



## Silicon and aluminium in groundwater of the Kłodzko Region (the Sudetes, SW Poland) — partial geochemical equilibrium with secondary solid phases

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The chemistry of shallow, cold groundwater in the eastern part of the Kłodzko Region (the Sudetes, SW Poland) was investigated. Groundwaters occur in the short turn-over time zone of the hydrogeological systems. The aquifers are composed of various bedrock types (metamorphic, igneous and sedimentary). Silicon and aluminium concentrations in the waters of particular aquifers are documented. The aqueous chemistry is interpreted in terms of the solubility of solid phases that are responsible for silicon and/or aluminium solubility control. Locally and/or periodically (seasonally) partial geochemical equilibrium between the groundwater and the secondary solid phases might be reached and maintained. In groundwater with a pH below 6.7, aluminium activity is usually controlled by the reversible congruent dissolution of  $\text{Al}(\text{OH})_3$  forms, whereas silicon activity is probably controlled by the solubility the  $\text{SiO}_2$  form (chalcedony). At pHs above 6.7, the incongruent reaction between the hydroxyaluminosilicate colloid ( $\text{HAS}_B$ ) and forms of  $\text{Al}(\text{OH})_3$  controls both silicon and aluminium activities.

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Key words: Sudetes, groundwater geochemistry; aluminosilicate phases, hydroxyaluminosilicate HAS, silicon, aluminium.

### INTRODUCTION

Dissolved silicon occurs in groundwater at relatively high concentrations that depend upon different factors and processes, such as equilibrium with solid phases, adsorption onto solids (such as Al hydroxides, aluminosilicates), the kinetics of dissolution reactions, or steady-state conditions between weathering release and hydrological removal. The amount of silica released into shallow groundwater and surface water is conditioned by the bedrock reactivity, as well as by climatic factors, e.g. seasonal fluctuations of atmospheric precipitation and temperature. Dissolved silicate is considered to reflect weathering and water circulation conditions, and is used to estimate outflow components (e.g., Wels *et al.*, 1991; Scanlon *et al.*, 2001; Asano *et al.*, 2003). Research into aluminium solubility and environmental behaviour is focussed mainly on soils, as well as on soil and surface waters due to environmental concerns, e.g. soil fertility, aluminium toxicity to plants and aqueous organisms. The activity of dissolved silica affects the formation of aluminosilicate solute and solid species, and can reduce aluminium toxicity (e.g., Exley *et al.*, 1994, 1997).

The chemistry of groundwater from the weathered zone developed on different bedrocks in the eastern part of the Kłodzko Region was investigated. The groundwaters studied represent the short turn-over time zone of water in the hydrogeological system. Springs and drainage intakes that discharge from fissured and/or regolith aquifers were sampled. In the studied part of the Sudetes, the aquifers mentioned above are the main sources of drinking water supplies.

The aim of the research was to determine groundwater chemistry, and to analyse concentrations and solubility controls of silicon and aluminium dissolved in shallow, low-temperature, fresh groundwater. In the study area, thermal groundwaters also occur in Łądek Spa. In the paper, silicon and aluminium dissolved in groundwater is interpreted in terms of the solubility of secondary solid phases.

### METHODS AND SITE MINERALOGY

The research into the groundwater chemistry was carried out in the years 1998–2003 in the eastern part of the Kłodzko Region (Fig. 1). Shallow, cold groundwater discharged from

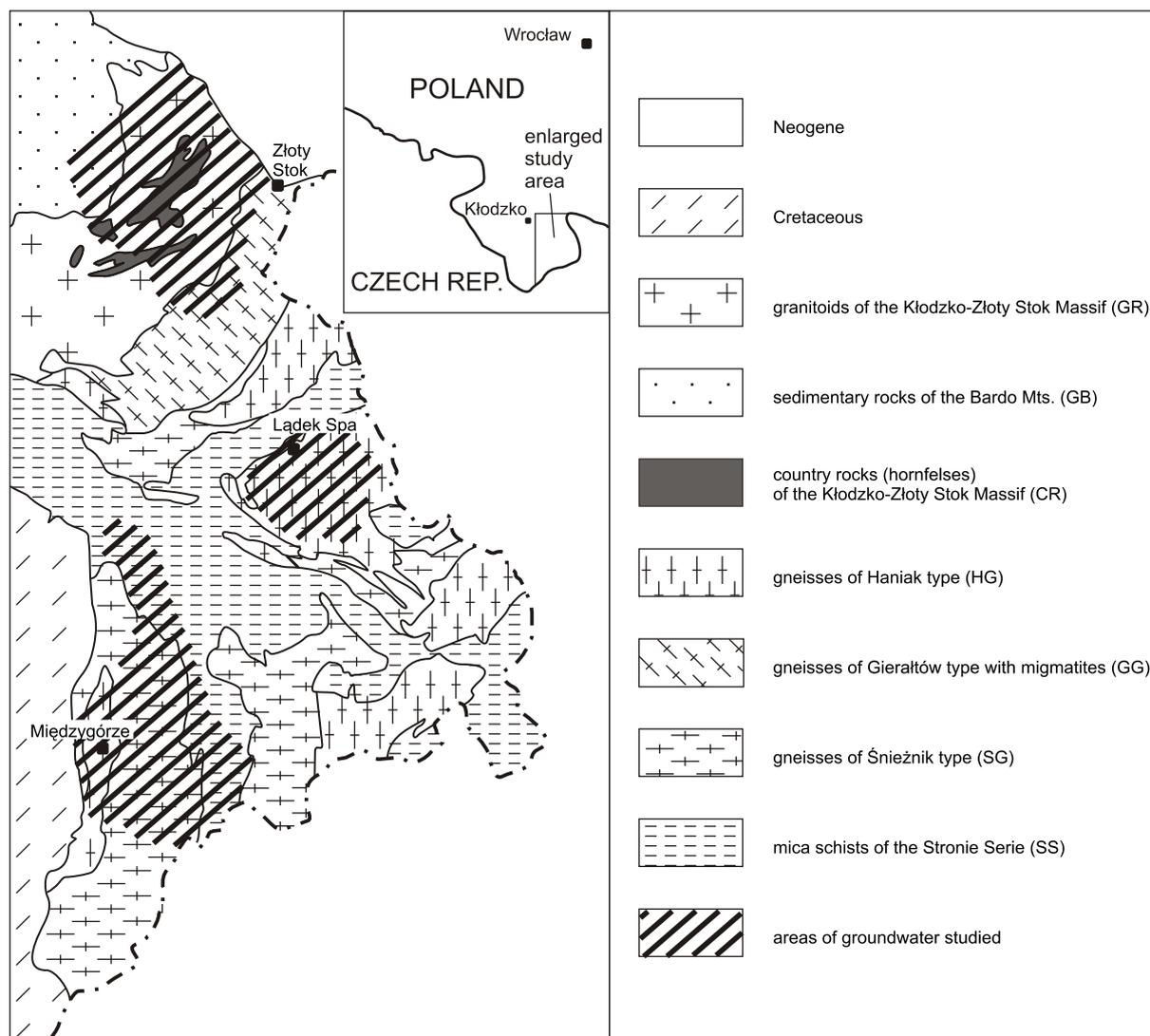


Fig. 1. Geological sketch of the eastern part of the Kłodzko Region (after Sawicki, 1995) with location of the areas studied

springs and drainage intakes was investigated. Water samples were filtered in the field by cellulose-nitrate 0.45  $\mu\text{m}$  membrane filters, and stored in LDPE bottles. Specific electric conductivity (SEC), pH, and T were measured in the field. Concentrations of Al (by ETA AAS),  $\text{SO}_4$ ,  $\text{NO}_3$ ,  $\text{PO}_4$ , F,  $\text{SiO}_2$  (by the spectrophotometric method),  $\text{HCO}_3$  and Cl (by the volumetric method), Ca, Mg, Na, K and trace elements (by ICP-AES) were determined in the lab. The calculation of species activity and saturation states was executed by the PHREEQC code (Parkhurst and Appelo, 1999). An Al-silicate  $(\text{H}_2\text{O})_5\text{AlOSi}(\text{OH})_3^{+2}$  complex was incorporated into the speciation model, using  $\lg K$  and  $\Delta H_f^\circ$  data given by Spadini *et al.* (2005) and Pokrovski *et al.* (1996). Calculation of saturation indexes also included dissolution reactions of the following aluminosilicates: allophane of Al/Si ratio = 2.0 ( $\lg K_{25} = 14.20$ ; Su and Harsh, 1998), allophane of Al/Si = 1.26 ( $\lg K_{25} = 11.27$ ; Su and Harsh, 1998), natural imogolite ( $\lg K_{25} = 13.60$ ; Su and Harsh, 1996), synthetic imogolite ( $\lg K_{25} = 13.08$ ; Su and Harsh, 1996), proto-imogolite ( $\lg K_{25} = 7.02$ ,  $\Delta H_f^\circ = -96.8$  kJ/mol; Lumsdon and Farmer, 1995).

The general descriptions of groundwater quality are also based on the data collected by Chmielewska (2000), Stępień (2000), Bąk (2002) and Bieliń (2002).

Bedrock in the area studied is composed of different kinds: sedimentary, igneous, and (mainly) metamorphic (Fig. 1, Table 1). Lower Carboniferous greywackes and conglomerates (with mudstones and shales) occur in the Bardo Mts., in the northern part of the area. Sedimentary rocks of the Bardo Mts. (GB) adjoin Variscan granitoids of the Kłodzko-Złoty Stok Massif (GR). Metamorphic rocks predominate in the area studied. Locally, above the granitoids, country rocks (CR) mainly composed of hornfels are preserved. In the east granitoids abut onto the metamorphic complex consisting of Haniak-type gneisses (HG) with mylonites and cataclasites. The central and southern parts of the area studied are composed of different gneisses and crystalline schists (the "Śnieżnik-Lądek metamorphic complex"). Three main metamorphic rock types can be distinguished in the complex: (1) mica schists with plagioclase gneisses, graphite schists and quartzites of the Stronie Serie (SS), (2) finely banded gneisses and migmatites of the

Table 1

Mineral composition of bedrocks in the area studied (after Butkiewicz, 1968; Wojciechowska, 1975; Wierzchołowski, 1976; Cwojdzński, 1977; Frąckiewicz and Teisseyre, 1977; Smulikowski, 1979; Borkowska *et al.*, 1990)

	Stronie Series (SS)	Gneisses of Gierałtów type (GG)	Gneisses of Śnieżnik type (SG)	Gneisses of Haniak type (HG)	Sedimentary rocks of the Bardo Mts. (GB)	Granitoids of Kłodzko-Złoty Stok Massif (GR)	Country rocks of Kłodzko-Złoty Stok granitoids (CR)
Minerals	Mica schists with plagioclase gneisses, graphite schists and quartzites	Fine banding gneisses with migmatites	Coarser, oligoclase-microcline granite-gneisses	Plagioclase-microcline gneisses with mylonites, cataclases, biotite gneisses	Greywackes, conglomerates, mudstones, clay shales	Granodiorites, granites with syenodiorites, monzonites, tonalities	Hornfels, hornfels gneisses, biotite schists
Quartz	♦♦♦	♦♦♦	♦♦♦	♦♦♦	♦♦♦	♦♦♦	♦♦♦
Plagioclases	♦♦ (0–30 An)	♦♦♦ (0–30 An)	♦♦♦ (10–30 An)	♦♦♦ (10–50 An)	♦♦	♦♦♦ (0–30 An)	♦♦
K-Feldspars	♦/♦♦	♦♦♦/♦♦	♦♦♦	♦♦	♦♦	♦♦	♦♦
Muscovite, sericite	♦♦/♦♦♦	♦♦/♦	♦♦/♦	♦/♦♦	♦♦	♦	♦♦
Biotite	♦♦♦	♦/♦♦	♦♦	♦♦	♦	♦/♦♦	♦/♦♦
Chlorites	♦/♦♦	♦/♦♦	♦/♦♦	♦/♦♦	♦	♦	♦/♦♦
Pyroxenes, amphiboles	♦					♦♦/♦	♦
Fe-oxides	♦	♦♦/♦	♦	♦	♦	♦	♦
Garnets	♦♦	♦	♦				♦
Zircon	♦	♦	♦			♦	♦
Titanite	♦	♦	♦			♦	
Apatite	♦	♦	♦			♦	
Staurolite	♦♦/♦						
Epidote		♦	♦			♦	♦
Graphite	♦/♦♦						
Tourmaline	♦						♦

Minerals: ♦♦♦ — main, ♦♦ — secondary, ♦ — accessory

Gierałtów type (GG), (3) coarser granite-gneisses of the Śnieżnik type (SG). Main features of the bedrock mineral composition are given in Table 1.

#### BASIC FEATURES OF SILICON AND ALUMINIUM HYDROGEOCHEMISTRY

Silicon and aluminium are — besides oxygen — the most abundant elements of the continental lithosphere (Si — 27.7%, Al — 8.1%). The geochemistries of these elements in natural waters contrast with each other. In the most groundwaters, especially in cold low-mineralised groundwater, concentration of dissolved silicon considerably exceeds that of aluminium. Hydrolytic decay of (alumino)silicates is regarded as the main source of Si and Al dissolved in natural waters. This process releases significant amounts of silicon, but relatively low amounts of aluminium, into waters. Silicon usually occurs in groundwater at concentrations of  $10^{-4} \div 10^{-3}$  mol/L, whereas aluminium concentrations are  $10^{-7} \div 10^{-5}$  mol/L (Hem, 1989; Svarcev, 1998). The geochemical behaviour of both elements is related to each other in some environments (e.g., in soils and the weathered zone).

Aluminium occurs usually in aqueous solution in ionic forms, as in many minerals, at octahedral (or tetrahedral) coordination with different ligands. The aluminium solubility is governed mainly by pH. Effects of water pH and hydrolysis of  $\text{Al}(\text{H}_2\text{O})_6^{+3}$  complex ions is modified by the formation of soluble, stable complexes with other inorganic or organic ligands, such as fluorides, sulphates, phosphates or carboxylates. As a consequence of its amphoteric properties, aluminium shows its highest solubility in acid and basic conditions. Silicon predominantly occurs in waters in the form of dissolved mono- and polymeric acids. Usually, the main form of silicon in low-mineralised non-alkaline waters is undissociated, orthosilicic acid  $\text{H}_4\text{SiO}_4$ . Silicon in solutes, like as many solids, occurs mainly in the tetrahedral coordination. An increase in pH causes dissociation of silicic acids, and an increase in silicon solubility. In alkaline waters (with pH above 9.5) silicon also occurs as silicate anions and/or polymeric acid species. Silicon and aluminium might form numerous complexes among them also the common complexes: hydroxyaluminosilicates (HAS). The formation of HAS depends on environmental conditions (Swaddle, 2001). In acidic and neutral conditions hydroxyaluminosilicates are mainly formed due to reactions of undissociated acid  $\text{H}_4\text{SiO}_4^0$  with Al cations  $(\text{Al}(\text{H}_2\text{O})_6^{+3})$ ,

$\text{Al}(\text{H}_2\text{O})_5(\text{OH})^{+2}$ ,  $\text{Al}(\text{H}_2\text{O})_4(\text{OH})_2^+$ ), whereas in alkaline conditions HASs are formed due to the reaction of  $\text{H}_4\text{SiO}_4^0$  and/or silicate anion  $\text{H}_3\text{SiO}_4^-$  with aluminate anions,  $\text{Al}(\text{H}_2\text{O})_2(\text{OH})_4^-$ . Apart of monosilicate complexes, polysilicate complexes also are formed and exist in natural waters (Dietzel, 2000).

The formation of hydroxyaluminosilicates has been the subject of numerous investigations. Farmer and Lumsdon (1994), Lumsdon and Farmer (1995) and Pokrovski *et al.* (1996) worked on the formation and solubility of  $\text{AlOSi}(\text{OH})_3^{+2}$  complex. In many soils proto-imogolite sol  $(\text{HO})_3\text{Al}_2\text{O}_3\text{SiOH}$  has been identified and considered as a precursor of allophane/imogolite minerals, playing an important role in soil formation (e.g., Farmer *et al.*, 1980; Farmer and Fraser, 1982; Gustafsson *et al.*, 1998). Recently, the formation and the structure of two kinds of HASs (named  $\text{HAS}_A$  and  $\text{HAS}_B$ ) has been described (Doucet *et al.*, 2001; Exley *et al.*, 2002). Both kinds of HASs have the composition and idealised Si:Al ratios of 0.5 and 1.0, respectively, identical to proto-imogolite or allophane/imogolite minerals. It is conceivable that HAS solutes may play an important role in the formation of amorphous/short range-ordered aluminosilicate solid phases (Farmer and Lumsdon, 1994; Lumsdon and Farmer, 1995; Doucet *et al.*, 2001; Exley *et al.*, 2002). Aluminosilicate solids (allophanes, imogolite) are widely identified, especially in soils developed on volcanic rocks (e.g., Parfitt and Kimble, 1989; Wada, 1989; Ugolini and Dahlgren, 1991; Ndayiragije and Delvaux, 2003), but also developed on sedimentary and metamorphic bedrock (e.g., Farmer *et al.*, 1980; Gustafsson *et al.*, 1998, 1999).

During irreversible transformations of primary minerals in the weathered zone a wide assemblage of secondary (reversible and irreversible) solid phases can be formed. They can control the solubility of silicon and/or aluminium in natural waters. To explain their activity in water the role of different phases, such as  $\text{Al}(\text{OH})_3$  forms (Sullivan and Cosby, 1998), halloysite and/or microcrystalline gibbsite (Hem *et al.*, 1973), metastable aluminosilicates (Pačes, 1978; Neal *et al.*, 1986), or mixed phase amorphous  $\text{Al}(\text{OH})_3$  and aluminosilicate (Gustafsson *et al.*, 1998) has been proposed.

The solubility of kaolinite, halloysite,  $\text{Al}(\text{OH})_3$  forms and some of allophane/imogolite mineral phases is already quite well known. Unfortunately, unlike the above-mentioned phases, the solubility of aluminosilicate solutes is poorly recognized. The equilibrium constants of  $\text{AlOSi}(\text{OH})_3^{+2}$  complex and proto-imogolite sol  $(\text{HO})_3\text{Al}_2\text{O}_3\text{SiOH}$  are known due to the work of Lumsdon and Farmer (1995) and Pokrovski *et al.* (1996). The  $\text{HAS}_B$  solubility was estimated experimentally by Schneider *et al.* (2004) and on the basis of field hydrochemical data by Dobrzyński (2006a).

#### SILICON AND ALUMINIUM IN THE GROUNDWATER STUDIED

The groundwaters studied are low-mineralised, and their specific electric conductivity (SEC) usually does not exceed  $350 \mu\text{S}/\text{cm}$  (Table 2). The mean temperature of water from different aquifers ranges from  $6.1^\circ\text{C}$  to  $8.6^\circ\text{C}$  (Table 2). Ground-

water pH varies within a wide range, between 3.88 and 7.66, but usually between 5 and 6.5. Calcium, bicarbonate and sulphate ions prevail amongst the solutes.

The groundwater from granitoids (GR) and from hornfelses (CR) differs from other groundwaters in terms of many chemical parameters, i.e. pH, total dissolved solids, concentration of calcium, magnesium, potassium, bicarbonates, chlorides. It results from the higher content of reactive primary rock-forming minerals in GR and CR bedrocks than in gneisses, metamorphic schists, and sedimentary rocks (conglomerates).

Dissolved silicate concentrations (expressed as  $\text{SiO}_2$ ) range between 5.09 and 26.6 mg/L  $\text{SiO}_2$  (85–443  $\mu\text{mol}/\text{L}$ ), and aluminium concentrations range between 1 and 1800  $\mu\text{g}/\text{L}$  (0.037–67  $\mu\text{mol}/\text{L}$ ) (Table 2, Fig. 2). Silicon and aluminium concentrations in the groundwater depend on bedrock type (Figs. 3 and 4).

The mean silica concentration in groundwater from different bedrocks (from 10.7 to 16.8 mg/L  $\text{SiO}_2$ ; Table 2) is similar to its average concentration in shallow groundwater of temperate climate regions (13.3 mg/L  $\text{SiO}_2$ ) and in groundwater of mountain areas (15.2 mg/L  $\text{SiO}_2$ ) after Svarcev (1998). Aluminium and silica concentrations in the groundwater studied also are similar to concentrations found in shallow cold groundwater in other parts of the Sudetes (Dobrzyński, 1997, 2005, 2006b; Bocheńska *et al.*, 1997).

Water pH is the main variable that governs Al concentration. However, correlation between  $\text{Al}_{\text{total}}$  and pH in groundwater (Fig. 5) is weak because of the presence of numerous samples with pH within the range 6–7, where Al shows the lowest solubility. Aluminium forms stable soluble complexes with different ligands, such as hydroxyls, fluorides, sulphates and organics. Speciation calculation shows that Al occurs mainly as Al-OH and Al-F complexes (Fig. 6). Al-sulphate and Al-silicate complexes form at most a few percent of aluminium inorganic complexes. Al-organic complexes have not been taken into account in the speciation models due to lack of information on  $\text{C}_{\text{org}}$  in groundwaters. Dissolved organic carbon (DOC) in the groundwaters was usually below the analytical detection limit ( $\text{DL} = 0.5 \text{ mg}/\text{L} \text{ C}_{\text{org}}$ ). Silicon occurs in the groundwater studied mainly as  $\text{H}_4\text{SiO}_4^0$  species that in all samples take more than 99.65% of total molar Si concentration.

## RESULTS AND DISCUSSION

The ionic equilibrium of aluminium and/or silicon-bearing solids in groundwater has been analysed. Interpretation was based on the calculation for congruent and incongruent dissolution reactions.

The groundwaters studied occur in the zone of short turn-over time in the hydrogeological system and show disequilibrium with water-bearing rocks as a whole. The waters are undersaturated with respect to the rock-forming silicate minerals (Table 3), such as feldspars, biotites and chlorites. These minerals are important reactive phases and sources of solutes. Groundwaters usually show supersaturation with respect to muscovite and secondary layer-silicates (kaolinite, illite, smectites). Muscovite/sericite is a common mineral in

Table 2

## Selected physico-chemical characteristics of the groundwater

	Bedrock						
	SS (41)	GG (8)	SG (47)	HG (10)	GB (10)	GR (35)	CR (8)
SEC [ $\mu\text{S}/\text{cm}$ ]	82.0* 36.7–127.2**	122.2 67.8–154.2	81.6 53.1–182	155.0 98.8–235.0	150.1 107.5–195.5	292.7 109–514	328.4 161.9–973
pH	5.72 5.07–7.08	5.60 5.33–5.81	5.06 3.88–6.89	5.43 5.13–6.6	4.89 4.27–5.77	6.09 5.21–7.66	6.31 5.79–7.00
T [ $^{\circ}\text{C}$ ]	6.07 4.6–9.46	8.62 7.5–10.0	7.06 4.7–24.3	6.45 3.0–9.6	7.45 4.1–11.0	8.02 3.0–12.2	8.55 5.3–10.8
SiO <sub>2</sub>	10.70 5.09–17.0	16.75 10.21–22.9	12.12 6.88–18.3	14.77 11.3–19.6	11.91 9.8–14.1	14.55 7.4–26.6	15.37 9.9–26.0
Al [ $\mu\text{g}/\text{L}$ ]	121 1–1224	32 5–103	133 1–1800	18 4–89	26 2–96	13 1–46	11 1–33
Ca	11.53 3.22–20.84	11.67 5.23–20.04	8.22 2.4–25.11	18.56 10.5–27.1	15.61 10.74–23.40	37.94 8.5–70.8	32.01 14.11–60.36
Mg	1.21 0.44–2.6	2.00 1.08–2.9	1.11 0.19–2.84	9.02 2.2–16.2	5.49 1.80–10.07	9.45 2.9–17.17	12.13 5.11–37.02
Na	7.61 1.5–16.8	14.36 5.6–27.5	11.59 1.6–28.0	4.59 2.5–7.29	6.33 4.2–12.3	7.67 4.2–12.3	9.58 4.5–30.0
K	1.88 0.5–3.0	2.53 0.5–8.2	1.86 0.75–5.1	1.62 0.9–2.4	2.62 1.24–5.80	3.05 0.75–12.0	4.46 1.17–18.0
HCO <sub>3</sub>	29.49 0.05–67.2	12.90 0.05–29.29	14.10 0.05–80.93	22.31 9.0–55.62	13.19 8.3–20.1	72.25 8.18–160.9	84.65 41.87–238.1
SO <sub>4</sub>	10.89 2.86–42.3	33.27 10.0–45.6	17.18 3.03–67.47	44.23 16.2–100.64	53.99 36–82	57.74 19.1–209.83	42.83 21.5–80.0
Cl	3.52 0.5–13.83	3.46 2.15–5.24	3.34 0.5–9.23	6.28 5.2–8.58	7.51 6.38–10.21	13.04 5.1–50.7	13.64 5.74–38.07
F	n.a.	n.a.	n.a.	0.17 0.04–0.29	0.12 0.02–0.28	0.25 0.08–1.46	0.18 0.02–0.35
PO <sub>4</sub>	0.33 0.01–2.22	0.17 0.07–0.31	0.16 0.01–0.60	0.05 0.01–0.14	0.06 0.03–0.10	0.12 0.01–0.38	0.06 0.01–0.15
NO <sub>3</sub>	8.52 2.0–14.2	9.73 6.1–14.1	10.74 5.6–24.2	3.09 0.8–7.0	5.01 1.8–7.8	4.41 0.3–14.0	6.26 0.9–25.7

() — number of samples; SEC — specific electric conductivity; \* — mean concentration; \*\* — range of concentrations, n.a. — not analysed; concentrations (except Al) in mg/L; bedrock types as in Table 1

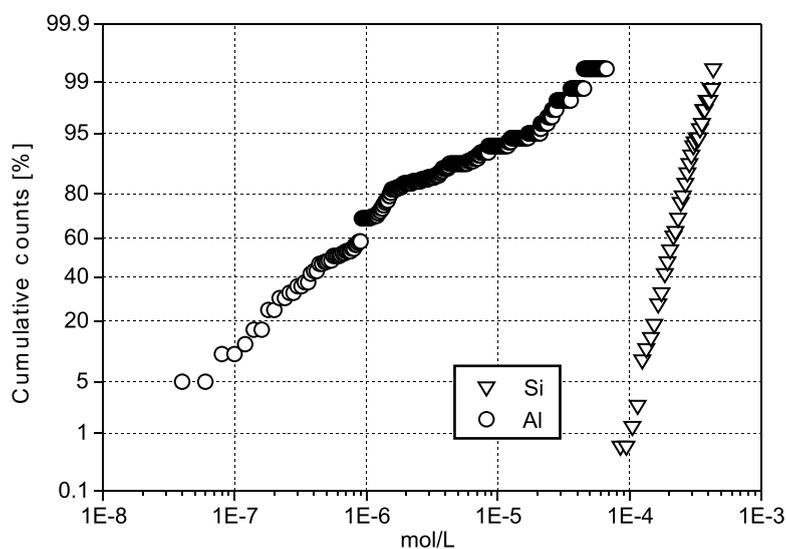


Fig. 2. Cumulative counts of silicon and aluminium molar concentration in the groundwater

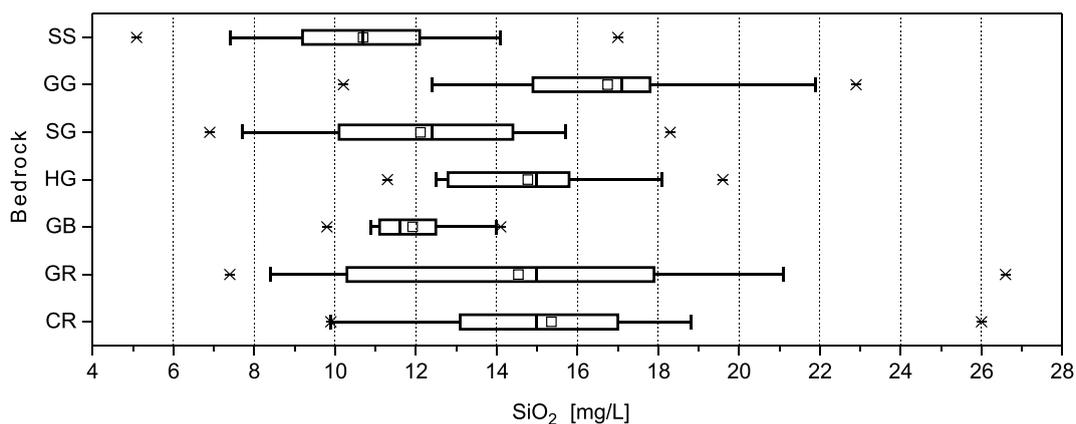


Fig. 3. Box charts of silica concentration in the groundwater

For bedrock types abbreviations see Table 1

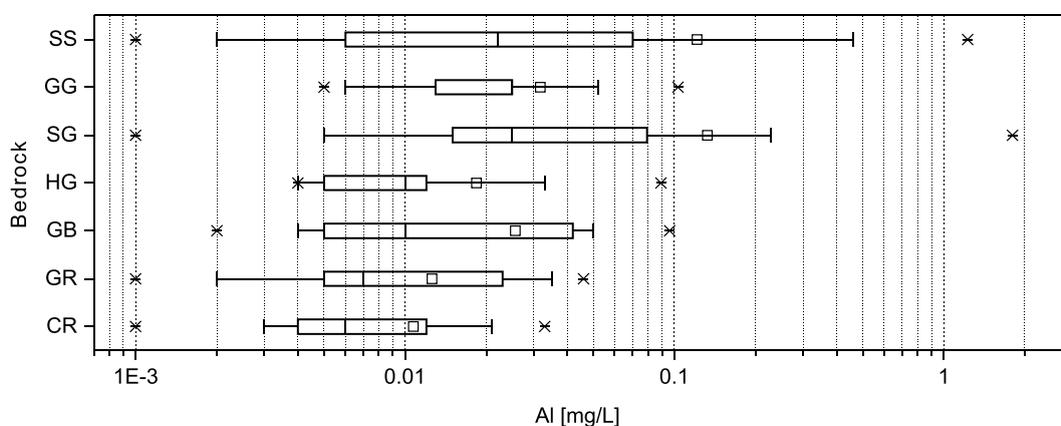


Fig. 4. Box charts of aluminium concentration in the groundwater

For bedrock types abbreviations see Table 1

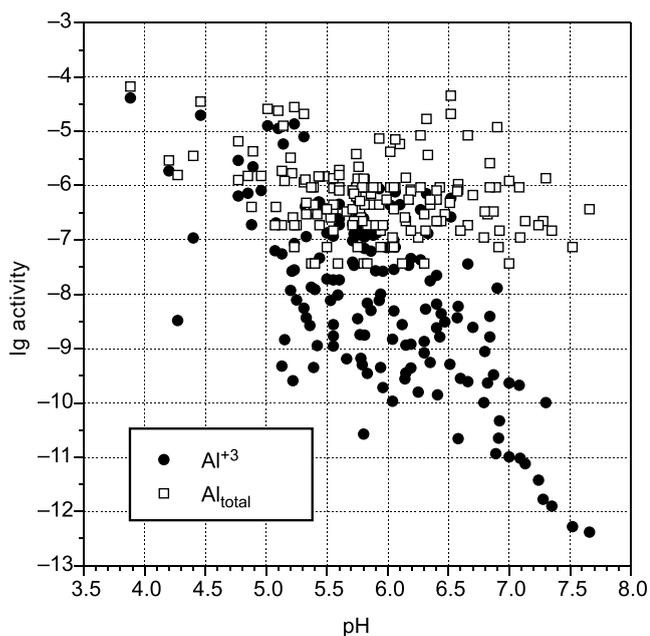


Fig. 5. Activity of Al<sub>total</sub> and Al<sup>3+</sup> vs. pH in the groundwater

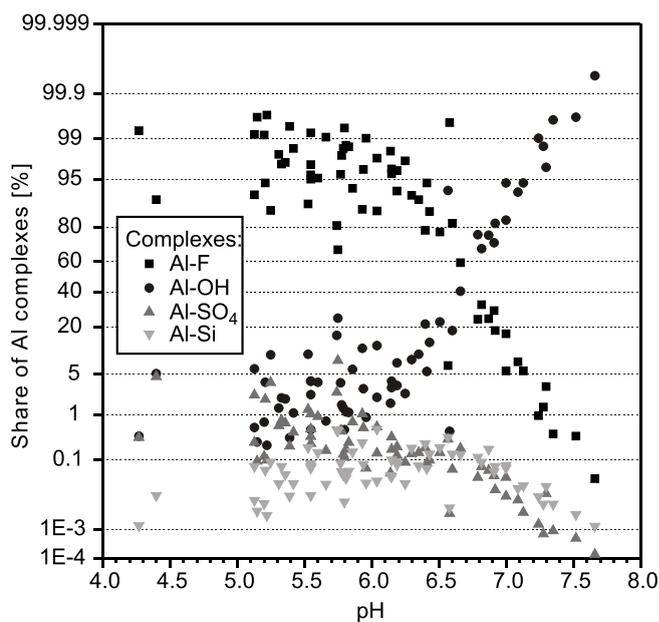


Fig. 6. Share of Al-F, Al-OH, Al-SO<sub>4</sub> and Al-Si complexes vs. pH in the groundwater

the bedrock (Table 1) and is stable in the most of the aquifers investigated (Table 3). Most waters also show supersaturation with respect to secondary reversible amorphous/short-range ordered aluminosilicates (allophane/imogolite). This might indicate the tendency of those solids to be formed in the weathered zone. Saturation indexes (SI) calculated by the geochemical code relate to the reaction of congruent dissolution. These better reflect the geochemical behaviour of reversible secondary phases (such as kaolinite, halloysite, allophane/imogolite,  $\text{Al}(\text{OH})_3$  forms and  $\text{SiO}_2$  forms) during weathering than the irreversible reactions of primary minerals. The latter ones usually dissolve incongruently. SI values suggest that the silica activity in groundwater might be controlled by chalcedony (Table 3).

Aluminium ( $\text{Al}^{+3}$ ) activity plotted vs. pH (Fig. 7) is scattered within a wide range, between the amorphous  $\text{Al}(\text{OH})_3$  and kaolinite solubilities. Groundwater from granitoids of the Kłodzko-Złoty Stok Massif (GR) and their country rocks, hornfels (CR) shows a regular pattern and indicates that locally and/or temporary a geochemical equilibrium with respect to microcrystalline gibbsite, gibbsite and the phases of solubility intermediate between halloysite and kaolinite phases might be maintained.

Interpretation of the ion activity quotient (IAQ) for solid phases was applied with regard to the activity of both elements (silicon and aluminium) in groundwater. IAQ curves were established for the following solids: allophanes by Su and Harsh (1998) (allophane-2.0 of Al/Si ratio = 2.0 and allophane-1.26 of Al/Si ratio = 1.26), proto-imogolite of composition by Lumsdon and Farmer (1995), kaolinite, and  $\text{Al}(\text{OH})_3$  forms. Due to the same Al/Si molar ratio, the curve for allophane-2.0 also relates to imogolite, and the curve for kaolinite to halloysite. The IAQ curve for  $\text{Al}(\text{OH})_3$  forms relates to the composition of gibbsite, microcrystalline gibbsite or amorphous aluminium hydroxide. The curves were calculated at mean values of  $\text{Al}^{+3}$  and activities in groundwater from particular bedrocks. The reaction quotient ( $\lg$  IAQ) for selected solids in groundwater from different bedrocks was plotted on Figure 8A–G and compared with the theoretical IAQ curves.

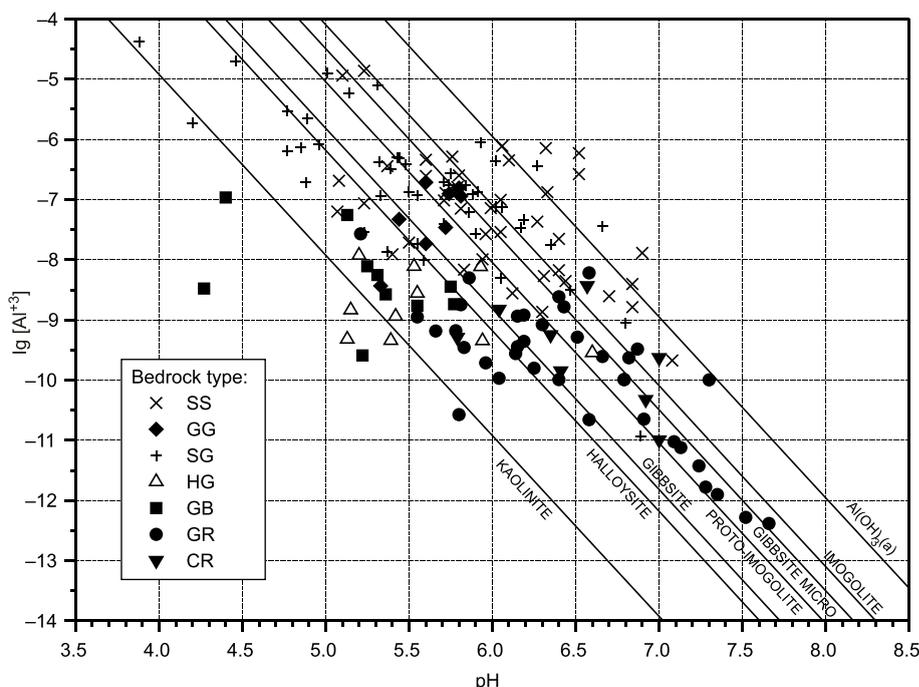
The power of the chemical data set for groundwaters from particular types of bedrock shows marked differences. This affects the reliability of interpretation. The chemical data

Table 3

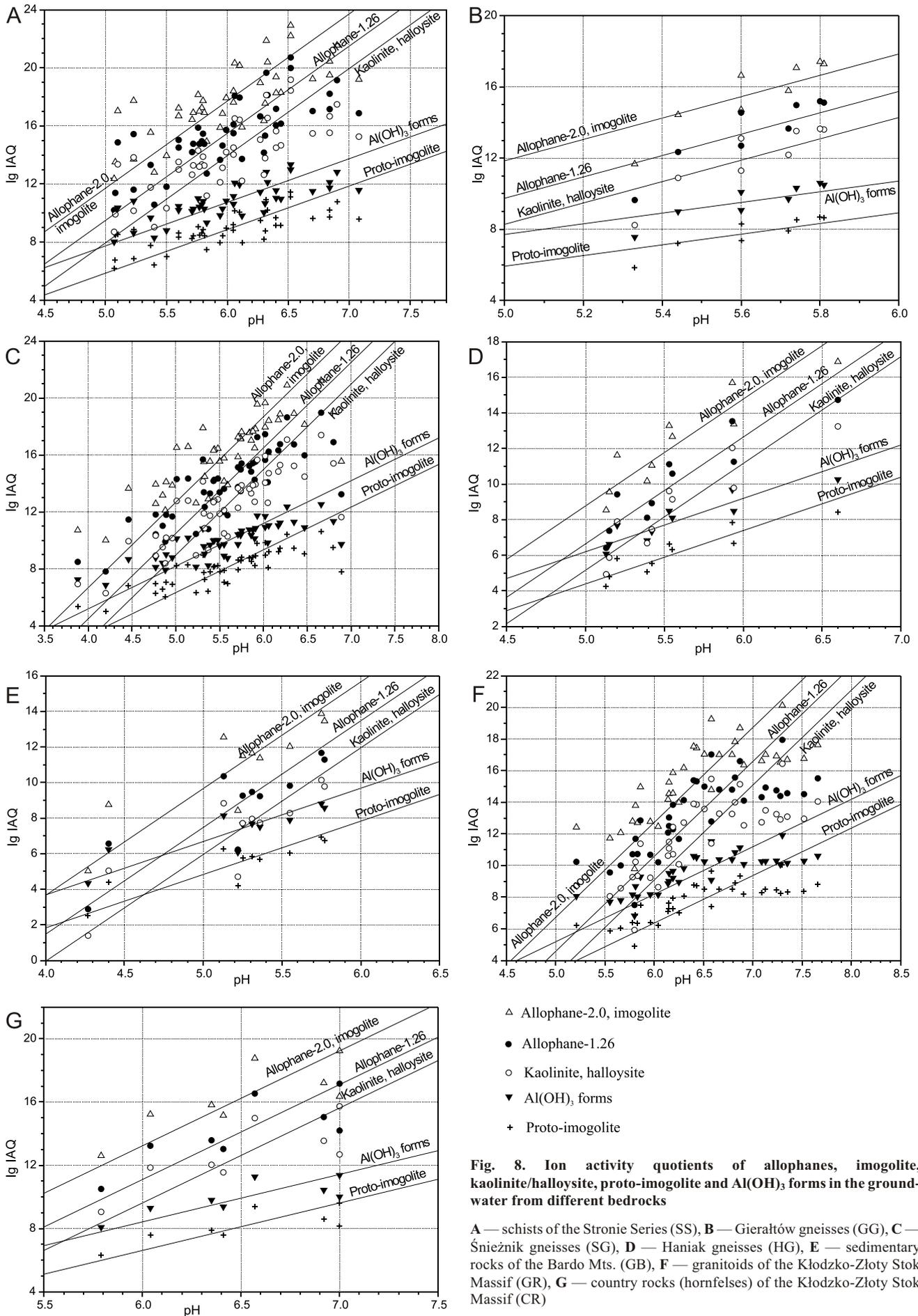
Mean saturation indexes (SI) of the groundwater with respect to solid phases

Solid phases	Bedrock						
	SS	GG	SG	HG	GB	GR	CR
K-feldspar	-1.61	-2.46	-2.64	-4.41	-5.51	-1.79	-1.12
Albite	-3.65	-4.15	-4.49	-6.53	-7.67	-3.84	-3.25
Anorthite	-7.01	-9.09	-9.27	-12.84	-14.98	-7.35	-6.35
Muscovite	6.86	4.09	4.38	-1.45	-3.74	4.60	6.14
Annite	-7.86	-10.83	-12.10	-14.89	-17.20	-6.71	-5.81
Phlogopite	-21.67	-23.82	-25.18	-24.36	-28.33	-16.36	-15.16
Chlorite	-27.99	-31.10	-33.26	-32.79	-38.89	-20.26	-18.35
Illite	<b>0.35</b>	<b>-1.61</b>	<b>-1.63</b>	-5.76	-7.84	<b>-0.90</b>	<b>0.32</b>
Ca-beidelite	2.74	<b>1.00</b>	<b>1.05</b>	-3.25	-5.15	<b>0.91</b>	<b>2.01</b>
Kaolinite	4.73	3.12	3.36	-0.49	-1.90	2.83	3.73
Halloysite	<b>-0.56</b>	-2.14	-1.92	-5.78	-7.17	-2.44	-1.53
Imogolite-natural*	4.08	2.03	2.56	-1.32	-2.74	1.87	2.69
Imogolite-syntet.*	4.60	2.55	3.08	-0.80	-2.22	2.39	3.21
Allophane-2.0*	3.48	1.43	1.96	-1.92	-3.34	1.27	2.09
Allophane-1.26*	4.19	2.25	2.70	-1.13	-2.59	2.05	2.89
Proto-imogolite	0.67	<b>-0.19</b>	<b>-0.03</b>	-2.01	-2.65	<b>-0.31</b>	<b>0.13</b>
Gibbsite	1.48	0.52	0.75	-1.27	-1.87	0.43	0.87
Gibbsite micro	<b>0.15</b>	-0.80	-0.57	-2.60	-3.19	-0.88	-0.45
$\text{Al}(\text{OH})_{3(a)}$	-1.39	-2.33	-2.11	-4.14	-4.73	-2.42	-1.98
Quartz	0.52	0.67	0.55	0.66	0.55	0.60	0.62
Chalcedony	<b>0.02</b>	0.18	<b>0.07</b>	<b>0.17</b>	<b>0.06</b>	<b>0.12</b>	<b>0.14</b>
$\text{SiO}_{2(a)}$	-0.88	-0.71	-0.84	-0.74	-0.84	-0.78	-0.76

\* — imogolites and allophanes after Su and Harsh (1996, 1998); bolded SI values relate to values within the equilibrium state range assumed ( $\pm 5\%$  lgK); shadowed cells indicate over-saturation ( $\text{SI} > +5\%$  [lgK]); bedrock types as in Table 1

Fig. 7. Activity of  $\text{Al}^{+3}$  vs. pH compared with the solubility of selected mineral phases, at 7°C

For bedrock types abbreviations see Table 1



**Fig. 8.** Ion activity quotients of allophanes, imogolite, kaolinite/halloysite, proto-imogolite and Al(OH)<sub>3</sub> forms in the groundwater from different bedrocks

**A** — schists of the Stronie Series (SS), **B** — Gierałtów gneisses (GG), **C** — Śnieżnik gneisses (SG), **D** — Haniak gneisses (HG), **E** — sedimentary rocks of the Bardo Mts. (GB), **F** — granitoids of the Kłodzko-Złoty Stok Massif (GR), **G** — country rocks (hornfels) of the Kłodzko-Złoty Stok Massif (CR)

for groundwater from the Stronie Series (SS), Śnieżnik gneisses (SG) and granitoids (GR) are more abundant than the hydrochemical data from other bedrock types.

The patterns of IAQs in groundwater from the metamorphic bedrocks dominated by gneisses and schists (SS, SG, GG, HG) show similarities. The IAQs for  $\text{Al}(\text{OH})_3$  forms and proto-imogolite sol show better agreement with the curves (especially in waters with pH between 5 and 6.5) than the IAQ of other solids (Fig. 8A–D). Moreover, IAQ patterns in groundwater from GG and HG bedrocks also conform to the solubility of kaolinite/halloysite and allophane-2.0/imogolite, but hydrochemical data here are not numerous. Groundwater from granitoids (GR) and hornfelses (CR) essentially show the same pattern (Fig. 8F and G). At pHs below 6.7 the IAQs are consistent with the solubility of  $\text{Al}(\text{OH})_3$  forms and proto-imogolite. Also in groundwater from sedimentary rocks of the Bardo Mts. (GB) the IAQs correlate to  $\text{Al}(\text{OH})_3$  forms and proto-imogolite, but hydrochemical data are few (Fig. 8E).

Despite the different bedrock mineralogies, the chemistry of the groundwater shows some common features. The ion activity quotient of  $\text{Al}(\text{OH})_3$  forms and aluminosilicate sol (proto-imogolite) shows the strongest agreement with the theoretical composition, especially in groundwater of pH below 6.5. Proto-imogolite relates to hydroxyaluminosilicate of the  $\text{HAS}_A$  type, and can form when the silica concentration in solution is close to that of aluminium (Doucet *et al.*, 2001; Exley *et al.*, 2002). Therefore, the formation of  $\text{HAS}_A$  or proto-imogolite in the aquifers studied is rather doubtful (Fig. 2).

The IAQ plots indicate a hypothetical equilibrium of groundwater with both aluminosilicates and  $\text{Al}(\text{OH})_3$  forms. This suggests that the groundwater studied might be in equilib-

Table 4

Reactions of incongruent dissolution between aluminosilicate solids and the  $\text{Al}(\text{OH})_3$  forms considered

Reactions	
(kaolinite, halloysite, $\text{HAS}_B$ ) $\leftrightarrow \text{Al}(\text{OH})_{3(s)}$	$\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 + 5\text{H}_2\text{O} = 2\text{Al}(\text{OH})_{3(s)} + 2\text{H}_4\text{SiO}_4^0$
imogolite $\leftrightarrow \text{Al}(\text{OH})_{3(s)}$	$\text{Al}_2\text{SiO}_5(\text{OH})_4 = 2\text{Al}(\text{OH})_{3(s)} + \text{H}_4\text{SiO}_4^0$
proto-imogolite $\leftrightarrow \text{Al}(\text{OH})_{3(s)}$	$0.5(\text{HO})_3\text{Al}_2\text{O}_3\text{SiOH} = \text{Al}(\text{OH})_{3(s)} + 0.5\text{H}_4\text{SiO}_4^0$

rium with more than one secondary solid. Simultaneous geochemical equilibrium of the groundwater with different secondary phases suggests incongruent transformation and an equilibrium state between them. Hypothetical incongruent reactions between the different aluminosilicates and the  $\text{Al}(\text{OH})_3$  forms of various crystallinity were considered (Table 4). Amongst the  $\text{Al}(\text{OH})_3$  forms gibbsite, microcrystalline gibbsite, and amorphous  $\text{Al}(\text{OH})_3$  were taken into consideration, whereas kaolinite, halloysite, imogolite, and proto-imogolite were taken into account amongst aluminosilicates. Apart from the above-mentioned aluminosilicate phases the hypothetical reaction of incongruent dissolution between hydroxyaluminosilicate  $\text{HAS}_B$  and  $\text{Al}(\text{OH})_3$  forms was also considered. This incongruent reaction was ascertained by Schneider *et al.* (2004) during the laboratory experiments on  $\text{HAS}_B$  dissolution. In the absence of a precisely determined  $\text{HAS}_B$  solubility constant, the value ( $\lg K_7 = 14.0 \pm 0.7$ ) estimated by Dobrzyński (2006a) was used in the calculation. The allophane-2.0 and the allophane-1.26 after Su and Harsh (1998) were not considered due to the lack of enthalpy of reaction ( $\Delta H_r^\circ$ ) data. The calculation was performed for 7°C, as a temperature close to mean values in groundwater (Table 2). The thermodynamic data applied to calculate the equilibrium constants for the incongruent reactions are given in Table 5. An equilibrium constant (Table 6) was used to calculate silica activity in solution that should be maintained by the particular re-

Table 5

Thermodynamic data used in calculation of the equilibrium constant for incongruent reactions

Reaction	$\lg K_{25}$	$\Delta H_r^\circ$ [kJ/mol]	$\lg K_7$	Source
Quartz, $\text{SiO}_2 + 2\text{H}_2\text{O} = \text{H}_4\text{SiO}_4^0$	-3.98	22.7	-4.235	a
Chalcedony, $\text{SiO}_2 + 2\text{H}_2\text{O} = \text{H}_4\text{SiO}_4^0$	-3.55	20.3	-3.778	a
$\text{SiO}_2$ amorphous, $\text{SiO}_2 + 2\text{H}_2\text{O} = \text{H}_4\text{SiO}_4^0$	-2.71	15.5	-2.884	a
Gibbsite, $\text{Al}(\text{OH})_3 + 3\text{H}^+ = \text{Al}^{+3} + 3\text{H}_2\text{O}$	8.11	-95.395	9.184	a
Microcrystalline gibbsite, $\text{Al}(\text{OH})_3 + 3\text{H}^+ = \text{Al}^{+3} + 3\text{H}_2\text{O}$	9.35	-102.508	10.504	a
$\text{Al}(\text{OH})_3$ amorphous, $\text{Al}(\text{OH})_3 + 3\text{H}^+ = \text{Al}^{+3} + 3\text{H}_2\text{O}$	10.8	-110.876	12.048	a
Kaolinite, $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 + 6\text{H}^+ = 2\text{Al}^{+3} + 2\text{H}_4\text{SiO}_4^0 + \text{H}_2\text{O}$	7.435	-147.695	9.097	a
Halloysite, $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 + 6\text{H}^+ = 2\text{Al}^{+3} + 2\text{H}_4\text{SiO}_4^0 + \text{H}_2\text{O}$	12.498	-167.025	14.378	b
Imogolite, $\text{Al}_2\text{O}_3\text{Si}(\text{OH})_4 + 6\text{H}^+ = 2\text{Al}^{+3} + \text{H}_4\text{SiO}_4^0 + 3\text{H}_2\text{O}$	12.10	-206.99 <sup>1</sup>	14.430	c
Proto-imogolite, $0.5(\text{HO})_3\text{Al}_2\text{O}_3\text{SiOH} + 3\text{H}^+ = \text{Al}^{+3} + 0.5\text{H}_4\text{SiO}_4^0 + 1.5\text{H}_2\text{O}$	7.02	-96.8	8.109	d
Hydroxyaluminosilicate $\text{HAS}_B$ , $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 + 6\text{H}^+ = 2\text{Al}^{+3} + 2\text{H}_4\text{SiO}_4^0 + \text{H}_2\text{O}$	-	-	14.0 ( $\pm 0.7$ )	e

a — Nordstrom *et al.* (1990); b — Ball and Nordstrom (1991); c — Wada and Kakuto (1999); d — Lumsdon and Farmer (1995); e — Dobrzyński (2006a);  $\Delta H_r^\circ$  — enthalpy of reaction calculated after enthalpy of formation data:  $\Delta H_{f, \text{Al}^{+3}}^\circ = -540.9$  kJ/mol (Palmer and Wesolowski, 1992),  $\Delta H_{f, \text{H}_2\text{O}}^\circ = -285.83$  kJ/mol (Robie and Hemingway, 1995),  $\Delta H_{f, \text{H}_4\text{SiO}_4^0}^\circ = -1457.3$  kJ/mol (Ball and Nordstrom, 1991),  $\Delta H_{f, \text{imogolite}}^\circ = -3189.6$  kJ/mol (Farmer *et al.*, 1979)

Table 6

Equilibrium constants ( $\lg K_7$ ) calculated for the incongruent reactions

	Al(OH) <sub>3</sub> amorphous	Gibbsite microcrystalline	Gibbsite
Kaolinite	-14.999	-11.911	-9.271
Halloysite	-9.718	-6.630	-3.990
Imogolite	-9.666	-6.578	-3.938
Proto-imogolite	-3.939	-2.395	-1.075
Hydroxylaluminosilicate HAS <sub>B</sub>	-10.096	-7.008	-4.368

Table 7

Silica activity ( $\lg[H_4SiO_4^0]$ ) in equilibrium with incongruent reactions, at 7°C

	Al(OH) <sub>3</sub> amorphous	Gibbsite microcrystalline	Gibbsite
Kaolinite	-7.500	-5.956	-4.636
Halloysite	-4.859	-3.315	-1.995
Imogolite	-9.666	-6.578	-3.938
Proto-imogolite	-7.878	-4.790	-2.150
Hydroxylaluminosilicate HAS <sub>B</sub>	-5.048 ( $\pm 0.35$ )*	-3.504 ( $\pm 0.35$ )*	-2.184 ( $\pm 0.35$ )*

\* — silica activity relates to the uncertainty range of  $\lg K_{HAS-B,7} = 14.0 \pm 0.7$  (Table 5)

actions at the equilibrium state (Table 7). Afterwards, the silica equilibrium activities calculated were compared with the silica activities in groundwater. The correctness of equilibrium constants depends upon the thermodynamic data quality. Moreover, the value of reaction constant for incongruent reactions varies with the temperature and the crystallinity of solid phases. The poorer the arrangement of Al(OH)<sub>3</sub> structure and/or the

better arrangement of aluminosilicate structure and/or the higher temperature, the lower is the silica equilibrium activity.

The silica equilibrium activities calculated fluctuate within a wide range (Table 7). Figure 9 shows only the values close to the field data. Silica equilibrium activities that are higher than amorphous silica solubility (as for the halloysite  $\leftrightarrow$  gibbsite reaction) are unrealistic, because they conform to metastable conditions.

The silica activities in groundwater are situated between the solubility of quartz and the solubility of amorphous silica (Fig. 9). Two hypothetical incongruent reactions (imogolite  $\leftrightarrow$  gibbsite and HAS<sub>B</sub>  $\leftrightarrow$  microcrystalline gibbsite) have solubilities closest to the field data on silica concentration. The mean silica activity in groundwater ( $\lg[H_4SiO_4^0] = -3.6704$ ) is higher than the solubility of chalcedony (Fig. 9), and lower than the silica activity at the equilibrium state in the incongruent reaction between HAS<sub>B</sub> and microcrystalline gibbsite. In most groundwater samples, the silica activity found is between the equilibrium with chalcedony congruent dissolution and the equilibrium in the incongruent reaction HAS<sub>B</sub>  $\leftrightarrow$  microcrystalline gibbsite.

Assuming that the geochemical equilibrium with the above-mentioned phases is maintained in the systems studied, the concentration of silica can be explained in different ways. The silica activity in groundwater might result from: (1) the HAS<sub>B</sub>  $\leftrightarrow$  microcrystalline gibbsite reaction; (2) dissolution of chalcedony; or (3) effects of both reactions.

The value of equilibrium silica activity calculated for the reaction (1) is affected by the quality of thermodynamic data used. The solubility of microcrystalline gibbsite was taken after Nordstrom *et al.* (1990), and the solubility of HAS<sub>B</sub> ( $\lg K_7 = 14.0 \pm 0.7$ ) after Dobrzyński (2006a; Table 5). The discrepancy between the equilibrium silica activity and the mean activity in groundwater can originate from uncertainty in the estimation of the HAS<sub>B</sub> solubility. The equilibrium silica activity fits very well to the field hydrochemical data when a HAS<sub>B</sub> solubility with the uncertainty range  $\pm 0.7$  is considered (Fig. 9). Most groundwaters show silica activities between that for

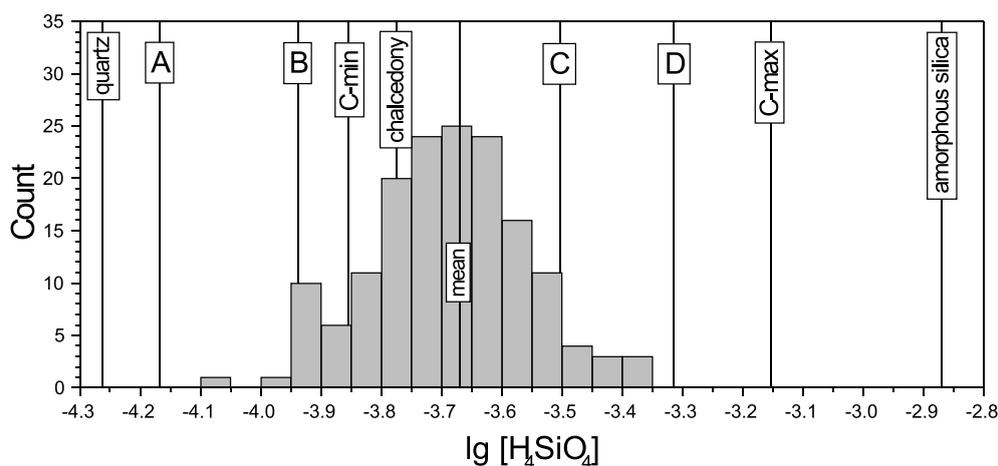


Fig. 9. Comparison of  $H_4SiO_4^0$  activity in the groundwater with equilibrium activity for incongruent reactions between aluminosilicates and Al(OH)<sub>3</sub> forms, and solubility of silica forms, at 7°C

Explanations of incongruent reactions: A — allophane 2.0  $\leftrightarrow$  gibbsite; B — imogolite  $\leftrightarrow$  gibbsite; C — hydroxylaluminosilicate HAS<sub>B</sub>  $\leftrightarrow$  microcrystalline gibbsite; D — halloysite  $\leftrightarrow$  microcrystalline gibbsite; C-min and C-max — silica activities relate to the uncertainty range of  $\lg K_{HAS-B}$  (Table 7)

$\lg K_{\text{HAS-B}, 7} = 14.0$  and for  $\lg K_{\text{HAS-B}, 7} = 13.3$ , “C” and “C-min” activities on Figure 9, respectively. This pattern might suggest uncertainty in the estimation of  $\lg K_{\text{HAS-B}}$ . However, it also can result from the solubility of the  $\text{Al}(\text{OH})_3$  form. Lower equilibrium silica activity suggests that in the geochemical system the  $\text{HAS}_B$  can dissolve forming  $\text{Al}(\text{OH})_3$  forms that are slightly more disordered and more soluble than microcrystalline gibbsite taken after Nordstrom *et al.* (1990).

The role of chalcedony solubility might also be significant, especially in groundwater with lower silica activity. However, the distribution of silica concentration in the groundwater is close to the normal one (Figs. 2 and 9). This suggests that the same process may be responsible for silica control in groundwater from different bedrocks. Geochemical equilibrium of the incongruent reaction between  $\text{HAS}_B$  and forms of  $\text{Al}(\text{OH})_3$  seems to be the most probable controlling process in the geochemical systems studied. Analysis of the extensive set of hydrochemical data in terms of hydroxyaluminosilicate  $\text{HAS}_B$  solubility indicated that the solid phase may play role, especially in groundwater of pH above 6.7 (Dobrzyński, 2006a).

The aquifer rocks differ in mineral reactivity and neutralisation capacity, which crucially affects groundwater pH. Water pH — especially in the shallow unconfined aquifers — shows seasonal fluctuations. Silicate minerals dissolve predominantly by reactions that depend on  $\text{H}^+$  activity in the solution. Changes of pH might cause the different phases to play an important role in controlling the solute activity.

The results of the ionic equilibrium analysis (based on saturation indices, solubility curves, quotients of reaction) allowed indication the phases that probably are responsible for the solubility control of silicon and aluminium. The main assumption is that locally and/or periodically (seasonally) a partial geochemical equilibrium between groundwater and the secondary phases might be reached and maintained.

In groundwater from gneisses and crystalline schists of the Śnieżnik-Lądek metamorphic complex (SS, SG, GG) aluminium is likely controlled by the dissolution of  $\text{Al}(\text{OH})_3$  forms at pHs below 6.5(6.7). In waters from SS and SG bedrocks at pHs above 6.7 an incongruent reaction between hydroxyaluminosilicate  $\text{HAS}_B$  and a  $\text{Al}(\text{OH})_3$  form is responsible for the control of aluminium and silicon activity. Both elements in groundwater from the Gierałtów gneisses (GG) also might be controlled by the solubility of kaolinite/halloysite and/or an allophane-like phase, but the quantity of the data available is very low.

The granitoids of the Kłodzko-Złoty Stok (GR) and their country rocks — hornfels (CR) — are rocks that are more reactive than the other bedrocks studied, which results in the highest pH of the groundwater (Table 2). The chemistry of groundwater from GR and CR bedrocks present a pattern similar to that found in the Śnieżnik-Lądek metamorphic complex. In groundwater with pH below 6.7, aluminium might be controlled by the solubility of  $\text{Al}(\text{OH})_3$  forms, whereas in water with pH above 6.7 by the incongruent dissolution between  $\text{HAS}_B$  and  $\text{Al}(\text{OH})_3$  forms. The latter reaction also plays a role in the silicon activity control.

The power of a set of hydrochemical data for groundwater from the Haniak gneisses (HG) is very low. Aluminium activity in is probably controlled by the  $\text{Al}(\text{OH})_3$  form.

Sedimentary rocks (mainly conglomerates) of the Bardo Mts (GB) are poorly weatherable. Groundwaters occur mainly in the regolith aquifer, and are not efficiently neutralised. Their chemical composition probably illustrates the most chemical disequilibrium conditions amongst the geochemical systems studied. Silicon and aluminium concentrations in groundwater likely result from kinetics or steady-state conditions between the weathering release and the hydrological removal.

It is conceivable that chalcedony might be responsible for the silicon activity control in all the groundwater studied, especially if the pH does not exceed 6.5(6.7).

## CONCLUSIONS

The chemistry of the groundwater studied is at disequilibrium with the aquifer rocks. During irreversible weathering transformation of primary rock-forming minerals an assemblage of secondary reversible and irreversible solid phases is formed in the weathered zone. The latter phases usually are more soluble than the primary minerals. Despite the short-time nature of water transit in the hydrogeological system, locally and/or periodically groundwater reaches partial geochemical equilibrium with some of secondary phases. Interpretation of the aqueous chemistry from the viewpoint of solid solubilities allows indication of the phases that are probably responsible for silicon and/or aluminium solubility in groundwater.

Groundwater chemistry depends upon the reactivity of the minerals in the water-bearing rocks. Granitoids of the Kłodzko-Złoty Stok Massif (GR) with their country rocks composed of hornfels (CR) are the most reactive amongst the bedrocks studied, whereas the sedimentary rocks (mainly conglomerates) of the Bardo Mts. (GB) are the least weatherable. Bedrock reactivity affects the chemistry and pH of the solution, and governs the solubility and the stability of the secondary solid phases.

Groundwater chemistry was interpreted in terms of solids solubilities with the main assumption that the partial geochemical equilibrium between the groundwater and the secondary phases locally and/or periodically (seasonally) might be reached and maintained in the systems studied.

Silicon and aluminium activities in the groundwater are mainly controlled by the equilibrium of congruent dissolution of the reversible secondary phases (such as  $\text{Al}(\text{OH})_3$  forms and chalcedony) and/or by the incongruent reaction between the hydroxyaluminosilicate colloid  $\text{HAS}_B$  and the hydroxyaluminium forms.

Groundwaters from the Śnieżnik-Lądek metamorphic complex (gneisses and crystalline schists), and those from the granitoids of the Kłodzko-Złoty Stok Massif and their country rocks (hornfels) show similar features of aquatic chemistry. Where groundwater pH is below 6.7, aluminium is likely controlled by the reversible congruent dissolution of  $\text{Al}(\text{OH})_3$ . In groundwater of pH above 6.7 the equilibrium of the incongruent dissolution of hydroxyaluminosilicate colloid,  $\text{HAS}_B$  with the production of  $\text{Al}(\text{OH})_3$  forms is responsible for the control of aluminium and silicon activity in the solution. It is conceivable that the silicon activity in groundwater with pH below 6.7 is controlled by the reversible solubility of chalcedony.

Silicon and aluminium in groundwater from the Gierałów gneisses (that belong to the Śnieżnik-Lądek metamorphic complex) also might be controlled by the solubility of kaolinite/halloysite and/or an allophane-like phase. However, interpretation is difficult because the hydrochemical data set is very small.

The power of a set of hydrochemical data for groundwater from the Haniak gneisses (HG) also is very low. Aluminium activity in these groundwaters is probably controlled by the  $\text{Al}(\text{OH})_3$  form.

Sedimentary rocks (conglomerates) of the Bardo Mts. (GB) are poorly weatherable. Groundwaters in that bedrock are not efficiently neutralised. The chemical composition shows chemical disequilibrium with respect to the solid phases. The silicon and aluminium concentrations in the groundwater probably result from kinetics or a steady-state situation between the weathering release and the hydrological removal.

The concentration of silica and aluminium in the groundwater can also be affected by other than equilibrium processes, such as adsorption, kinetics or a steady-state condition between

weathering release and hydrologic removal. The results shown are based on mineral solubilities. Future chemical and mineralogical examinations should focus on the presence of  $\text{Al}(\text{OH})_3$  forms and amorphous/short-range ordered aluminosilicates (allophanes/imogolite) in the weathered zone developed on bedrock in the eastern part of the Kłodzko Region to verify the conclusions based on the aqueous chemistry and the species solubility. In the light of the results obtained here the presence of hydroxyaluminosilicate HAS in groundwater is also a promising research subject.

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