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The main hydrogeochemical processes affecting the composition of certain naturally carbonated waters of southwestern Poland

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Kłodzko region is a historical region in southwestern Poland, cutting into the territory of the Czech Republic. In geological terms, it contains (within the Polish borders) the Upper Nysa Kłodzka Graben and the Orlica–Śnieżnik Metamorphic Unit. The region abounds in naturally carbonated waters, whose composition is dominated by HCO_3^-, Na^+, Ca^{2+} and Mg^{2+} ions. This study concerns the chemical composition of waters from particular intakes situated in Kudowa-Zdrój, Jeleniów, Duszniki-Zdrój, Polanica-Zdrój and Gorzanów. Chemical data were analysed mathematically and by hydrochemical modelling performed with the help of the *AquaChem5.1* and *PhreeqC* codes. The chemical composition of the waters studied is shaped chiefly by hydrolysis of aluminosilicates. The major ion composition is also influenced by ion exchange (adsorption and desorption) with and dissolution of carbonate minerals. Analysis of saturation indexes showed that these waters are in equilibrium with kaolinite. Generally speaking, the chemical composition of waters in this region is determined by dissolution and precipitation of carbonates (mostly secondary) and aluminosilicates in the presence of carbon dioxide, as well as by ion exchange.

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Key words: Poland, Kłodzko Region, groundwater, ion exchange, water-rock interaction, mineral equilibrium.

INTRODUCTION

The occurrence of mineral waters across Kłodzko Region was described as early as in the early 20th century. Detailed research into the hydrogeological conditions was not launched until the 1960s. This is when, based on Frech's hypotheses (1904, 1912), Fistek (1977) proposed a pattern of mineral water and carbon dioxide (CO_2) migration in this part of the Sudetes.

The area discussed contains two large tectonic units: the Orlica–Śnieżnik Metamorphic Unit and the Upper Nysa Kłodzka Graben (Fig. 1). The former is built chiefly of metamorphic rocks of amphibole facies. These are mostly Paleozoic rock complexes: mica, mica-graphite, quartzite, carbonate and chlorite schists, quartzites and crystalline limestones, amphibole rocks, as well as gneisses and granite-gneisses (Żelaźniewicz, 2003). Don (1996) classified these rock units into one very large rock formation (Liber and Kiełczawa, 2009). It should be added that gneisses around Duszniki-Zdrój contain large amounts of secondary calcite, iron compounds (hematite), plagioclase (commonlly completely replaced by calcite), and kaolinized potassium feldspar (Fistek and Fistek, unpubl.).

In the northwestern part of the Orlica–Śnieżnik Metamorphic Unit, in the area of Kudowa-Zdrój, there are two smaller tectonic units, the Kudowa granitoid and the Kudowa depression. The elongated granitoid delimits a subsidence basin, filled with Permian and Upper Cretaceous strata, situated to the east. The Permian is represented by sandstones and conglomerates (Tęsiorowska and Fistek, 1971).

The Upper Nysa Kłodzka Graben is a unit filled with Upper Cretaceous strata (Cenomanian, Turonian and Coniacian). The Cenomanian deposits are chiefly of sandy facies. In the bottom part, these are clay-calciferous sandstones, with underlying quartz conglomerates. The next unit comprises quartz sandstones, the "lower jointed sandstones". The upper Cenomanian is represented by marly sandstones (Radwański, 1975). These are overlaid by Turonian strata, predominantly clay and clay-silicic marls interstratified with jointed sandstones, and interbeds of sandy marls, claystones and sandy limestones. The Coniacian succession is dominated by flysch deposits: alternating sandstones, mudstones and claystones.

Neogen and Paleogen deposits in the area of Kłodzko Region comprise varved clays (Kiełczawa, 2001*a*).

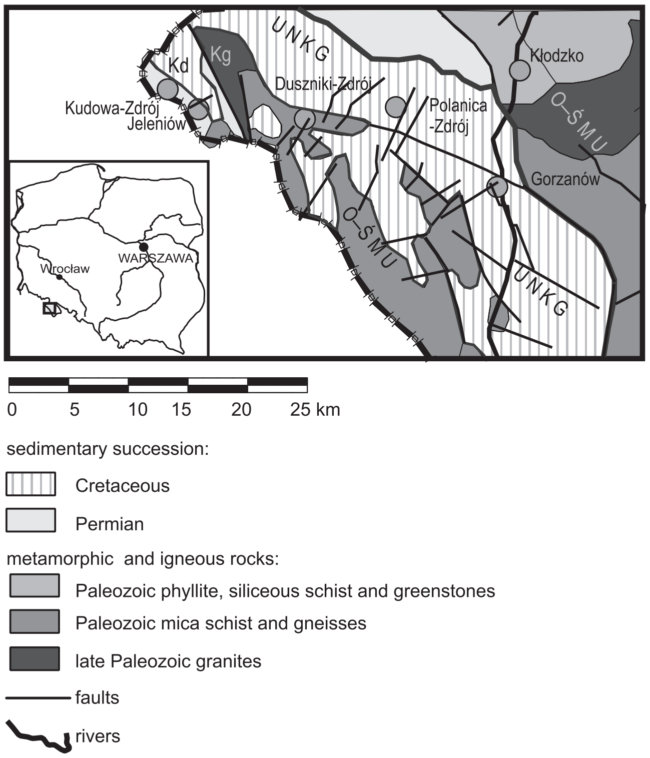

Fig. 1. Simplified geological sketch-map of the research area with location of the health resorts (on base Sawicki *et al.*, 1986)

UNKG – Upper Nysa Kłodzka Graben; O-ŚMU – Orlica-Śnieżnik Metamorphic Unit; Kg – Kudowa granitoid; Kd – Kudowa depression

Quaternary deposits form a discontinuous cover of post-glacial, fluvioglacial, fluvial, slope and aeolian sediments.

The present arrangement of tectonic units in Kłodzko Region reflects uplift contemporaneous with and following deposition of the sediment infill of the Upper Nysa Kłodzka Graben (Oberc, 1972).

The units discussed are separated by fault systems. Important faults, such as the NW–SE oriented Pstrążna–Gorzanów Fault, also intersect Cretaceous deposits within the Upper Nysa Kłodzka Graben. It is generally accepted that this is a dislocation zone built of two roughly parallel faults, displacing the sedimentary cover together with its crystalline bedrock (Fistek, 1977). The crystalline formations have been uplifted to form a horst. In the literature, this zone is also referred to as the Duszniki-Zdrój–Gorzanów–Waliszów Fault (Don, 1996). It is the southeastern part of a discontinuity stretching from Hronov (on the Czech side) through Pstrążna and Kudowa-Zdrój to Gorzanów (Kiełczawa, 2005).

The present investigations are based a chemical analyses of waters from particular intakes in Kudowa-Zdrój, Jeleniów, Duszniki-Zdrój, Polanica-Zdrój and Gorzanów. Groundwaters from these places have been classified as medicinal and potentially medicinal (Dz.U. nr 32, poz. 220 z 2006 r.). In chemical terms, they are all naturally carbonated waters varying in the contents of principal cations. In Duszniki-Zdrój there are calcium-sodium-magnesium (boreholes: Jan Kazimierz, No. 39, Agata, Pieniawa Chopina, B-1 and B-4) and calcium-magnesium (B-2, B-3 and Zimny Zdrój boreholes) carbonated waters. Sodium-calcium carbonated waters are characteristic of Kudowa-Zdrój (K-200, Marchlewski boreholes and Górne intake) and Jeleniów (Sarenka intake) and in the former place there are also calcium-sodium carbonated waters (Śniadecki and Moniuszko intakes). The waters in Polanica-Zdrój and Gorzanów, on the other hand, (Fig. 2) are dominated by calcium (Józef II, Żelaziste, Józef Stary) and calcium-sodium carbonated waters (Wielka Pieniawa, P-300 and Józef I boreholes and the bottom water level in borehole No. 5 in Gorzanów), as well as calcium bicarbonate waters (Kaczka, No. 2, 3, 4, 4a, b, 6, 7M and 10R boreholes). These carbonated waters are drawn from Permian (in Jeleniów) and Upper Cretaceous deposits (Polanica-Zdrój, Kudowa-Zdrój, Gorzanów except for the bottom level in intake No. 5). The intakes in Duszniki draw waters from Paleozoic crystalline rocks.

The chemical types of waters in Duszniki-Zdrój and their position on a Piper diagram suggest they should be regarded as “transitional”, between the waters of Kudowa-Zdrój and Polanica-Zdrój and Gorzanów.

RESULTS AND DISCUSSION

It was decided that amongst all medicinal and potentially medicinal waters found in Kłodzko Region, only those mentioned above would be analysed, as their source deposits are found in similar tectonic conditions and lie close to each other. Moreover, the availability of analytical results concerning the physicochemical properties of waters, provided by the Kłodzko Health Resorts Group Joint Stock c.o., was also significant.

Analyses of waters from particular localities (Fig. 3) demonstrate that the highest amount of total dissolved solids (TDS) can be found in naturally carbonated waters from Kudowa-Zdrój (K-200, Moniuszko, Śniadecki). Carbonated waters from Duszniki-Zdrój (Agata), and Polanica-Zdrój (P-300) come next. Carbonated waters from the Kaczka intake in Gorzanów has the chemical composition closest to that of rainwater.

As for the ionic composition, the highest amounts of sodium are characteristic of waters from Kudowa-Zdrój (K-200, Moniuszko, Śniadecki), then from Duszniki-Zdrój (except for intake B-3), Jeleniów, Polanica-Zdrój and Gorzanów. The lowest contents of sodium (*ca.* 30 mg/L) are found in waters from intake B-3 in Duszniki-Zdrój. The highest concentrations of calcium ions are recorded in waters from Polanica-Zdrój (P-300, Wielka Pieniawa) and Duszniki-Zdrój (Agata, Pieniawa Chopina), then Gorzanów and Kudowa-Zdrój (Marchlewski and Górne). The least calcium is contained in waters from the Kaczka intakes – *ca.* 70 mg/L (in Gorzanów) and waters from Jeleniów (J-150 – *ca.* 85 mg/L). The highest amounts of chlorine have been observed in waters from Kudowa-Zdrój. Relatively high concentrations (up to *ca.* 62 mg/L) of this ion have also been observed in Gorzanów. The waters of Kudowa-Zdrój, Duszniki-Zdrój and Jeleniów are also characterized by the highest contents of metasilicic acid, while there is much variation in the concentration of this component in waters from Duszniki-Zdrój. Genarally speaking, when analysing the concentrations of metasilicic acid and the total dissolved forms of inorganic carbon (TDIC), one can ob-

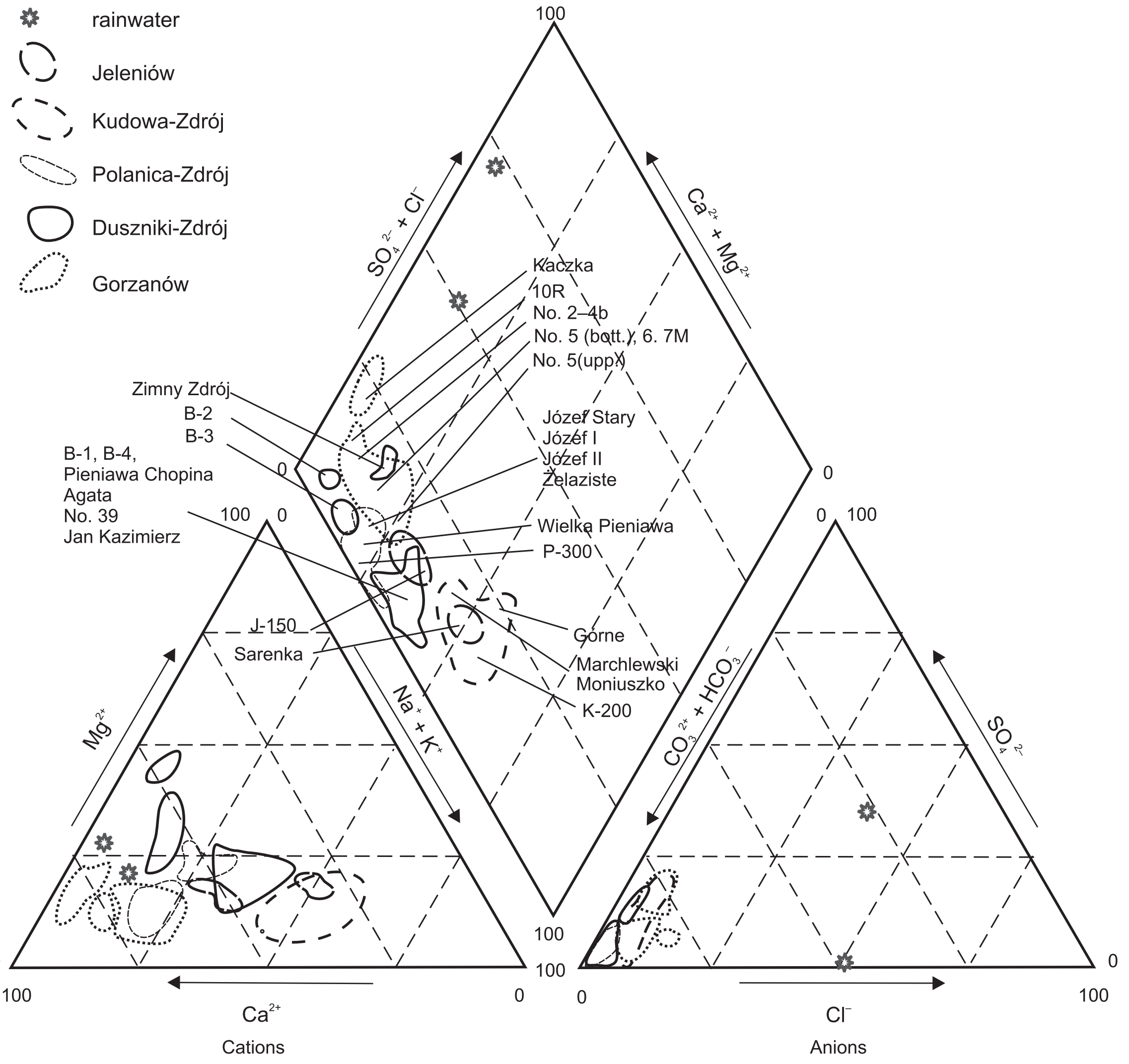

Fig. 2. Piper's diagram showing the chemical composition of waters in the study area

serve a gradual rise in the amount of these components in the waters discussed. According to Gi-Tak *et al.* (2006) such a situation indicates a predominance of feldspar hydrolysis among the processes determining the composition of these waters.

The co-ocurrence, in particular localities, of waters with varying proportions of cations, forming slightly different chemical types, raises a question about correlations between these waters. What changes them more – mixing different compositions of waters or geochemical reactions?

Ciężkowski *et al.* (unpubl.) and Kiełczawa (2001*a*, *b*, 2005) have observed that waters from the deposits discussed are mixtures of deep system waters and waters of contemporary circulation. The mixing of waters from two circulation systems can be inferred from the analyses of their isotope composition. Medicinal water deposits of Kudowa-Zdrój and Duszniki-Zdrój have their recharge areas located higher (from 540 to 800 m a.s.l.) than those in Jeleniów (Table 1), Polanica-Zdrój and Gorzanów (Ciężkowski *et al.*, unpubl.). This is why the former ones have longer and deeper circulations. The latter two deposits have their recharge areas in lower-lying parts of Kłodzko Region (290–640 m a.s.l.). Hence, the conclusion is that these are two separate water systems.

The percentages of deep, highly mineralised waters, determined through chemical analyses, vary considerably (Table 1). However, analyses of tritium content in waters from particular intakes have shown the presence of tritium-free waters in Kudowa-Zdrój (K-200 and Górne intakes) and Polanica-Zdrój (P-300 and Wielka Pieniawa boreholes; Ciężkowski *et al.*, 1996). Significant amounts of water-dissolved CO_2 (*ca.* 2900 mg/L at the most) confirm the possible inflow of deep-circulation waters, and indirectly also the possibility of their mixing with shallow waters.

The fissures in cracked crystalline bedrock in the area of Duszniki-Zdrój are filled with clay minerals and calcite (Fistek and Fistek, unpubl.). One could expect that such a situation is not just local, but also occurs in other crystalline rock zones in Kłodzko Region. The presence of these minerals is probably a result of the hydration of aluminosilicates building the Orlica–Śnieżnik crystalline structure. Moreover, secondary calcite also crystallises in fissures as an ion exchange deriva-

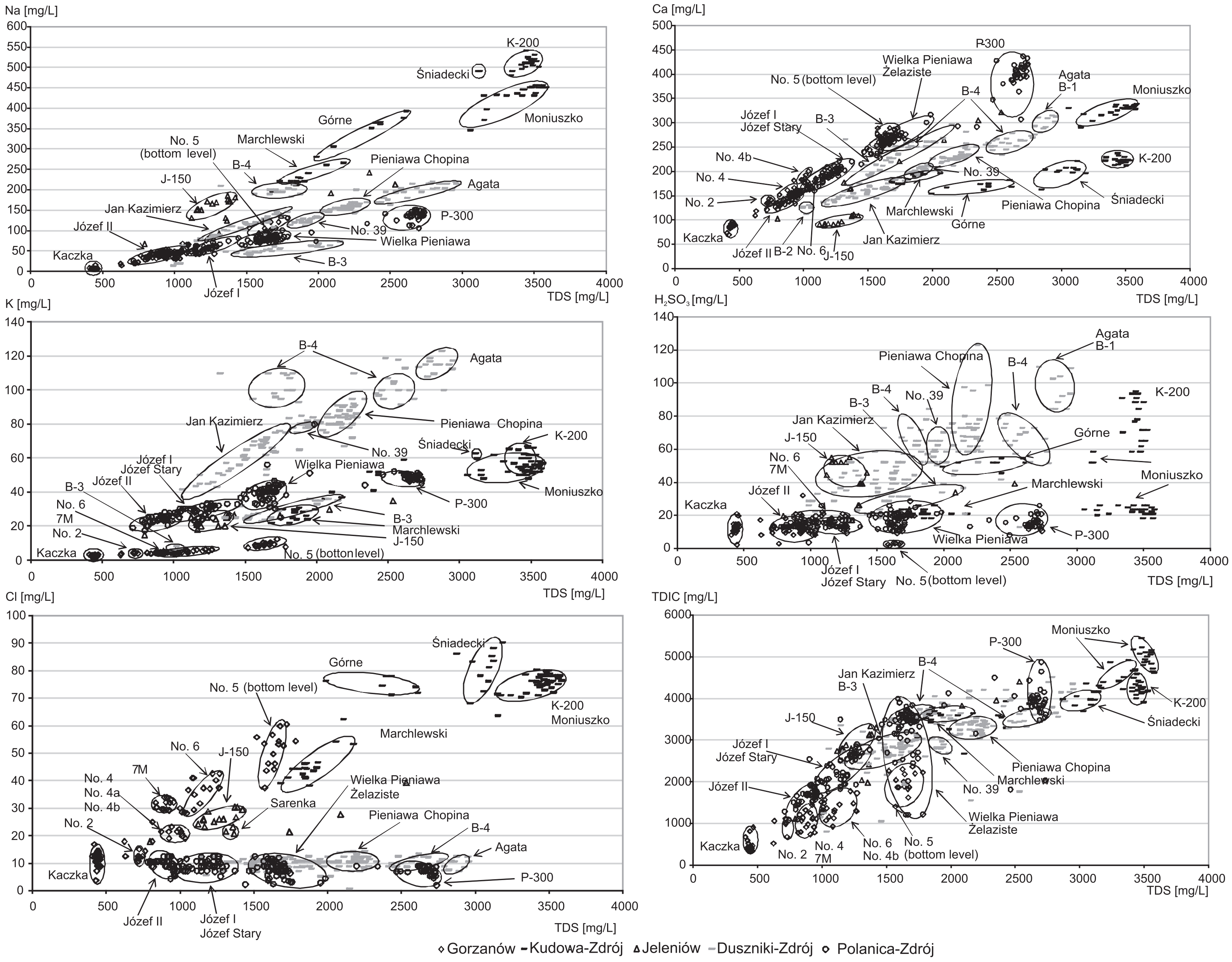

Fig. 3. The relationships between TDS (total dissolved solids) concentration and physicochemical parameters for waters in the study area

Table 1

Location of recharge areas (based on isotope composition analyses of waters) and percentage of deep circulation waters (based on hydrochemical data) in waters from particular localities (according to Ciężkowski *et al.*, 1996; Kiełczawa, 2001*a*)

Locality	Intake name	Location of recharge area [m a.s.l.]	Percentage of deep- circulation waters
Kudowa-Zdrój	K-200, Górne	644–689	36–55
	Moniuszko, Marchlewski	537–559	30–87
Jeleniów	J-150	412–480	34–91
Duszniki-Zdrój	Agata, B-1, B-4, Jan Kazimierz, No. 39, Pieniawa Chopina	745–805	34–92
	Zimny Zdrój, B-2, B-3	715–797	24–60
Polanica-Zdrój	P-300	530–537	100
	Wielka Pieniawa		38–72
	Józef I, Józef II		30–65
	Józef Stary		42–45
Gorzanów	Kaczka, 3, 10	287–644	22–37
	2		40–53
	4, 4a, 4b		55–62
	5, 6		32–97
	7		70

tive. It should be noted that metamorphic rocks in this area of the Sudetes contain lenses of crystalline limestones. These rocks are also an important source of Ca^{+2}, Mg^{+2}, HCO_3^- and CO_3^{2-} ions. The influence of dissolution of crystalline limestones on water composition, e.g. in Gorzanów, has been suggested by Dowgiałło (1978) and Kiełczawa (2005).

A simple method of finding out whether the exchange of Na^+, Ca^{2+} i Mg^{2+} ions influences the chemistry of groundwaters is to compare their principal ion complexes, i.e. $Ca + Mg–HCO_3–SO_4$, in relation to Na-Cl (in meq/L). If the values of the relations determined form a straight line with a slope of –1 (or lie near it) on the graph (Fig. 4), it shows a predominance of ion exchange processes in the water-rock system (Fisher and Mullican, 1997; Rajmohan and Elango, 2004; Srinivasamoorthy *et al.*, 2008). Figure 4 shows that waters from particular health resorts define a straight line with a slope between –1.36 ($R^2 = 0.99$) and a maximum of –1.07 ($R^2 = 0.97$). The results obtained imply that generally all the principal cations (Na^+, Ca^{2+}, Mg^{2+}) can participate in ion exchange reactions.

Similar conclusions could be drawn from the analysis of the relation between $Ca + Mg$ and $HCO_3 + SO_4$ (in meq/L). The ion exchange line, due to the enrichment of waters in sulphate and bicarbonate ions, “shifts” the points to the right of the 1:1 line (Fig. 5). If reverse ion exchange occurs (sodium and potassium from waters are replaced by calcium and magnesium found in rocks), there is an increase in the number of Ca and Mg ions in waters, so the points lie to the left of the straight line. When the points lie near the 1:1 line, the system is dominated by the processes of dolomite, calcite and gypsum dissolution (Rajmohan and Elango, 2004; Srinivasamoorthy *et al.*, 2008).

All the waters studied are distributed in the field below the 1:1 line (Fig. 5). This fact is most likely linked to the considerable predominance of bicarbonate ions in their chemical composition. This, in turn results from the interaction of CO_2 (of a deep origin) supplied to the intake area, with aluminosilicates in the rock medium in the aqueous environment. Notably, intakes B-2 and B-3 in Duszniki-Zdrój (Fig. 5) and waters from Gorzanów and Polanica-Zdrój (except for intake P-300) are distributed closest to the dissolution line. Therefore, it is possible that dissolution of carbonate minerals may influence the chemical composition of these waters (these intakes draw waters directly from Cretaceous strata, Polanica-Zdrój, Gorzanów, Kudowa-Zdrój) or that waters enriched in the products of such reactions flow into the intake (Duszniki-Zdrój).

The biggest shift to the right can be observed for water analyses from Kudowa-Zdrój and Jeleniów, which may be evidence of advanced ion exchange between calcium and magnesium cations from waters, and Na^+ ions from hydrated sodium plagioclases or clay minerals (Fisher and Mullican, 1997; Rajmohan and Elango, 2004; Srinivasamoorthy *et al.*, 2008).

Examining the relation between $(Ca + Mg)/HCO_3$ and Cl (in mmol/L) resulted in dividing the analysed waters into two sets: one comprising waters from Kudowa-Zdrój, Jeleniów and Gorzanów and the other with waters from Duszniki-Zdrój and Polanica-Zdrój (Fig. 6). The contents of Cl^- ions change linearly within both water sets, but the former case shows distinct variation in the concentration of the component discussed.

The image obtained may demonstrate the accuracy of the hypothesis concerning recharging deposits, e.g. in Kudowa-Zdrój and Gorzanów, with deep circulation waters flowing to these places along the Hronov–Kudowa-Zdrój–Pstrążna–Gorzanów tectonic zone. The intakes in Polanica-Zdrój and Duszniki-Zdrój, on the other hand, are situated along faults transverse to this dislocation (and simultaneously subordinate to it). Therefore, it may be concluded that the inflow of deep system waters is smaller in this case. Large amounts of CO_2, both in waters and in the soil air of Duszniki-Zdrój (Żak *et al.*, 2008), as well as increased water temperatures, indicate the proximity of that zone.

The values of the calculated relation $(Ca + Mg)/HCO_3$ falling below 0.5 show the replacement of Ca^{2+} and Mg^{2+} by Na^+ from clay minerals. When the calculated values are higher,

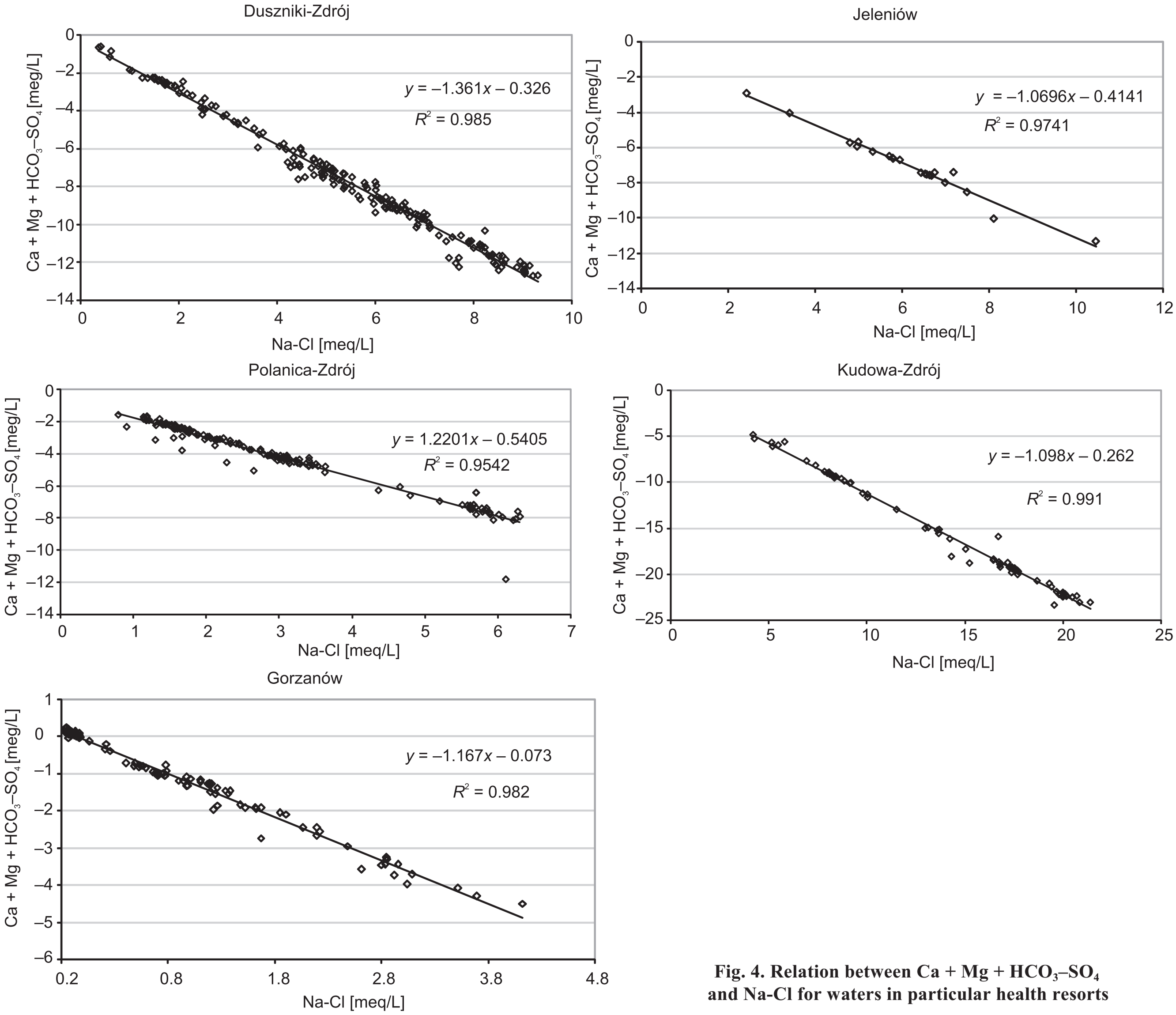

Fig. 4. Relation between Ca + Mg + HCO_3–SO_4 and Na-Cl for waters in particular health resorts

the influence of reverse exchange is observed (Rajmochan and Elango, 2004). The values obtained imply simple ion exchange developing in most of the waters studied. Only in one intake (Kaczka), situated in Gorzanów, the values reach 0.5–0.68. At this stage it is difficult to state explicitly whether reverse ion exchange occurs in these waters.

The determination of ion exchange direction can be facilitated by Schoeller's indices. These are sodium-chloride indices CAI 1 and CAI 2 where:

$$\text{CAI 1} = \text{Cl} - \frac{\text{Na} + \text{K}}{\text{Cl}} \qquad [1]$$

$$\text{CAI 2} = \text{Cl} - \frac{\text{Na} + \text{K}}{\text{SO}_4} + \text{HCO}_3 + \text{CO}_3 + \text{NO}_3 \qquad [2]$$

(by Rajmochan and Elango, 2004 after Schoeller).

One can talk about simple ion exchange when Ca^{+2} and Mg^{+2} ions found in waters are replaced by Na^{+} and K^{+} ions from the rock medium, when both of these indices have negative values. Their positive values are a sign of reverse ion exchange processes.

The values calculated for the waters studied do not clearly show the exchange direction, as all the waters analysed have values CAI 1 <0 and CAI 2 >0. Most probably, simple exchange processes dominate, and positive values of the latter index are related to high numbers of HCO_3^- ions in the composition of the waters studied. Isolated results from intakes P-300 in Polanica-Zdrój and B-4 in Duszniki-Zdrój, give an indication of reverse ion exchange, i.e. the sodium from water is replaced by calcium and magnesium found in rocks.

The mineral composition of crystalline rocks includes silica minerals (quartz, chalcedony), silicates (olivines), aluminosilicates (pyroxenes, potassium feldspars, plagioclases) and hydrated aluminosilicates (amphiboles, micas). It is generally known that chemical weathering of these minerals produces clay minerals (kaolinite, illite, montmorillonite), calcite as well as oxides and hydroxides (e.g., gibbsite, hematite). Consequently, the waters studied may be expected to show a state of equilibrium or supersaturation with respect to these minerals.

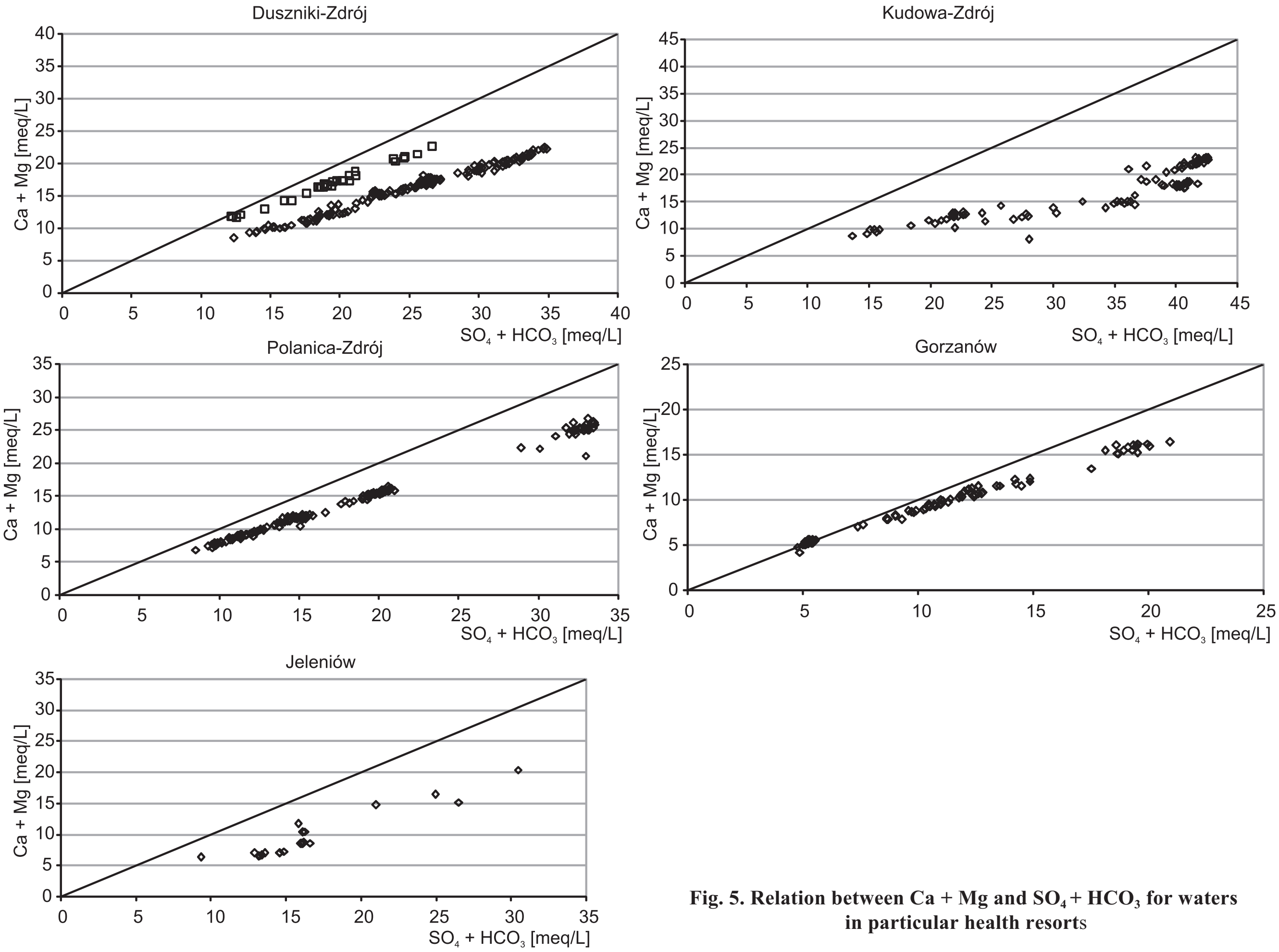

Fig. 5. Relation between Ca + Mg and SO_4 + HCO_3 for waters in particular health resorts

Physicochemical properties of medicinal waters have been studied in health resorts for many years. Data collections contain results gathered back in the late 19th century. Unfortunately, due to the often dubious accuracy of these analyses and selectivity of the ion components examined, not all this data can be used directly for particular analyses. This is why only few results have been employed for determining the activity and saturation indices of probable mineral forms present in these waters. The data used come from the Wielka Pieniawa and P-300 intakes in Polanica-Zdrój, B-4 and No. 39 in Duszniki-Zdrój, the K-200, Moniuszko and Górne intakes in Kudowa-Zdrój, as well as J-150 in Jeleniów. The parameters discussed were determined with the help of the *PhreeqC* code (Parkhurst and Appello, 1999).

The values of saturation indices defined (SI; Table 2) support the above deductions. All the waters analysed are characterized by supersaturation with respect to micas, kaolinite and chalcedony. Waters from intakes B-4, No. 39 and K-200 exhibit slight supersaturation with respect to potassium aluminosilicates (feldspars), illite and montmorillonite. In all these cases dissolution of dolomite and plagioclases occurs. Except for waters from intake J-150, all the others are marked by equilibrium or slight undersaturation with respect to calcite. Equilibrium with this mineral is observed in waters with a higher contribution of Na^+ ions to their ionic composition. Presumably, their interaction with the rock medium lasted longer. Their deeper circulation and subsequent greater interaction with the rock medium and CO_2, resulted in releasing HCO_3^- ions (as a result of hydrolysis of silicates and aluminosilicates). This, in turn may lead to removed of Ca^{+2} from the solution as a result of secondary calcite crystallisation.

On the other hand, calcium ions can be removed from these waters through ion exchange with Na^+ or K^+ coming from secondary aluminosilicates (i.e., clay minerals formed through hydration of e.g., feldspars).

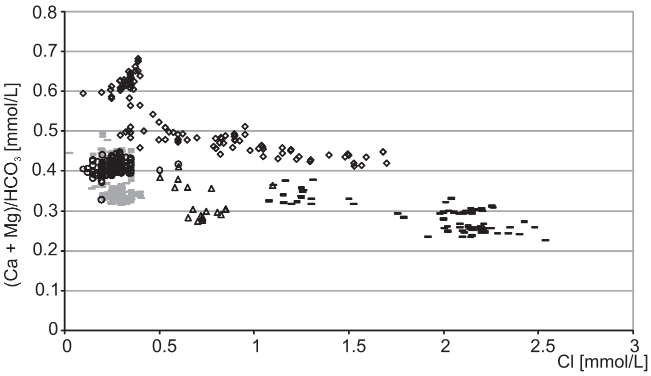

Fig. 6. Relation between (Ca + Mg)/HCO_3 and salinity for waters in particular health resorts

Explanations as in Figure 3

Table 2

Values of saturation indices (SI) for waters from selected intakes (based on recent chemical composition analysis comprising data on Al^{3+} ion concentrations) with respect to principal minerals found in rock units in the research area

Mineral	Locality							
	Duszniki-Zdrój		Jeleniów	Kudowa-Zdrój			Polanica-Zdrój	
	Intake name							
	No. 39	B-4	J-150	K-200	Moniuszko	Górne	P-300	Wielka Pieniawa
$Al(OH)_{3(a)}$	–2.8	–2.41	–3.6	–2.9	–3.2	–3.14	–2.8	–3.18
Albite	–2.01	–1.4	–3.14	–1.36	–3.24	–1.95	–3.6	–4.4
Anorthite	–8.02	–5.75	–9.16	–6.96	–8.52	–7.84	–7.57	–9.1
Aragonite	–0.32	–0.11	–0.77	–0.22	–0.12	–0.51	**0.02**	–0.66
Ca-montmorillonite	1.5	2.48	–0.84	1.56	–0.96	0.75	–0.35	–1.2
Calcite	–0.17	**0.04**	–0.62	**–0.07**	0.04	–0.36	0.17	–0.5
Chalcedony	0.56	0.56	0.42	0.61	0.12	0.56	**0.04**	0.06
Dolomite	–0.76	–0.24	–1.62	–0.45	–0.49	–1.17	–0.31	–1.84
Gibbsite	**–0.04**	0.36	–0.79	–0.1	–0.4	0.34	**–0.04**	–0.37
Illite	0.38	1.44	–2.29	0.38	–2.16	–0.55	–1.58	–2.7
K-feldspar	0.24	0.83	–1.45	0.29	–1.6	–0.26	–1.5	–2.1
K-mica	5.73	7.12	2.5	5.64	3.15	4.62	3.98	2.69
Kaolinite	2.73	3.55	0.97	2.75	1.16	2.16	1.71	1.09
Quartz	1.01	1.02	0.89	1.08	0.59	1.03	0.5	0.53
Rhodochrosite	–0.45	–0.24	–0.9	–0.74	–0.77	–0.86	–0.29	–1.18
Siderite	0.36	0.54	**0.04**	0.36	0.26	0.14	0.37	–0.18
$SiO_{2(a)}$	–0.31	–0.31	–0.46	–0.27	–0.76	–0.32	–0.83	–0.83
Barite	–1.1	–0.17	**0.03**	0.1	0.21	**0.0**	0.01	–0.2

Values close to the equilibrium state are typed in bold

The waters discussed are naturally carbonated with a substantial predominance of HCO_3^- (bicarbonate) ions in their composition. This is characteristic of waters whose chemistry is formed as a result of aluminosilicate hydration in the presence of CO_2. Hence the notion that these processes also determined directly the presence of Na^+ ions in the waters studied.

The degree of saturation or undersaturation of the solution with respect to aluminosilicates is depicted by stability diagrams for particular minerals (Figs. 7 and 8). The division of these waters into two groups is clear: one with a considerable proportion or predominance of calcium ions (intakes P-300, Wielka Pieniawa and Moniuszko), and the other one characterized by a

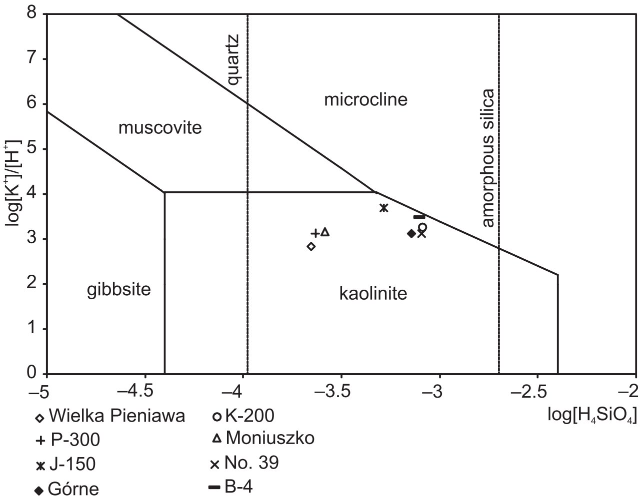

Fig. 7. The stability diagram of K-feldspar (microcline) and its possible weathering products (gibbsite, kaolinite and muscovite)

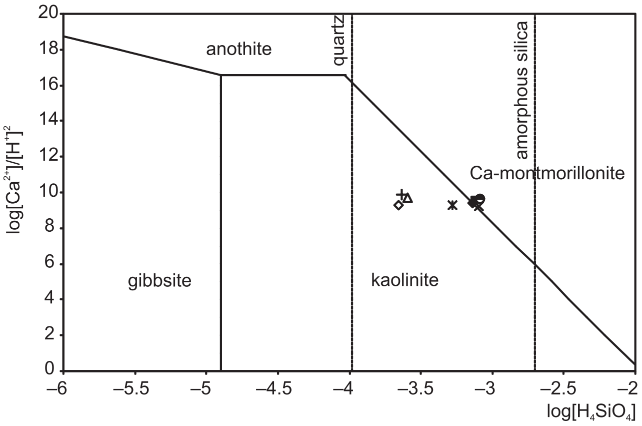

Fig. 8. The stability diagram for anorthite and its weathering products gibbsite, kaolinite and Ca-montmorillonite

Explanations as in Figure 7

predominance of Na^+ ions (in the case of Kudowa-Zdrój) or their high percentage (in Duszniki-Zdrój) in their cation complex. The waters in this group show supersaturation with respect to montmorillonite and a state close to equilibrium with microcline (potassium feldspar). In both groups, kaolinite is the stable form of secondary aluminosilicates. The waters from Duszniki-Zdrój and Kudowa-Zdrój are distributed on the boundary of the kaolinite/montmorillonite phases. This suggests the influence of dissolution of incongruous aluminosilicates on the chemistry of these waters (Appello and Postma, 2007). In the first of these deposits, where waters are found in crystalline rocks, the development of such processes is very likely. In the case of Kudowa-Zdrój, this possibility is confirmed by the inflow of waters from the crystalline bedrock, i.e. deep circulation waters.

CONCLUSIONS

The chemical composition of the naturally carbonated waters of Kłodzko Region is determined chiefly by their interaction with the rock medium and with carbon dioxide (of deep origin) moving towards the discharge area. It is most influenced by dissolution of primary aluminosilicates, silicates and crystalline limestones, as well as by crystallisation of secondary calcite and clay minerals (kaolinite). Hydrolysis of silicates and aluminosilicates has a direct influence on the concentrations of the main ion components, i.e. Na^+, Ca^{+2}, Mg^{+2} and HCO_3^-.

Variations in the content of Ca ions may result from ion exchange on one hand, and from the precipitation of secondary calcite in rock fissures on the other. As hydrolysis of silicates and aluminosilicates prevails in a deep circulation system, the resultant HCO_3^- ions can be balanced with Na^+ and K^+, which is most likely to result in calcite precipitation. Additionally, calcium ions can be replaced by Na^+ ions from secondary clay minerals. Shallower parts of the system may be dominated by reverse ion exchange between sodium from waters of the deep circulation system and Ca^{+2} and Mg^{+2} from Cretaceous strata.

Moreover, the chemical composition of the waters studied is also influenced by the mixing of shallow (type HCO_3-Ca) and deep circulation (type HCO_3-Na) waters.

The calculated saturation indices imply that the stable mineral form in the waters studied is kaolinite (a product of hydration of silicate and aluminosilicate minerals). Dissolution of carbonate minerals is indicated by the values of saturation indices (SI) of the solution.

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