Ciężkowski *et al.*, 1996) 100% modern water.

The positive correlations of Ge with boron (B) and tungsten (W), also indicated by statistics, differ in detail.
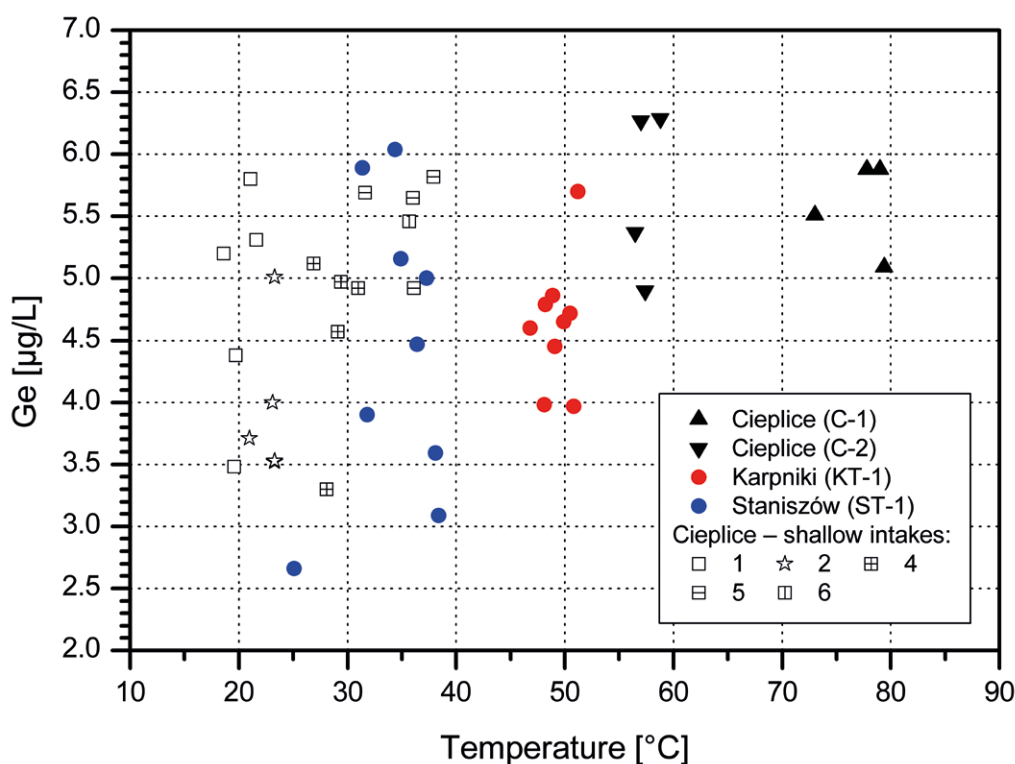

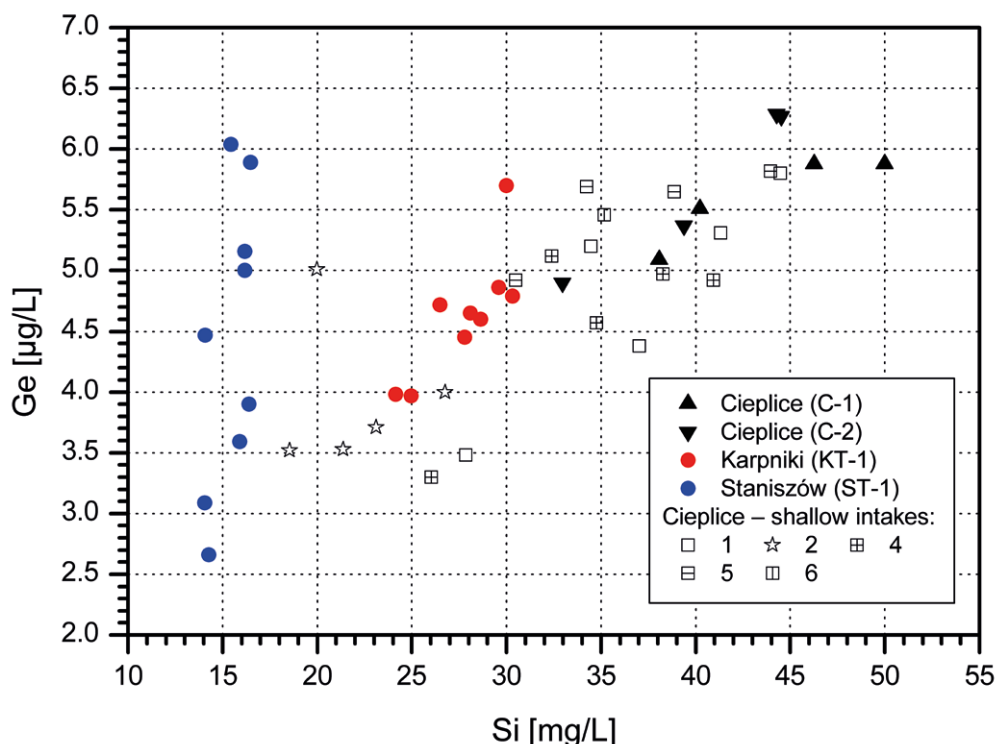**Fig. 4.**   Germanium concentration versus temperature in the thermal waters studied.

Fig. 5. Germanium concentration versus silicon concentration in the thermal waters studied.

The Ge-B relationship unifies all the waters studied, while the Ge and W relationship reveals marked differences between the waters (Supplementary material 4, Figs S3, S4). Naturally, a relationship between elements exhibiting close association may not be the result of a cause-and-effect relationship. The link of germanium migration to tungsten in thermal waters has long been pointed out (Kraynov, 1965; Pentcheva, 1975). However, there is a lack of in-depth, contemporary research on this topic. The relationship of Ge to Mo is similar in nature to Ge-W (Supplementary material 4, Fig. S5). The concentrations of Mo and W in thermal waters depend on the extent of water-rock interaction, which is determined by the temperature and age of the water (Arnórsson and Óskarsson, 2007). The highest Mo and W concentrations in the KT-1 water (Supplementary material 4, Fig. S6) do not confirm the decisive influence of temperature in this case. Of the main silicate rock-forming minerals, the sources of both elements (Mo, W) in the waters are most likely to be biotites, amphiboles, as well as calcic plagioclases, against which the waters are unsaturated (next section). The same minerals can also be sources of germanium.

Germanium shows a weak negative correlation with zinc (Supplementary material 4, Fig. S7), an element, to which it shows geochemical affinity, particularly in solid phases from reductive environments with elevated sulphide activities. The positive correlation between germanium and vanadium (V), indicated in the literature (e.g., Arnórsson, 1969), was not found in the thermal waters studied. The negative correlation between Ge and V, shown by Kendall's test (Fig. 3), does not imply the relationship valid for the entire data population, and this is because the clearly different relationship between the two parameters in the water no. 2 (Supplementary material 4, Fig. S8).

As far as the relationships between germanium and halides (F, Cl, Br) are concerned, the general positive relationship is only apparent for fluorides (Supplementary material 4, Figs S9–S11). The dissimilarity of water no. 2 becomes apparent for each halide (Supplementary material 4, Figs S12, S13). The deep thermal waters studied contain from 8.5 to 13.4 mg/L of F, shallow thermal waters between 7.2 and 12.0 mg/L, and water of no. 2 only 2.3–3.5 mg/L (Tab. 1). Mineral source phases for fluoride solute are proposed to be biotite and fluorite (next section).

The Cl/Br [M/M] ratio in the waters studied (varying between 113 and 1352; Tab. 1) is similar to the Cl/Br [M/M] ratio found in fluid inclusions extracted from hydrothermal quartzes of the Karkonosze massif (170–1200; Kozłowski and Karwowski, 1974). This indicates that, hypothetically, the main source of both anions in the waters could be salts mobilised from inclusions, which could be an alternative scenario to the influence of atmospheric deposition or halide release from micas. The F/Cl [mM/M] ratio in quartz from veins and pegmatites ranges between 0 and 44, whereas in quartz from granite it is between 12 and 210 (Kozłowski, 1978). The same F/Cl ratio in the deep thermal waters studied is much higher (393–895 mM/M; Tab. 1), indicating a significant supply of fluoride from other sources, such as biotite or fluorite.

Halides are very sensitive parameters of hydrogeochemical conditions. For example, the relationship to bromides with ionic strength in an excellent manner differentiates the waters studied (Supplementary material 4, Fig. S14). The halides in the JGS thermal waters require detailed study. The presence and role of the chloride-sodium component and halides in groundwater, occurring in the crystalline rocks of the Karkonosze-Izera complex, including

the Karkonosze granites, so far is poorly studied. The occurrence of such waters is evidenced by interesting recent finds of Na-(Ca)-Cl radon cold mineral water in two springs at Albrechtice near Frýdlant (Czechia) on the westernmost edge of this crystalline complex (Goliáš *et al*., 2014, 2022).

Owing to the strong affinity of Ge for Si, the Ge/Si ratio is a used measure of the behaviour and sources of both elements in near-surface environments. On the basis of the mean Si (31.13%) and Ge (1.4 µg/g) concentrations (Rudnick and Gao, 2014), the mean Ge/Si ratio in the Earth's upper continental crust is 1.74 µM/M. Fresh stream waters with low Ge/Si ratios, commonly below 1 µM/M, are depleted in Ge relative to bedrock (Mortlock and Froelich, 1987; Evans and Derry, 2002). The Ge/Si ratios in thermal waters are often higher, ranging from 2 to above 1000 µM/M (e.g., Criaud and Fouillac, 1986; Evans and Derry, 2002). In the

thermal waters studied the Ge/Si ratio varies between 45.5 and 151.3 (Tab. 1) and confirms a strong Ge enrichment, relative to bedrock and fresh water.

The Ge/Si versus Si concentration relationship reveals a clear bipartite nature of the waters studied (Fig. 6A). Thermal waters from Cieplice and Karpniki present a slight gradual decrease in the Ge/Si ratio with increasing Si, while the Staniszów water shows a large Ge/Si variation (72.1–151.3 µM/M) with almost constant Si concentration (average 15.44 mg/L). The quasi-constant concentrations of Si in the Staniszów water indicates the release of Ge from a non-silicate mineral (more reactive than silicates) into this water, even though temperatures are similar to those, found in the water from shallow intakes (Fig. 6B). The Ge/Si ratio does not show a relationship with pH or redox potential of the waters studied (Supplementary material 4, Figs S15, S16).
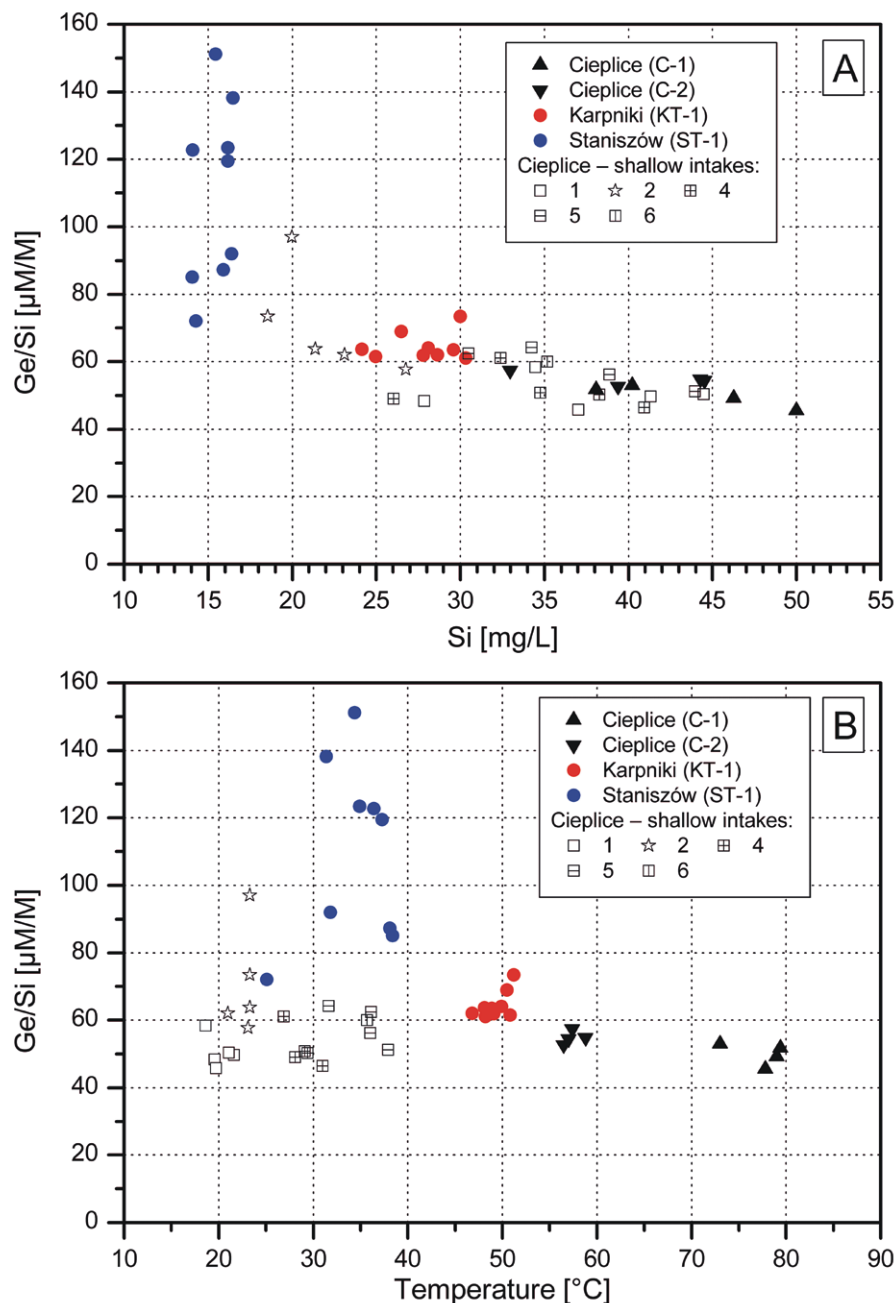

Fig. 6. Ge/Si ratio versus Si concentration (**A**) and temperature (**B**) in the thermal waters studied.

The focus was on the analysis of the relationships between germanium and selected elements, to which it usually shows a high affinity, like silicon, arsenic, zinc and iron. The ratio of germanium to the aforementioned elements may help to explain the origin of both germanium and these elements. By analysing the possible relationships between the ratios of Si to two different elements (e.g., Ge/Si versus Ge/As), basic conclusions can be drawn. Quasi-constant values of one of the Ge/X-element ratios indicate that: (1) two elements other-than-germanium originate from different source phases, and (2) germanium (principally) comes from the same phase as the second chemical element (included in a quasi-constant ratio). Secondly, the directly proportional relationship between Ge/X-element ratios indicates that: (1) both elements other-than-germanium probably were derived from the same phase (or phases), and (2) germanium might originate from the same phase(s) as (both?) elements other-than-germanium. Naturally, one should be aware that the patterns obtained may be influenced and obscured by other processes, such as the immobilisation of element(s) by sink phase(s) and/or dynamic equilibrium between reactions or processes, responsible for release into solution and those, which immobilise individual elements from a solution.

Diagrams of the relationship of germanium ratios to the elements (Si, As, Zn, and Fe) are presented in Supplementary material 5. These accounts, too, demonstrated significant similarities between the deep water of Cieplice (C-1, C-2) and the deep water of Karpniki (KT-1), and a clear difference between the water from Staniszów (ST-1) in relation to the two aforementioned waters. The diagrams show that in the deep thermal waters from Cieplice, Ge comes mainly from the same phase(s) as silicon, i.e., silicate minerals (Supplementary material 5, Figs S1–S3). The Ge/As – Ge/Fe and Ge/As – Ge/Zn relationships indicate that some Ge might also be provided by an As-bearing phase. The same conclusion can be drawn for the Karpniki water. The water from Staniszów reveals different patterns. Ge in this water could have originated from both the As- and Si-bearing source phases. Moreover, Ge also could have come from both the Si- and Fe-bearing phases. This could have been silicate minerals containing Fe (biotites, amphiboles). However, consideration of the possible role of Fe-bearing phases requires caution, given that the waters investigated are very poor in Fe. As many as 74% of the samples tested had Fe concentrations < DL (10 ppb), and 5 ppb Fe was used to calculate the ratio.

The range of values of the Ge/X ratio(s) can be a measure of the variability of hydrogeochemical conditions on the scale of the recharge area of an individual intake or on the scale of the entire aquifer under consideration. A broader analysis of the relationship between such ratios is proposed as a simple tool for deciphering the hydrogeochemical conditions.

Saturation state of thermal waters

The assessment of the saturation state of the studied thermal waters focused on the results for the main rock-forming minerals and those of the secondary and accessory minerals that tend to show enrichment in Ge, and those which were encountered in the aquifer under study. So far as regards the main granite-forming minerals are concerned, the thermal waters show supersaturation with respect to quartz, alkali feldspars and muscovite (Fig. 7). Plagioclases are unstable, owing to undersaturation with respect to the anorthite-end member (Fig. 8A), and the waters are undersaturated with respect to biotite (Fig. 8B).

Calcic amphiboles occur in the porphyritic granites and hybrid rocks. Using the thermoddem thermodynamic database, it was possible to calculate the saturation indices for two calcic amphiboles, tremolite, $(Ca_2Mg_5)Si_8O_{22}(OH)_2$ and ferrotremolite, $(Ca_2Fe_5)Si_8O_{22}(OH)_2$. Almost all deep waters and all shallow waters are undersaturated, relative to these amphiboles (Supplementary material 6, Fig. S1).

Secondary and accessory minerals, including ore minerals, present varying states of equilibrium with aqueous solutions. The waters investigated show supersaturation with respect to epidote, while the deep circulation waters (C-1, C-2, KT-1, ST-1) are undersaturated with respect to fluorite (Supplementary material 6, Fig. S2). Waters that are a mixture of deep circulation thermal water and shallow cold waters are enriched in Ca (Tab. 1) and show equilibrium or even supersaturation with respect to fluorite. Deep circulation thermal waters contain markedly elevated concentrations of fluoride (8.5–13.4 mg/L; Tab. 1), which is an important component that gives the waters at Cieplice their therapeutic value. The origin of fluoride in the hydrogeochemical system studied still needs to be investigated. Kozłowski and Matyszczak (2022) report that biotites contain between 0.49 and 0.85 wt.% of fluorine, and are the main F-carrier mineral in Karkonosze granite. Following these findings and the state of saturation, it can be assumed that unstable biotites are the main mineral source-phases supplying fluoride to the studied thermal waters. However, the role of dissolving fluorite as an F-source phase is also a possibility.

Deep circulation waters (C-1, C-2, KT-1, ST-1) are supersaturated, relative to pyrite, while most shallow thermal waters are undersaturated, relative to it (Supplementary material 6, Fig. S3). The studied waters are strongly undersaturated, relative to arsenopyrite. All the thermal waters studied are significantly supersaturated, relative to other major sulphides, as sphalerite (SI between 3.0 and 6.8), chalcopyrite (SI 7.0 to 15.2), galena (SI 1.9 to 5.1), and bornite (SI 18.0 to 41.0). Deep-circulation thermal waters also show supersaturation with respect to calcite (Supplementary material 6, Fig. S4), which is favoured by the alkaline environment.

Potential equilibrium model for controlling germanium

The thermal waters studied can be divided into two main groups, deep-circulation old waters (from intakes C-1, C-2, KT-1, ST-1) and thermal waters with a modern water component (from shallow intakes at Cieplice). It can be assumed that the waters of the first group, owing to their age, present conditions of chemical equilibrium with the aquifer rocks.

Considering the theoretical temperature-dependent equilibrium model of water with Ge-containing quartz (proposed by Evans and Derry, 2002), the temperature dependence of the Ge/Si ratio is observed in deep circulation geothermal
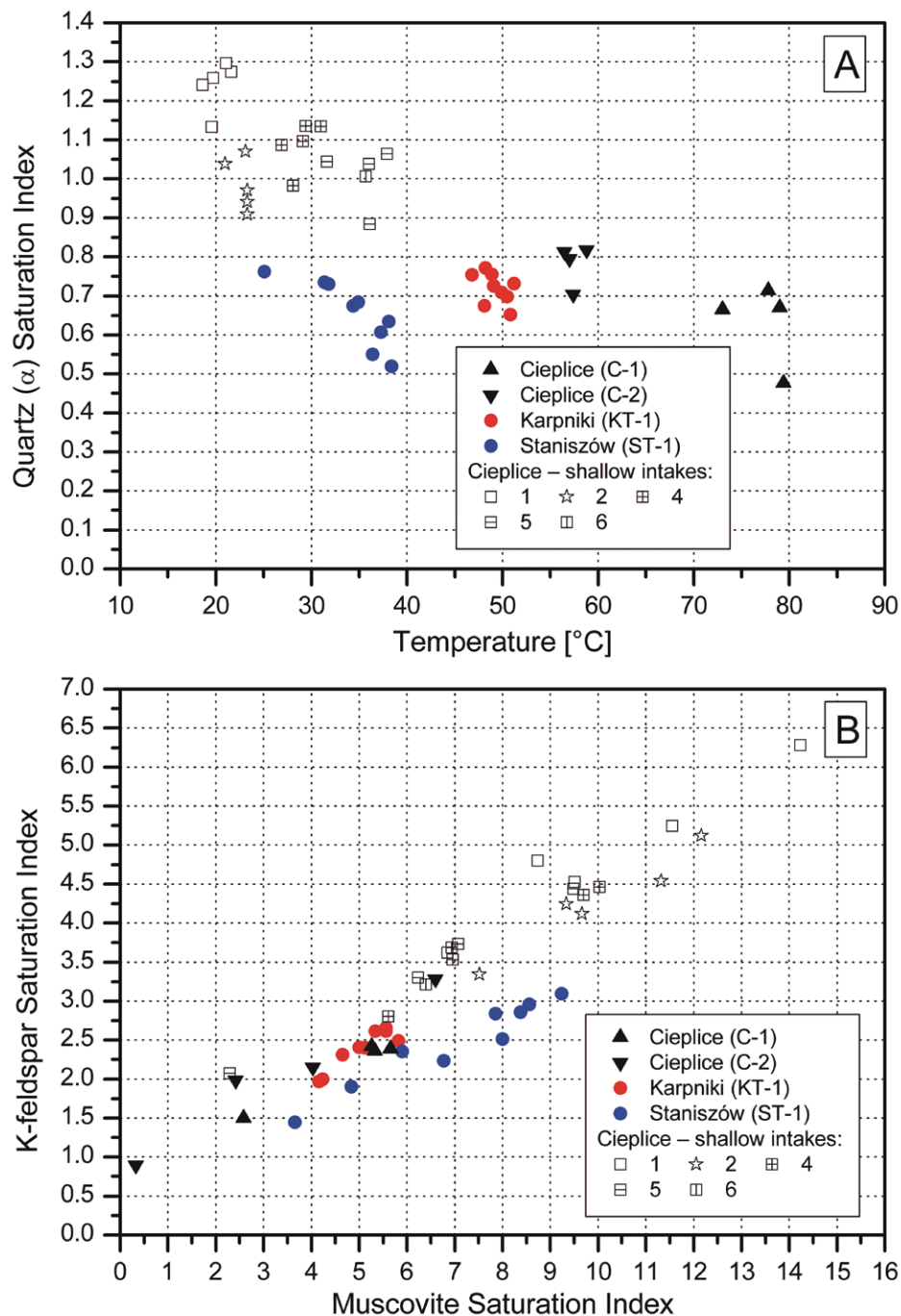
Fig. 7.   Saturation index (SI) of thermal waters with respect to quartz versus temperature (**A**), and for K-feldspar versus muscovite (**B**).

waters from Cieplice (C-1, C-2) and Karpniki (KT-1; Fig. 9). In a compatible model, the Ge content of the controlling quartz should average around 1.5 µg/g. The various types of quartz from the Karkonosze pluton contain from 0.6 to 5.2 µg/g of Ge (Tab. 3). Karkonosze granite quartzes have 0.7 to 0.9 µg/g, hydrothermal vein and druse quartzes - 0.6–1.3 µg/g, while the greatest diversity is represented by pegmatite quartzes (1.0 to 5.2 µg/g Ge). Solubility control by quartz containing Ge at 1.5 µg/g is realistic and plausible, as the eastern part of the Karkonosze pluton through which transit paths of the Cieplice and Karpniki groundwaters run is much richer in pegmatites than the central and western parts of the pluton (Aleksandrowski *et al.*, 2019).

The highly variable Ge/Si ratio in the Staniszów ST-1 water (72.11–151.25 µM/M) is not consistent with the quartz equilibrium model, which is a further argument for concluding that the germanium in this water is probably derived mainly from a non-silicate mineral phase. The relatively lower Ge/Si ratios in waters from shallow intakes are due to the mixing of geothermal water with cold groundwater.

Concluding discussion

The recharge area of the deep, old thermal waters at both Cieplice (C-1, C-2) and Karpniki (KT-1) has been proposed in the mountain range of Rudawy Janowickie (Ciężkowski
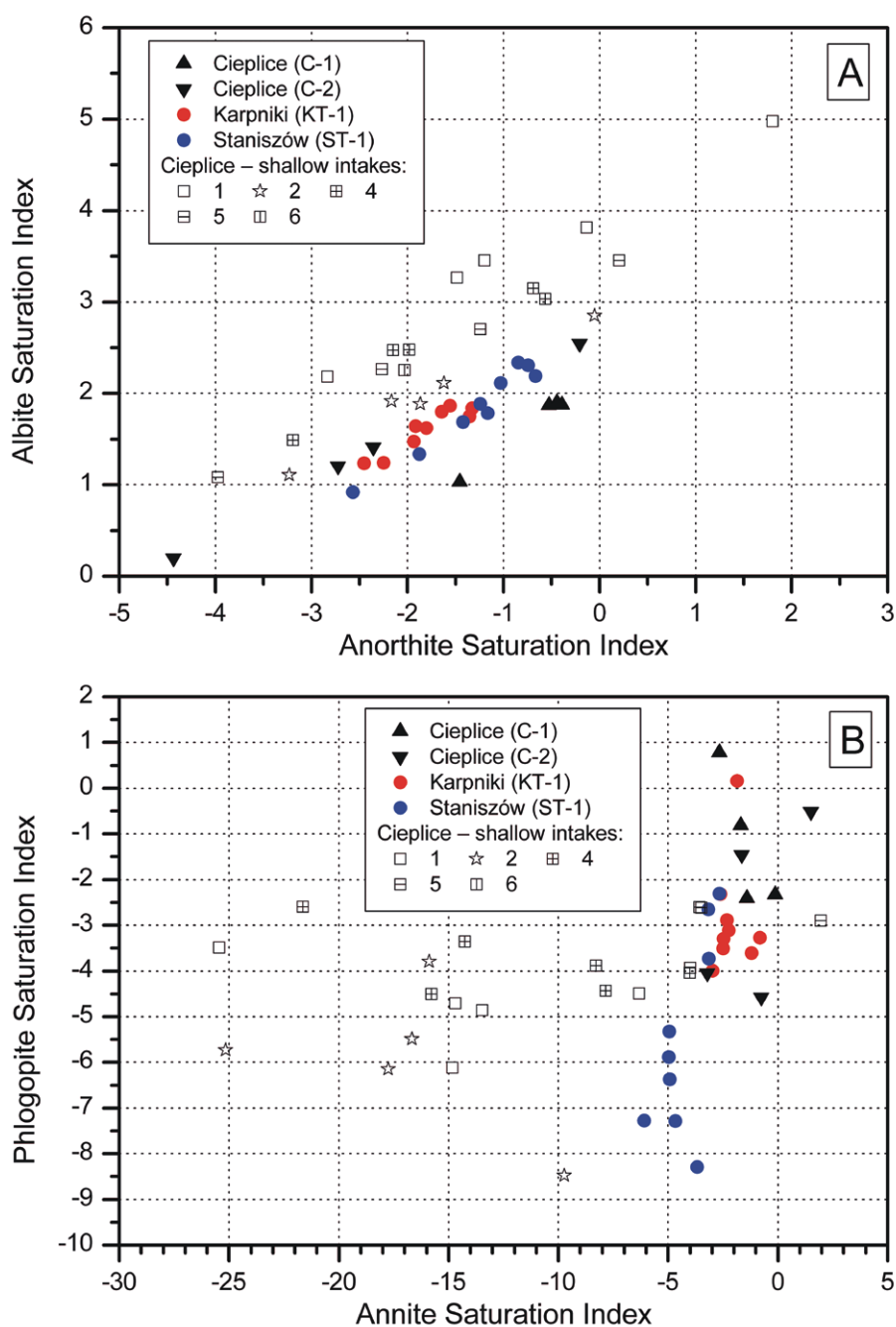
Fig. 8.   Saturation indices of thermal waters. **A.** Albite versus anorthite. **B.** Phlogopite versus annite.

et al., 1996; Łukaczyński and Polaczek, 2014a), located on the eastern edge of the Karkonosze pluton. In Karpniki, which is closer to the Rudawy Janowickie Mountains than Cieplice, the water temperature (50 °C) is lower than at Cieplice. Originally, the highest temperature after drilling was 68 °C in C-2 and 87.8 °C in C-1; while thermal logging in C-1 revealed 97.7 °C at 1,870 m. (Dowgiałło, 2000). Both the KT-1 and C-1 waters have artesian flow. Elemental relationships and saturation indices indicate that ferromagnesian minerals (biotites and amphiboles) of the porphyritic granite are important source phases for germanium in these waters. Another confirmation of biotite as an important Ge-source is provided by the marked depletion of altered biotite in germanium (Tab. 3). However, the temperature-dependent

equilibrium model shows that germanium activities in the deep thermal waters of Cieplice and Karpniki are controlled by the solubility of germanium-containing quartz (most likely at a Ge content of about 1.5 µg/g).

The waters of the shallow intakes at Cieplice (intakes nos. 1, 2, 4–6) have temperatures between 19 °C and 38 °C. A common feature of these waters is that they contain a proportion of modern water components. As a result, the characteristics typical of deep thermal waters are somewhat obliterated in them and the concentrations of a number of constituents, especially trace elements, and temperature are reduced. The shallow waters are distinguished chemically from the deep old waters, also clearly shown in the results of the statistical analyses. The next consequence of

mixing is that the shallow waters do not present a chemical equilibrium with regard to minerals. The concentration of germanium in the shallow Cieplice waters (3.3–5.8 µg/L) is only slightly lower than in the deep Cieplice waters (4.9–6.3 µg/L). However, the concentration of germanium in the former is probably not due to control by the mineral phases but is the result of a dynamic equilibrium between the mixing water components. This is confirmed by the Ge/Si ratio values, lying below the 1.5 µg/g solubility line (Fig. 9).

In the group of shallow waters, water from intake no. 2 stands out clearly, which is also very evident in the results of the statistical analyses. This water is probably 100% modern water (Ciężkowski *et al.*, 1996). The dissimilarity of the composition of water no. 2 is very intriguing, when it is compared with the composition of waters of other shallow intakes (intakes nos. 4, 5, 6), located nearby, on the same local fault (Fig. 1). The next interesting feature is that water no. 2 shows some geochemical similarities to the old Staniszów water. The germanium in water no. 2 is probably derived from ferromagnesian minerals (biotites, amphiboles), although the influence of sulphide phases cannot be excluded. The chemical composition of water no. 2 may be influenced by hybrid rocks, probably lamprophyres, the presence of which in this part of the batholith was confirmed in the nearby boreholes C-1 and C-2.

The ST-1 intake is deep (well to 1,501 m), but the water temperature at the outflow (median 35.7 °C) is surprisingly low, when compared with the deep waters of Cieplice and

Karpniki. The maximum temperature found at the bottom of this borehole was 45.1 °C (Łukaczyński and Polaczek, 2014b). The relatively reduced temperature, measured at the surface may have been somewhat influenced by the fact that the borehole was operated intermittently between 2015 and 2021, mainly during the autumn and winter seasons. However, the low yield of the borehole also may have had an influence. An expression of the hydrogeological conditions prevailing in the active zone of the ST-1 well, is the very low specific discharge of the well (0.21 m³/h/1mS; with well discharge Q = 20.5 m³/h and depression S = 97.4 m (Łukaczyński and Polaczek, 2014b). The concentration of germanium in ST-1 water shows greater variability (2.7–6.0 µg/L) than totally in the other deep waters studied (4.0–6.3 µg/L). A characteristic feature of the ST-1 water is that the variability in Ge concentrations occurs with quasi-stable values of other important parameters, such as temperature and dissolved silicon concentration. The next notable feature of the composition of the ST-1 water is that germanium shows a strong correlation with arsenic.

Analysis of the Ge/Si ratio and the Ge relationship with other elements indicates that Ge in ST-1 water is not mainly derived from silicate mineral phases, and that its activity is not controlled by the solubility of a silicate mineral phase such as quartz. It is hypothesised that the source of Ge in this water is probably an arsenic-bearing sulphide mineral, perhaps arsenopyrite. The germanium content of arsenopyrite is reported to range from 0.1 to 6 µg/g (Ivanov, 1996).

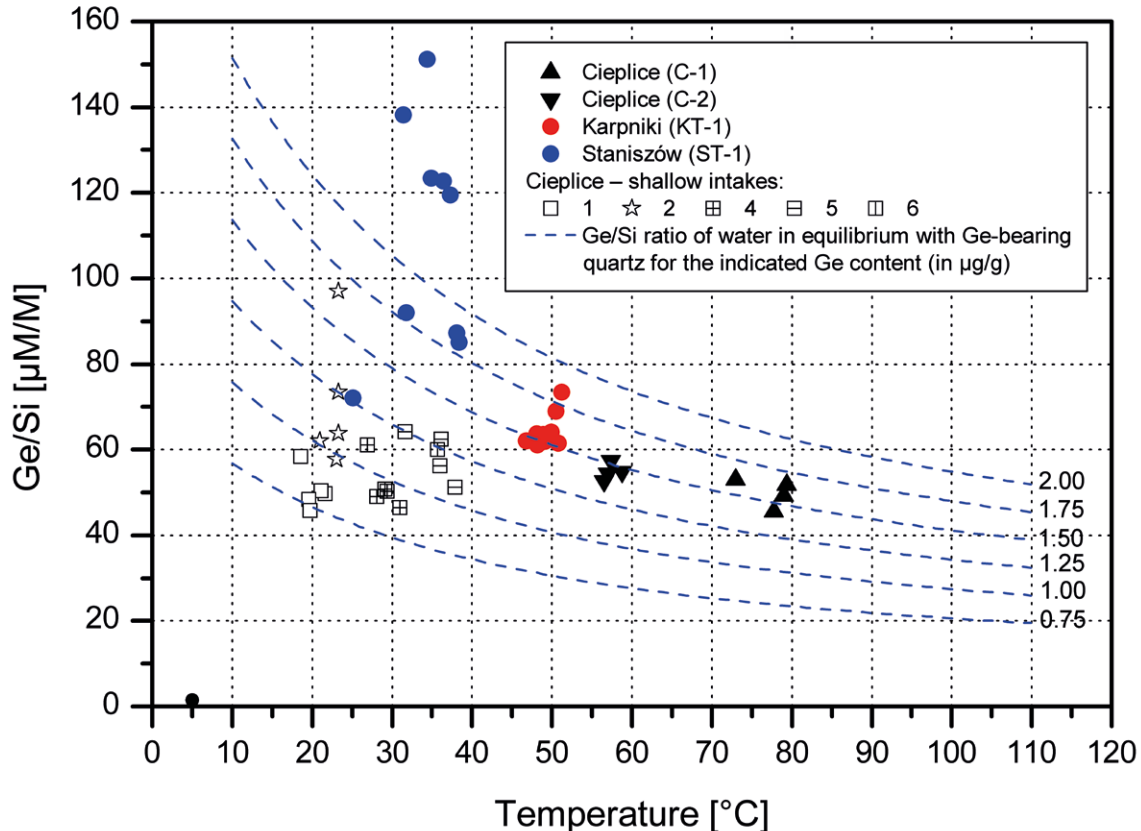**Fig. 9.** Ge/Si (µM/M) ratio versus temperature in the thermal waters studied in relation to Ge/Si of fluid in equilibrium with Ge-bearing quartz. The Ge/Si equilibrium curves were calculated by using PHREEQC programme with the thermoddem database. The average value of the Ge/Si ratio (filled circle) in cold fresh waters from springs located in Rudawy Janowickie Mountains (in the presumed thermal water recharge zone) is shown for comparison.

The Staniszów water is richer in hydrogen sulphide than other waters (Tab. 1). The significant changes in S^{-2} concentration (0.33–5.30 mg/L) in the ST-1 water may have been due to the impact of periodic operating conditions (yield changes), indicating that reactions with sulphide minerals take place at a short distance in the active zone of the well.

In addition to biotites, amphiboles common in porphyritic granites may be a possible source of Ge. Biotites and amphiboles are more abundant in hybrid rocks than in porphyritic granites. Ge concentrations in amphiboles (mainly hornblende) of granitoids are given between 1.6 and 3.4 µg/g, average 2.4 µg/g (Lyakhovich, 1972). Leaching experiments on crystalline rocks (granite, pegmatite, gneiss) and their main rock-forming minerals, using alkaline solutions of a composition mimicking that of common thermal waters (Na-HCO$_3$, Na-HCO$_3$/CO$_3$, Na-SO$_4$-HCO$_3$/CO$_3$), have shown that Ge is supplied to the solution mainly by the decomposition of biotites, amphiboles and muscovites (Pentcheva, 1973).

In the case of the ST-1 water, the possibility that some Ge is derived from ferromagnesian minerals (biotites, amphiboles) cannot be dismissed. On the one hand, this would explain the association of Ge with Fe indicated by the GeX$_1$-GeX$_2$ type relations (section "Hydrochemical relations" and Supplementary material 5). On the other hand, it could indicate the presence of hybrid rocks in the ST-1 well active zone.

Throughout the profile of borehole ST-1, porphyritic granite, with several zones of fine-grained equigranular granite, pegmatites and quartz veins were noted. The borehole is filtered at a depth of 1360–1405 m. However, the petrographic description of the granite core samples relates only to three zones between depths of 194 and 605 m and does not provide information on the presence of ore minerals (Łukaczyński and Polaczek, 2014b). Of the sulphide minerals, for which it was possible to calculate the saturation state, only arsenopyrite shows undersaturation in deep thermal waters, including the ST-1 water (Supplementary material 6, Fig. S3). Arsenopyrite is sometimes found in the form of ore mineralisation, disseminated throughout the Karkonosze granite and related to magma intrusion. However, primarily it occurs in vein-type and disseminated, polymetallic mineralisation of Cu, As, Fe, Bi, Au, Sn, W, and U associated with (pneumo)hydrothermal activity (Mochnacka *et al.*, 2015). Arsenopyrite has been found in abandoned mines, prospects, and mineral occurrences in the Kowary-Karpacz area, which are located in the probable recharge zone of the ST-1 well.

CONCLUSIONS

A study of germanium in the rocks and minerals of the Karkonosze pluton and thermal waters of the Jelenia Góra geothermal system was carried out. Germanium concentrations ranging from 1.40 to 1.89 µg/g were found in granites, with 1.34–1.73 µg/g of Ge occurring in hybrid rocks. Ge concentrations in the main rock-forming minerals, i.e., quartzes, alkali feldspars, plagioclases, and biotites, lie in the ranges of: 0.71–0.78 µg/g, 1.16–1.62 µg/g, 1.05–1.22 µg/g and 3.02–6.97 µg/g, respectively.

Interpreting a large set (n = 46) of chemical analyses of thermal waters, it can be concluded:

1. The concentration of germanium in the thermal waters of the Jelenia Góra geothermal system is between 2.7 and 6.3 µg/L.

2. In the deep old thermal waters at Cieplice and Karpniki (intakes C-1, C-2, KT-1), germanium is derived from silicate mineral phases (most probably biotites and amphiboles) and its activity is controlled by the solubility of Ge-bearing quartz.

3. The chemical composition of the shallow thermal waters at Cieplice (intakes nos. 1, 2, 4–6) results from the mixing of deep old thermal waters with modern cold waters. This results in differences from the deep thermal waters at Cieplice. Germanium in the shallow waters is mainly derived from silicate mineral phases. However, its concentrations are the result of the mixing of the two above-mentioned water components, so that they do not show chemical equilibrium with aquifer minerals, including Ge-bearing quartz.

4. The deep old thermal water at Staniszów (ST-1) shows a significant difference in terms of many physicochemical parameters from the other waters. Germanium in this water probably comes mainly not from the silicate mineral phases, but from the As-bearing sulphide phase(s). It is hypothesised that the probable main source mineral phase is arsenopyrite. However, in the case of this water, the possibility that some Ge is derived from ferromagnesian minerals (biotites, amphiboles) cannot be fully dismissed. This would explain the association found of Ge with Fe, and indicates the presence of hybrid rocks in the ST-1 well active zone.

5. The modern water from shallow intake no. 2 at Cieplice, apart from its similarities to other shallow waters of Cieplice, shows a number of chemical dissimilarities. The composition of this water might be formed by the influence of the aquifer rocks, which have a distinctly different composition to the porphyritic granite, as is the case with the other Cieplice waters and Karpniki waters. The chemical composition of water no. 2 may be influenced by hybrid rocks, probably lamprophyres, the presence of which in this part of the batholith was confirmed in the nearby boreholes C-1 and C-2. Despite significant differences, water no. 2 shows puzzling chemical similarities to the old water from the ST-1 intake (at Staniszów). Ge in water no. 2 is presumably derived mainly from ferromagnesian minerals (biotites, amphiboles). The significant fluctuations in Ge concentration and other parameters indicate that they are due to the influence of dynamic equilibrium in the active water turn-over zone, rather than a chemical equilibrium.

6. The equilibrium of the deep thermal waters with Ge-bearing quartz could be a useful tool in future regional analyses of this geothermal system.

7. In terms of hydrogeochemical conditions, the Jelenia Góra geothermal system can be regarded as a mosaic-like area, with a significant influence of local conditions. This is illustrated particularly by the waters from intake ST-1 at Staniszów and intake no. 2 at Cieplice. In addition to lithological variation, tectonic conditions and significant

batholith dislocation are largely responsible for the hydrogeochemical mosaic.

8. It should be emphasised that owing to the small number of thermal water intakes, the geochemical recognition of Jelenia Góra geothermal system is still very sparse, which prevents its satisfactory hydrogeochemical characterisation. More extensive geochemical studies of the minerals, including accessory and ore minerals, are also required.

Contributions

Conceptualisation, DD; Methodology, DD, KT, JK, AT, ES; Field works and water lab analysis, DD, MS; Rock and mineral analysis, KT, JK, AT, ES; Chemical modelling, DD; Modelling validation, DD; Statistical analysis, DD; Writing – original draft, DD, KT; Writing – review and editing, DD, KT, MS, JK, AT, ES; Visualisation, DD, MS. All authors have read and agreed on the version of the manuscript submitted for publication.

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