

Silica solubility in groundwater from Permian volcanogenic rocks (the Sudetes Mts., SW Poland) — the role of reversible aluminosilicate solids

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The chemistry of groundwater in Permian volcanic rocks (rhyolitic tuffs, trachyandesites) in two small headwater catchments (the Sudetes Mts., SW Poland) has been investigated. The calculated transfer of silica released during weathering is greater than the real concentration in groundwater, and indicates that part of the silica is immobilized in secondary aluminosilicates. Silica solubility is interpreted in terms of the solubility of reversible secondary aluminosilicates (allophanes, hydroxyaluminosilicates). Partial chemical equilibrium of these phases is sometimes locally achieved. In groundwaters with pH above 6.7 from trachyandesites of the Bukowiec Mt. type, chemical equilibrium with respect to the hydroxyaluminosilicate HAS_B is probably maintained. Its solubility constant, calculated accordingly to the method given by Schneider *et al.* (2004), is $\lg K_{\text{HAS}_B} = -44.74 (\pm 0.52)$, and indicates that this “field” HAS_B has a solubility lower than the published experimental value ($\lg K_{\text{HAS}_B} = -40.6 \pm 0.15$) for synthetic HAS_B (*op.cit.*). Non-equilibrium with respect to aluminosilicates in groundwaters from rhyolitic tuffs and from trachyandesites of the Stożek Wielki Mt. type is caused by the short turn-over time of groundwater in the system and by the poor neutralisation capacity of the bedrock. The silica concentration in these groundwaters results from steady-state conditions achieved between weathering release, hydrological removal and precipitation of secondary phases. The hydrogeochemical data are conducive to the presence of allophane minerals in the weathered rhyolitic tuffs.

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Key words: Sudetes Mts., groundwater chemistry, volcanic rocks, silicon, aluminium, hydroxyaluminosilicates (HAS), allophanes.

INTRODUCTION

The paper deals with conditions affecting the silica content of groundwater. Attention is focussed on silica sources and solubility, especially on the role of reversible metastable secondary aluminosilicate solid phases such as allophanes and hydroxyaluminosilicates. The hydrochemical data are interpreted in terms of the solubility of various aluminosilicate phases. The hydroxyaluminosilicate (HAS) colloids probably play an important role in formation aluminosilicate (allophane/imogolite) solids (Farmer and Lumsdon, 1994; Lumsdon and Farmer, 1995; Doucet *et al.*, 2001; Exley *et al.*, 2002). The formation of HAS phases is of environmental importance since they reduce aluminium toxicity (e.g., Exley *et al.*, 1997).

Research into the aluminosilicate solid and solute forms are focused mainly on soils, soil waters and surface waters because of environmental concerns, e.g. soil fertility, reduction of aluminium toxicity to plants and aqueous organisms. Groundwater is rarely examined from this viewpoint.

Groundwater chemistry has been investigated in two small forested headwater catchments located in the central part of the Sudetes Mts. (SW Poland). The main objects of research comprise relationships between bedrock and groundwater chemistry, and silicon geochemistry in the short turn-over time zone of the hydrogeological system.

METHODS

Groundwater was sampled in 17 (ephemeral and perennial) springs during different seasons. Water samples were filtered through cellulose-nitrate 0.45 µm membrane filters, and stored in LDPE bottles. Silica concentration was determined by the spectrophotometric silicomolybdate method, while aluminium concentration was measured by the ETA AAS method. The species activities were calculated by the PHREEQC code (Parkhurst and Appelo, 1999). In the constructing of solubility curves for mineral phases present thermodynamic data was used. Solubility curves for allophane/imogolite phases were based on data of al-

lophane of Al/Si molar ratio = 2.0 ($\lg K_{25} = 14.20$) and allophane of Al/Si = 1.26 ($\lg K_{25} = 11.27$) after Su and Harsh (1998), proto-imogolite ($\lg K_{25} = 7.02$, $\Delta H_r^0 = -96.8$ kJ/mol after Lumsdon and Farmer, 1995). Solubility of imogolite was calculated after $\lg K_{25} = 12.10$ (Wada and Kakuto, 1999) and the enthalpy of the solubility reaction $\text{Al}_2\text{O}_3\text{Si}(\text{OH})_4 + 6\text{H}^+ = 2\text{Al}^{+3} + \Delta H_r^0 + 3\text{H}_2\text{O}$ ($\Delta H_r^0 = -206.99$ kJ/mol) was calculated using enthalpy of formation data: ΔH_f^0 imogolite = -3189.6 kJ/mol (Farmer *et al.*, 1979), ΔH_f^0 Al⁺³ = -540.9 kJ/mol (Palmer and Wesolowski, 1992), ΔH_f^0 H₄SiO₄⁰ = -1457.3 kJ/mol (Ball and Nordstrom, 1991), ΔH_f^0 H₂O = -285.83 kJ/mol (Robie and Hemingway, 1995).

GEOLOGICAL SETTING AND HYDROGEOLOGY

The headwater catchments studied (Fig. 1) are located in the Kamienne Mts (a range in the central part of the Sudetes Mts., SW Poland). Altitude in catchment 1 ranges from 517.5 to 853.8 m a.s.l., and in catchment 2 from 580.0 to 901.7 m a.s.l. The mean annual temperature of air varied between 6.6 and 5.5°C, and annual precipitation usually ranged from 800 to 900 mm (Walczak, 1968). The catchments are for-

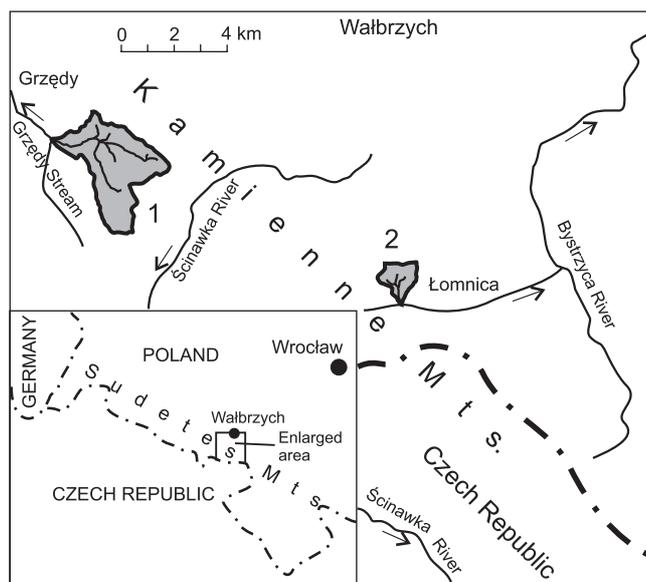


Fig. 1. Location of the catchments studied

1, 2 — number of catchment

ested, uninhabited, and with no point-sources of pollution. The catchments receive acid atmospheric deposition. Monthly weighted mean pH of wet deposition has varied between 4.60 and 5.19, with an average value of 4.79 (Dobrzyński, 1997). Spruce prevails in the forests, with some birch, sycamore, larch, and beech. Soils, predominantly inceptisols, are acid, $\text{pH}_{\text{KCl}} 2.90$ – 3.95 , and their sorption complex is dominated by aluminium cations that usually occupy from 53 to 86% of CEC (Dobrzyński, 1997).

The catchments are composed of Lower Permian volcanic rocks. Catchment 1 is composed of trachyandesites of the Stożek Wielki Mt. type (SW-trachyandesites) in the eastern part, and of a rhyolitic tuffs (bedded tuffs, massive non-welded and welded tuffs) in the western part (Awdankiewicz, 1999a, b). Catchment 2 is composed of trachyandesites of the Bukowiec Mt. type (B-trachyandesites) (*op.cit.*). The mineral composition of the bedrock is given in Table 1.

Two types of aquifer occur in the areas studied (Dobrzyński, 1997): (1) a shallower aquifer in the regolith, and (2) a deeper, fissured aquifer in the volcanic bedrock. The thickness of regolith is usually from 0 to about 2 metres with a low water retention capacity. The depth of the fractured zone in the Sudetes Mts. is estimated usually on at 50–80 metres (Kowalski *et al.*, 1986; Kowalski, 1992). Locally, hydraulic connections between these aquifers are present. Groundwater discharged in the ephemeral springs derives from and illustrates the chemistry of the regolith, whereas waters discharged in the perennial springs derive from the fissured aquifer. Seasonally some perennial springs discharge also water from the regolith, and ephemeral springs might discharge water from the fissured aquifer. Both the fissured aquifer and the regolith aquifer occur in catchment 1. Rocks of the tuffaceous succession vary from massive to porous structure, and from fissure-controlled to intergranular porosity. The SW-trachyandesites have fissure porosity. In catchment 2 groundwater in the B-trachyandesites forms fissure aquifer that is discharged by streams and by perennial springs only. Springs that occur in the areas studied are divided according to two criteria: (1) the bedrock types and (2) the outflow persistence (perennial or ephemeral springs).

ESTIMATION OF WEATHERING SILICA RELEASE

The groundwater has a TDS value between 63 and 214 mg/L (Table 2). Sulphate, bicarbonate and calcium ions dominate amongst solutes, and water is usually of SO₄-Ca or

Table 1

Mineral composition of the volcanic rocks in the study area (after Nowakowski, 1967, 1968; Awdankiewicz, 1999b)

Rhyolitic tuffs	SW-trachyandesites ^a	B-trachyandesites ^b
Clasts of quartz, volcanic glass, feldspars, with fragments of volcanic, detritic, metamorphic rocks, and dispersed clay-carbonate substances. Rock matrix (70–80%): feldspars, quartz, fragments of effusive rocks.	Plagioclase and anorthoclase phenocrysts, pseudomorphoses after pyroxenes and olivines. Rock matrix (70–90%): albitised plagioclases with relicts of andesine and overgrowths with alkaline feldspar.	Microcline crystals of plagioclases (andesine-labradorite). Rarely orthoclase phenocrysts, pseudomorphoses after pyroxenes and olivines, hornblende, Fe and Ti oxides, quartz, apatite, devitrified volcanic glass, secondary calcite.

a — trachyandesites of the Stożek Wielki Mt. type; b — trachyandesites of the Bukowiec Mt. type

Table 2

Physico-chemical characteristics of the groundwater studied (after Dobrzyński, 1997 updated)

		Rhyolitic tuffs		SW-trachyandesites		B-trachyandesites
		Aquifer		Aquifer		Aquifer
		fissure	regolith	fissure	regolith	fissure
SEC [$\mu\text{S}/\text{cm}$]	mean (N)	196.5 (102)	176.5 (24)	177.4 (66)	201.1 (22)	203.3 (89)
	range	85–312	107–222	150–247	173–246	80–310
TDS	mean (N)	124.9 (102)	116.2 (24)	111.7 (66)	126.0 (22)	138.6 (89)
	range	81–214	80–150	63–148	80–154	87–194
pH	mean (N)	6.19 (102)	5.96 (24)	5.29 (66)	4.80 (22)	7.06 (89)
	range	5.45–7.4	5.50–6.80	4.42–6.94	4.14–5.89	6.32–7.67
T [$^{\circ}\text{C}$]	mean (N)	6.20 (102)	5.67 (24)	6.75 (66)	6.82 (22)	7.01 (89)
	range	3.8–8.9	2.0–8.2	2.0–8.9	3.7–13.9	0.2–15.8
SiO ₂	mean (N)	12.00 (62)	11.38 (16)	17.05 (45)	16.51 (13)	12.88 (57)
	range	6.8–14.9	7.8–13.8	11.4–21.5	12–21.4	6.2–16.1
Al [$\mu\text{g}/\text{L}$]	mean (N)	10.6 (98)	19.8 (20)	215.1 (62)	880.3 (19)	9.9 (89)
	range	1–73	2.7–83	12–1500	23–3300	2–46
Ca	mean (N)	18.8 (94)	18.1 (19)	16.3 (60)	17.7 (17)	27.9 (85)
	range	12.8–29.8	13–24.5	10.5–24.1	8.3–29.5	19.7–44
Mg	mean (N)	5.14 (94)	4.69 (19)	5.67 (60)	7.14 (17)	3.84 (85)
	range	1.9–13.3	1.4–8.4	1.2–26.6	3.9–12.6	0.7–9.2
K	mean (N)	11.31 (94)	7.43 (19)	4.97 (60)	5.14 (17)	1.84 (85)
	range	5.2–21.2	2.2–11.1	3.3–13.5	4.1–8	0.2–14.1
Na	mean (N)	3.69 (94)	3.50 (19)	5.36 (60)	4.16 (17)	4.76 (85)
	range	1.4–6.2	2.2–4.8	2.6–8.3	2.5–6.0	1.7–8.8
HCO ₃	mean (N)	10.5 (94)	10.6 (19)	8.2 (60)	6.1 (17)	35.5 (85)
	range	0.5–32.5	0.5–22	0.5–14.6	0.2–18.3	3–67.7
SO ₄	mean (N)	51.9 (94)	46.2 (19)	39.9 (60)	54.9 (17)	41.8 (85)
	range	21–148.7	16.7–104.9	19.2–101.3	27.9–104.7	16.3–88.9
Cl	mean (N)	9.7 (94)	9.8 (19)	10.9 (60)	11.1 (17)	8.8 (85)
	range	2.1–18.8	7.1–12.4	6.0–27.6	8.2–17.7	3.5–14.7
PO ₄	mean (N)	0.09 (62)	0.14 (16)	0.14 (45)	0.16 (13)	0.13 (57)
	range	0.00–0.59	0.03–0.45	0.00–1.01	0.03–0.69	0.01–0.80
NO ₃	mean (N)	20.64 (24)	17.19 (6)	21.72 (18)	17.00 (17)	19.50 (20)
	range	14.17–27.9	8.85–22.13	8.41–28.33	15.5–19.04	13.72–27.89
F	mean (N)	0.10 (62)	0.10 (16)	0.16 (45)	0.15 (13)	0.13 (57)
	range	0.00–0.29	0.00–0.17	0.00–0.30	0.01–0.27	0.00–0.31

N — amount of water samples; concentrations in milligram per litre, except Al; SEC — specific electrical conductivity; TDS — total dissolved solids

SO₄-HCO₃-Ca hydrochemical types. Groundwater from particular bedrocks differs mainly in terms of potassium, calcium, silicon, and aluminium concentration (Table 2). Groundwater pH has a wide range, from 4.14 to 7.67. Aquifer rocks are characterised by different reactivities and neutralisation capacities against acid deposition. The regolith is depleted in easily reactive mineral phases, and groundwater in the regolith aquifer is neutralised poorer than groundwater in the fissured aquifer (Dobrzyński, 1997). Groundwater is the most effectively neutralised in B-trachyandesites (up to pH \approx 7), probably due to the presence of secondary calcite. Groundwater in rhyolitic tuffs acquires a pH of about 6, and groundwater in the SW-trachyandesites develops a pH of around 5 (Table 2). The latter groundwater has a pH only slightly higher than the

weighted mean pH (4.79) of wet atmospheric deposition in the area studied (Dobrzyński, 1997). Water pH is the main variable that governs aluminium solubility and affects the formation of aluminosilicates.

Silica concentration in the groundwater ranges from 6.2 mg/L SiO₂ to 21.5 mg/L SiO₂. Wet atmospheric deposition contained on average 0.227 mg/L SiO₂. Considering an evapotranspiration coefficient of about 2 (Dobrzyński, 1997), atmospheric-origin silica in groundwater comprises probably only 0.45 mg/L SiO₂. Therefore the silica from atmospheric precipitation is negligible in comparison to silica from weathering sources.

Inferred sequences of mineral weathering are evaluated by using solubility curves constructed in a co-ordinates system, two-ion parameter, “lg[Al³⁺] + 3pH” vs. silica activity (Fig. 2).

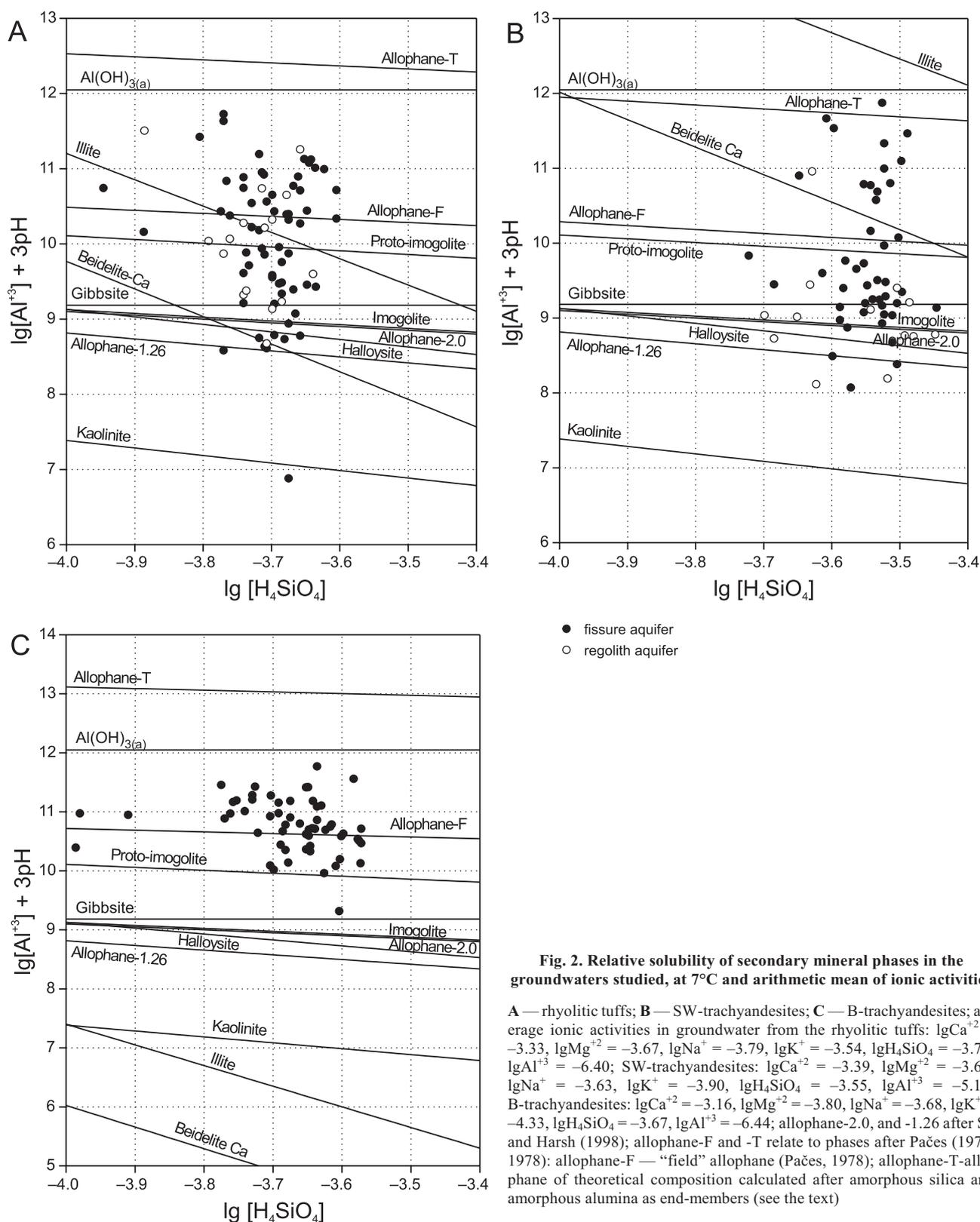


Fig. 2. Relative solubility of secondary mineral phases in the groundwaters studied, at 7°C and arithmetic mean of ionic activities

A — rhyolitic tuffs; **B** — SW-trachyandesites; **C** — B-trachyandesites; average ionic activities in groundwater from the rhyolitic tuffs: $\lg\text{Ca}^{+2} = -3.33$, $\lg\text{Mg}^{+2} = -3.67$, $\lg\text{Na}^+ = -3.79$, $\lg\text{K}^+ = -3.54$, $\lg\text{H}_4\text{SiO}_4 = -3.70$, $\lg\text{Al}^{+3} = -6.40$; SW-trachyandesites: $\lg\text{Ca}^{+2} = -3.39$, $\lg\text{Mg}^{+2} = -3.63$, $\lg\text{Na}^+ = -3.63$, $\lg\text{K}^+ = -3.90$, $\lg\text{H}_4\text{SiO}_4 = -3.55$, $\lg\text{Al}^{+3} = -5.10$; B-trachyandesites: $\lg\text{Ca}^{+2} = -3.16$, $\lg\text{Mg}^{+2} = -3.80$, $\lg\text{Na}^+ = -3.68$, $\lg\text{K}^+ = -4.33$, $\lg\text{H}_4\text{SiO}_4 = -3.67$, $\lg\text{Al}^{+3} = -6.44$; allophane-2.0, and -1.26 after Su and Harsh (1998); allophane-F and -T relate to phases after Pačes (1973, 1978); allophane-F — “field” allophane (Pačes, 1978); allophane-T-allophane of theoretical composition calculated after amorphous silica and amorphous alumina as end-members (see the text)

The curves for secondary phases in **Figure 2** illustrate the relative stability amongst them and indicate secondary mineral phases that are probably the most stable in the particular aquifer. Relative solubility suggests that in groundwater from the rhyolitic tuffs (**Fig. 2A**) and from the SW-trachyandesites (**Fig. 2B**) kaolinite is the most stable mineral, whereas in the

B-trachyandesites — smectite (Ca-beidelite) is the most stable solid (**Fig. 2C**).

The contribution of weathering to groundwater chemistry (**Table 3**) was quantified using the method described e.g. by Appelo and Postma (1993, p. 3–5), based on wet deposition chemistry data (Dobrzyński, 1997) and groundwater composition.

Table 3

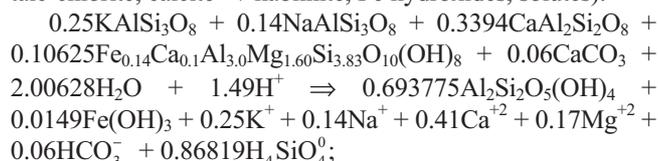
Weathering contribution to the chemical composition of the groundwater from the fissured aquifer in the volcanogenic rocks (after Dobrzyński, 1997 updated); concentrations in mmol/L

	Rhyolitic tuffs	SW-trachyandesites	B-trachyandesites
Na	0.14	0.21	0.19
K	0.25	0.08	0.02
Ca	0.41	0.34	0.64
Mg	0.17	0.18	0.12
HCO ₃	0.06	–	0.49
SO ₄	0.40	0.25	0.30

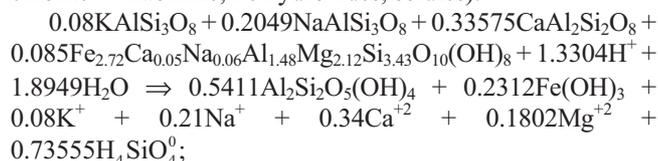
Summary reactions of irreversible mineral dissolution quantify the transfer of silica that is released during weathering. The following reactions relate to fissured aquifers because they reflect better the effects of bedrock composition on groundwater. The proposed simplified reactions consider the main source mineral phases (after Nowakowski, 1968; Awdankiewicz, 1999b) and the “chief” alteration secondary product phases (after weathering sequences; Fig. 2). The chemical composition of chlorites, pyroxenes, and plagioclases (in the B-trachyandesites) was calculated after chemical data given by Awdankiewicz (1999b). In reactions involving rhyolitic tuffs and SW-trachyandesites feldspars are included as the pure end-members because both rocks mainly consist of rock matrix, with partly devitrified volcanic glass. The composition of real feldspars (andesine-labradorite) was used in the reaction for B-trachyandesites. Stoichiometric coefficients of the primary minerals were calculated using the values of weathering contribution for the main cations (Table 3).

The proposed summary weathering reactions are the following:

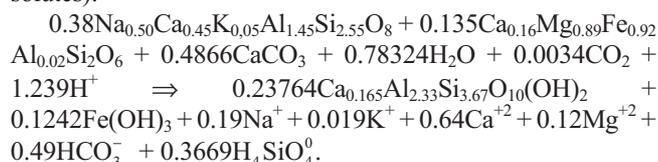
1) Groundwater in the rhyolitic tuffs (feldspars, talc-chlorite, calcite ⇒ kaolinite, Fe hydroxides, solutes):



2) Groundwater in the SW-trachyandesites (feldspars, chlorite ⇒ kaolinite, Fe hydroxides, solutes):



3) Groundwater in the B-trachyandesites (plagioclase, pyroxene (pigeonite), calcite ⇒ Ca-beidelite, Fe hydroxides, solutes):



During the weathering, part of the silica as well as basic cations are released into the groundwater. The calculated amount of silica is not consistent with the analytical data, and signifi-

Table 4

Comparison of calculated and analytical H₄SiO₄ concentration (mmol/L) in the groundwater

Bedrock	Calculated	Mean analytical	“Excess”
Rhyolitic tuffs	0.868	0.200	0.668
SW-trachyandesites	0.736	0.284	0.452
B-trachyandesites	0.367	0.214	0.153

cant “over-production” of silica is indicated (Table 4). The least stable silicate phase of the volcanic rocks is devitrified glass in the groundmass. The B-trachyandesites contain a small amount of volcanic glass (2–6%). The chemical composition of groundwater from the B-trachyandesites was probable formed by decay of the crystalline mineral phases (calcite, plagioclases, pyroxenes, amphiboles). In the SW-trachyandesites, the rock matrix is composed of albitised plagioclases (predominantly) and glass, and comprises 70–90 wt. %. The felsic rock matrix contributes to 70–80 wt. % of the rhyolitic tuffs, and is mainly composed of (mostly devitrified) volcanic glass. Probably, in the two latter rocks, solutes mainly originated from the decay of rock matrix phases.

Groundwater chemistry correlates with the presence of reactive mineral phases. The richer the rocks in volcanic glass, the higher alkali (Na + K) release into groundwater (0.39 mmol/L Na + K in rhyolitic tuffs, 0.29 mmol/L in SW-trachyandesites, 0.21 mmol/L in B-trachyandesites; Table 3). Calculated silica “over-production” (Table 4) shows the same pattern. The lowest calculated silica release is indicated in groundwater from the B-trachyandesites — the bedrock that is the poorest in the easily weatherable silicate solids. The difference between calculated and analytical silica concentrations contributes to the hypothesis that part of silica released during the weathering might be immobilised in the geochemical system as secondary aluminosilicate solids.

SOLUBILITY OF SECONDARY ALUMINOSILICATES

The weathering reactions proceed through many steps and involve unstable solid phases that exist due to partial equilibrium in the geochemical systems. For explanation of silicon and/or aluminium concentrations observed in natural waters equilibrium has been proposed between the solution and different secondary solids, such as clay minerals (mainly kaolinite, halloysite) or Al(OH)₃ forms. Equilibrium was also proposed between the solution and amorphous/poorly crystalline aluminosilicates (allophanes).

Allophanes are defined as naturally occurring short-range ordered hydrous aluminosilicates with a composition of (Al₂O₃)·(SiO₂)_{1–2}·(H₂O)_{2.5–3.0} (Wada, 1989). Their chemical composition varies in the range necessary to maintain Si-O-Al bonds. Similar to allophane minerals, with respect to the composition, is imogolite of ideal composition of (Al₂O₃)·(SiO₂)·2.5(H₂O). Allophanes usually have an Al/Si ratio of 1.0 to 2.0, but phases with ratios above 2.0 and below 1.0 may be also present (Wada, 1989). Many varieties of volcanic

Table 5

Equilibrium constants of aluminosilicate phases and Al(OH)₃ forms

Phase, reaction	lgK ₂₅	ΔH _f ⁰ [kJ/mol]	Source
Allophane-2.0, Al ₂ O ₃ ·SiO ₂ ·2.53H ₂ O + 6H ⁺ = 2Al ³⁺ + H ₄ SiO ₄ ⁰ + 3.53H ₂ O	14.20	–	b
Allophane-1.26, Al ₂ O ₃ ·1.59SiO ₂ ·2.63H ₂ O + 6H ⁺ = 2Al ³⁺ + 1.5H ₄ SiO ₄ ⁰ + 2.25H ₂ O	11.27	–	b
Imogolite, Al ₂ O ₃ Si(OH) ₄ + 6H ⁺ = 2Al ³⁺ + H ₄ SiO ₄ ⁰ + 3H ₂ O	12.10	–	c
Proto-imogolite, 0.5(HO) ₃ Al ₂ O ₃ SiOH + 3H ⁺ = Al ³⁺ + 0.5H ₄ SiO ₄ ⁰ + 1.5H ₂ O	7.02	–96.8	d
Allophane-T, [Al(OH) ₃] _(1-x) [SiO ₂] _x + 3(1-x)H ⁺ = (1-x)Al ³⁺ + xH ₄ SiO ₄ ⁰ + (3-5x)H ₂ O	-5.95 + 1.82 pH	–	e
Allophane-TG, [Al(OH) ₃] _(1-x) [SiO ₂] _x + 3(1-x)H ⁺ = (1-x)Al ³⁺ + xH ₄ SiO ₄ ⁰ + (3-5x)H ₂ O	-5.36 + 1.63 pH	–	e
Allophane-F, [Al(OH) ₃] _(1-x) [SiO ₂] _x + 3(1-x)H ⁺ = (1-x)Al ³⁺ + xH ₄ SiO ₄ ⁰ + (3-5x)H ₂ O	-5.89 + 1.59 pH	–	f
Allophane-FV, Al(OH) ₃ (SiO ₂) _x + 3H ⁺ = Al ³⁺ + xH ₄ SiO ₄ ⁰ + (3-2x)H ₂ O, (x = 0.5–1.0)	-13.55(±0.73) + 2.92(±0.12) pH ^a	–	e
Hydroxyaluminosilicate HAS _B , Al ₂ Si ₂ O ₅ (OH) ₄ + 6H ⁺ = 2Al ³⁺ + 2H ₄ SiO ₄ ⁰ + H ₂ O	14.0 (±0.7)	–	g
Kaolinite, Al ₂ Si ₂ O ₅ (OH) ₄ + 6H ⁺ = 2Al ³⁺ + 2H ₄ SiO ₄ ⁰ + H ₂ O	7.435	-147.695	h
Halloysite, Al ₂ Si ₂ O ₅ (OH) ₄ + 6H ⁺ = 2Al ³⁺ + 2H ₄ SiO ₄ ⁰ + H ₂ O	12.498	-167.025	i
Gibbsite, Al(OH) ₃ + 3H ⁺ = Al ³⁺ + 3H ₂ O	8.11	-95.395	h
Gibbsite (microcrystalline), Al(OH) ₃ + 3H ⁺ = Al ³⁺ + 3H ₂ O	9.35	-102.508	h
Al(OH) _{3(a)} , Al(OH) ₃ + 3H ⁺ = Al ³⁺ + 3H ₂ O	10.8	-110.876	h

a — lgK of hypothetical phase, allophane-FV at 7°C, mean temperature of the groundwater studied; b — Su and Harsh (1998); c — Wada and Kakuto (1999); d — Lumsdon and Farmer (1995); e — this work; f — Pačes (1978); g — lgK at 7°C (Dobrzyński, 2006); h — Nordstrom *et al.* (1990); i — Ball and Nordstrom (1991)

tuffs produce allophanes during weathering, but they are favoured in soil horizons of pH above 5.0.

Pačes (1973, 1978) proposed a hypothetical allophane of varied composition [Al(OH)₃]_(1-x)[SiO₂]_x, depending on pH according to the formula, x = 1.24 – 0.135 pH. Pačes gave the solubilities of two allophanes, a theoretical and an empirical one. The equation for the equilibrium constant for the allophane of theoretic composition (allophane-T) is lgK = -5.7 + 1.68 pH at 25°C (Pačes, 1973). The so-called “field” allophane (allophane-F) has lgK = -5.89 + 1.59 pH (Pačes, 1978), based on field and experimental water chemistry data. The solubility constant of allophane-T was recalculated by the author using the procedure given by Pačes (1978), and the present-day data for amorphous silica, SiO_{2(a)}, lgK₂₅ = -2.71, and for amorphous aluminium hydroxide, Al(OH)_{3(a)}, lgK₂₅ = 10.8 (Nordstrom *et al.*, 1990). The updated equation for lgK₂₅ allophane-T equals -5.95 + 1.82 pH (Table 5). This allophane might be regarded as a freshly precipitated amorphous aluminosilicate phase. During ageing, in hydroxyaluminosilicate precipitates a tendency of progressive arrangement occurs. Pačes (1973) found the deviation of the field data from the theoretical solubility, and explained it by the hypothesis, that aluminium atoms more easily assume co-ordinated positions during ageing, as opposed to silicon atoms. To take that inferred effect of the arrangement into account, the solubility of theoretical “aged” allophane was calculated using amorphous silica end-member solubility and microcrystalline gibbsite (lgK₂₅ = 9.35; Nordstrom *et al.*, 1990) end-member solubility instead of amorphous Al(OH)₃. The equilibrium equation of this modified “aged” allophane (allophane-TG) is lgK₂₅ = -5.36 + 1.63 pH.

The following allophane/imogolite and allophane-like phases are considered in the discussion: “field” allophane-F after Pačes (1978), allophanes after Su and Harsh (1998) of Al/Si molar ratio = 1.26 (allophane-1.26) and Al/Si = 2.0 (allo-

phane-2.0), imogolite after Wada and Kakuto (1999), and proto-imogolite of composition given by Lumsdon and Farmer (1995). Two other hypothetical solid phases (allophane-T and allophane-TG) are also considered in the present work. The equilibrium constants and the equations for the equilibrium constants for the above-mentioned phases are given in Table 5.

The groundwater chemistry data are analysed in terms of the ion activity quotient of different secondary solids that might control Si and/or Al solubility. Solubility curves (Fig. 3) were prepared at an arithmetic mean of activities of products (Al³⁺, H₄SiO₄⁰) in groundwater. Due to the same composition and Al/Si molar ratio, the curve for allophane-2.0 also relates to imogolite, and the curve for kaolinite to halloysite. The IAQ curve of Al(OH)₃ forms relates to the composition of gibbsite, microcrystalline gibbsite or amorphous aluminium hydroxide.

The relationship between the reaction quotient (lgIAQ) of the Pačes’ allophanes and pH (lgIAQ = (1-x) lg[Al³⁺] + xlg[H₄SiO₄⁰] + 3(1-x) pH) is linear as a consequence of the linear relationship between x and pH. However, the value of lgIAQ obtained does not make a linear plot across the whole pH range found. Field chemical data present a linear relationship within limited ranges only (Fig. 4). This indicates different conditions of silica activity control in the groundwater. Almost all water samples from the SW-trachyandesites plot along the allophane-F solubility line (Fig. 4), whereas waters from the B-trachyandesites are mainly scattered along the line of allophane-TG. Most of the waters from the rhyolitic tuffs and several water samples from the SW-trachyandesites lie between allophane-F and allophane-TG lines. In allophane of (Al₂O₃)(SiO₂)₁₋₂(H₂O)_{2.5-3.0} composition (Wada, 1989), the Al/Si molar ratio ranges between 1 and 2. The Al/Si ratio of the hypothetical reversible metastable allophane phase proposed by Pačes (1973, 1978) depends on the pH value, and varies within a wide range between pH 1.8 (point of zero charge

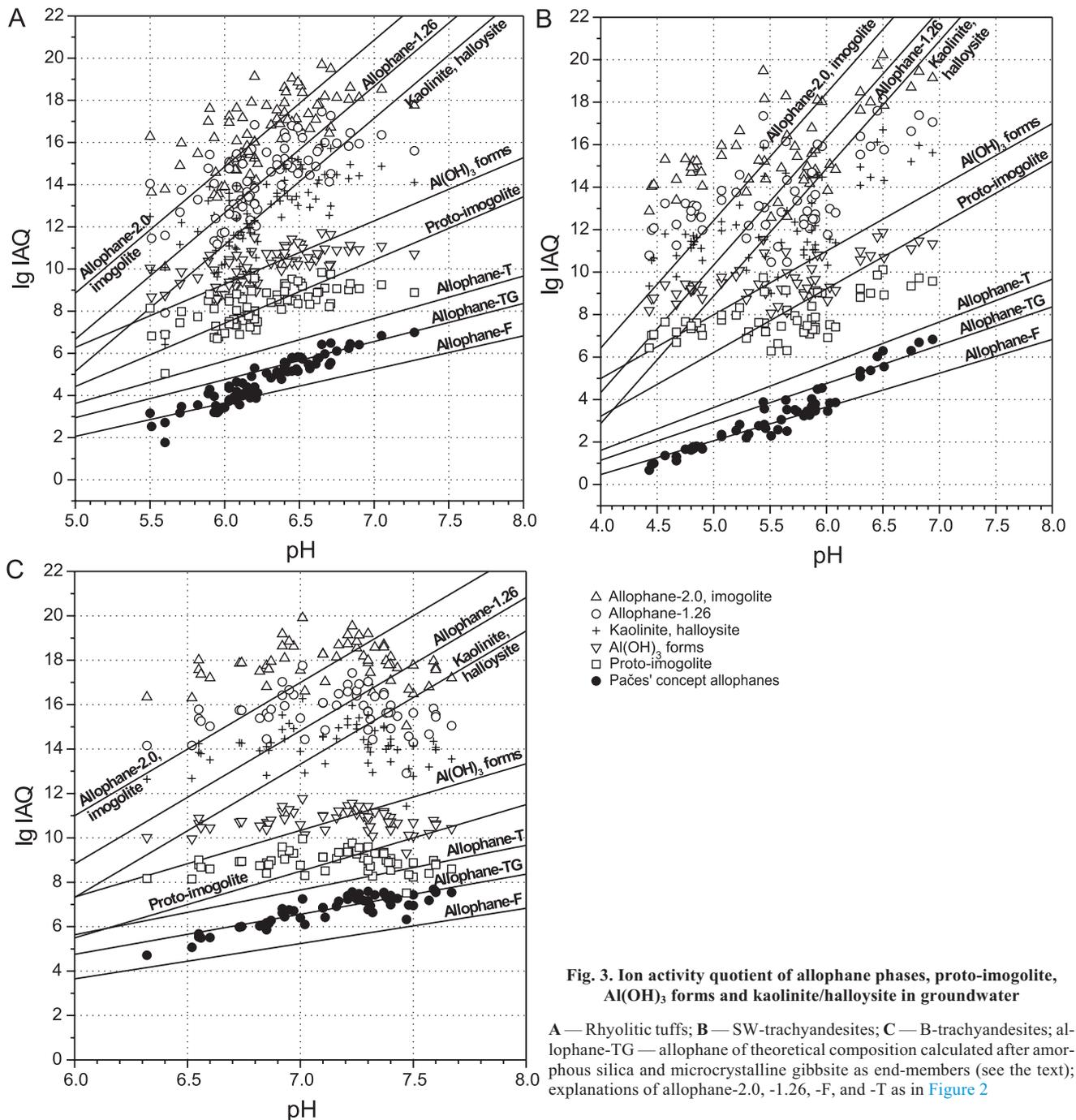


Fig. 3. Ion activity quotient of allophane phases, proto-imogolite, $\text{Al}(\text{OH})_3$ forms and kaolinite/halloysite in groundwater

A — Rhyolitic tuffs; B — SW-trachyandesites; C — B-trachyandesites; allophane-TG — allophane of theoretical composition calculated after amorphous silica and microcrystalline gibbsite as end-members (see the text); explanations of allophane-2.0, -1.26, -F, and -T as in [Figure 2](#)

(PZC) of amorphous SiO_2) and pH 9.2 (PZC of amorphous $\text{Al}(\text{OH})_3$). The Al/Si molar ratio of Pačes' allophane reaches the value of 1 at pH 5.50, and 2 at pH 6.73. In fact, most of the groundwater samples that plot between the allophane-F line and the allophane-TG line are included within the same pH range ([Fig. 4](#)).

Groundwater samples are divided into three groups with respect to pH: (1) samples with pH from 4.40 to 5.50, (2) samples with pH within the range 5.50–6.73, and (3) samples with pH from 6.73 to 7.7. These groups are fairly well related to the bedrock types ([Table 6](#)).

Within the pH 5.50–6.73 range, the IAQ of allophane can be fitted ([Fig. 4](#)) by the regression function $\lg \text{IAQ} = -13.55(\pm 0.73) + 2.92(\pm 0.12) \text{pH}$ ($R = 0.92$; $N = 108$).

If one assumes that the solubility relation corresponds to the solid phase, and that partial equilibrium is maintained, the composition of the solid might be inferred. The general solubility reaction for allophane can be written as: $\text{Al}(\text{OH})_3 \cdot (\text{SiO}_2)_x + 3\text{H}^+ = \text{Al}^{3+} + x\text{H}_4\text{SiO}_4^0 + (3-2x)\text{H}_2\text{O}$. An activity of water and solid that equals 1 is assumed. This leads to the solubility constant of $\lg K = \lg[\text{Al}^{3+}] + x\lg[\text{H}_4\text{SiO}_4^0] + 3 \text{pH}$, and to the conclusion that the hypothetical phase should have a composition of $\text{Al}(\text{OH})_3 \cdot (\text{SiO}_2)_{0.5-1.0}$. This hypothetical “field” phase is named allophane-FV. The water chemistry suggests that the allophane-FV might have a composition similar to that of allophane/imogolite minerals.

The ion activity quotient of Pačes' allophanes ($[\text{Al}(\text{OH})_3]_{(1-x)}[\text{SiO}_2]_x$) is affected by an artefact of the mathe-

Table 6

Percentage shares of groundwater samples within the pH ranges assumed

Bedrocks	pH < 5.50 (N = 26)	pH 5.50 – 6.73 (N = 108)	pH > 6.73 (N = 59)
SW-trachyandesites	100.0	26.9	5.1
Rhyolitic tuffs	–	66.6	10.2
B-trachyandesites	–	6.5	84.7

mathematical relation because the Al/Si ratio depends on pH according to the formula $x = 1.24 - 0.135 \text{ pH}$. The good correlation between $\lg \text{IAQ}$ and pH (Fig. 4) might result from the real equilibrium state and from the mathematical function. The dispersion of data points around equilibrium line is important. To check whether the equilibrium might be maintained, the deviation of the IAQ vs. pH was plotted with respect to the equilibrium line for theoretical “aged” allophane-TG (Fig. 5).

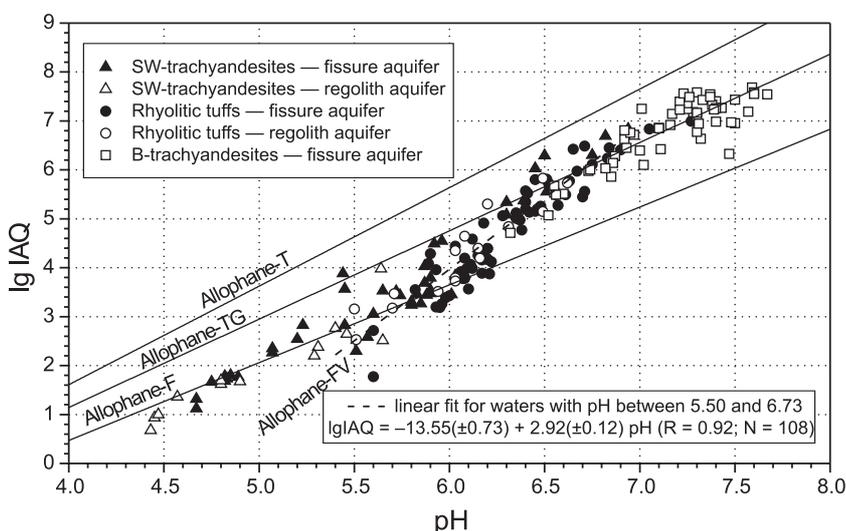


Fig. 4. Ion activity quotient of Pačes' concept allopahanes in groundwater vs. pH

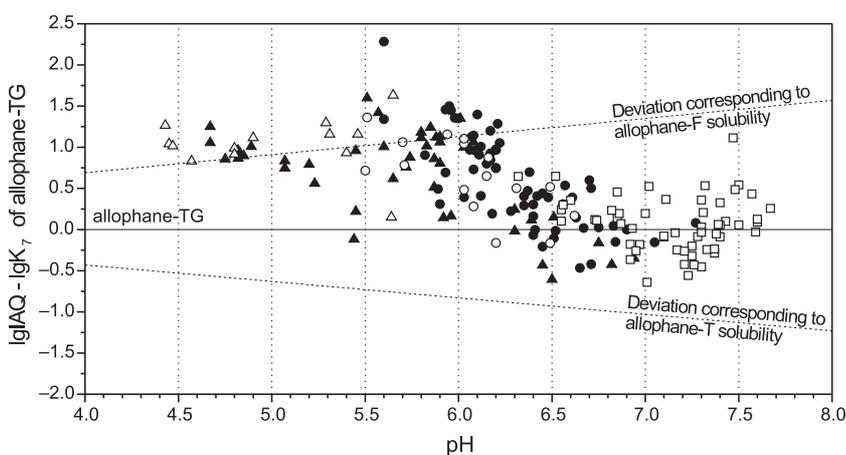


Fig. 5. Deviation of $\lg \text{IAQ}$ value for allopahanes of composition proposed by Pačes (1978) from the allopahane-TG solubility vs. pH

Explanations as in Figure 4

So-called proto-imogolite sol $(\text{HO})_3\text{Al}_2\text{O}_3\text{SiOH}$ has been identified in many soils and regoliths, which probably plays important role in soil formation (Farmer *et al.*, 1980; Farmer and Fraser, 1982; Gustafsson *et al.*, 1998, 1999). Hydroxyaluminosilicate (HAS) colloids are formed by the reaction of silicic acid with aluminium (Exley and Birchall, 1993). The formation and structure of two synthetic HASs, which were named HAS_A and HAS_B , have been documented in detail (Doucet *et al.*, 2001; Exley *et al.*, 2002). HAS_A and HAS_B have idealised Al/Si molar ratios of 2.0 and 1.0, respectively. Composition of both HASs conforms to the composition of phases noted in many soils, such as proto-imogolite or allophane/imogolite minerals. The HAS_A has a composition similar to that of proto-imogolite. It forms when the silica concentration in solution is close to the aluminium concentration. The HAS_B of idealised composition $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ forms in solution in which the silica concentration exceeds that of aluminium (Doucet *et al.*, 2001; Exley *et al.*, 2002). The solubility of synthetic HAS_B was estimated experimentally by Schneider *et al.* (2004).

It is conceivable that aluminium as well as silicon activity in the groundwaters studied may be controlled by HAS_B . It forms even at low aluminium concentrations as it is found in the groundwaters studied. The calculation method proposed by Schneider *et al.* (2004) was applied to quantify ion activity products of HAS_B in the groundwaters. As a result of the method that is used (*op.cit.*), $\lg \text{IAQ}_{\text{HAS-B}}$ achieves a constant value when the equilibrium conditions are fulfilled. The ion activity quotient of HAS_B plotted vs. H^+ , and Al^{3+} activities shows a regular pattern (Figs. 6 and 7). The equilibrium with HAS_B is likely maintained in groundwater over a wide range of chemical composition. Actually, IAQ of HAS_B is constant for $\lg[\text{Al}^{3+}]$ below -10.0 and for pH above 6.7. The arithmetic mean of $\lg \text{IAQ}_{\text{HAS-B}}$ in water samples with $\lg[\text{Al}^{3+}]$ below -10.0 equals -44.691 (SD = 0.476, N = 41), and in samples with pH above 6.7 it is of -44.744 (SD = 0.515, N = 63). Both values are close to the value that was found in groundwaters from sedimentary rocks in the same part of the Sudetes Mts., $\lg \text{IAQ}_{\text{HAS-B}} = -44.88 \pm 0.48$ (Dobrzyński, 2005). The similar value of $\lg \text{IAQ}_{\text{HAS-B}}$ (-44.7 ± 0.58) also was obtained by Dobrzyński (2006) after analysis of the wide chemical data set from surface and groundwaters in different (magmatic, sedimentary, metamorphic) bedrocks in the Sudetes.

The value of $\lg K_{\text{HAS-B}} = -40.6 (\pm 0.15)$ estimated experimentally by Schneider *et al.* (2004) is higher than is found in groundwater. Experimental $K_{\text{HAS-B}}$ (Schneider *et al.*, 2004) is likely overestimated because the fast-reacting aluminium $[\text{Al}_f]$ instead of

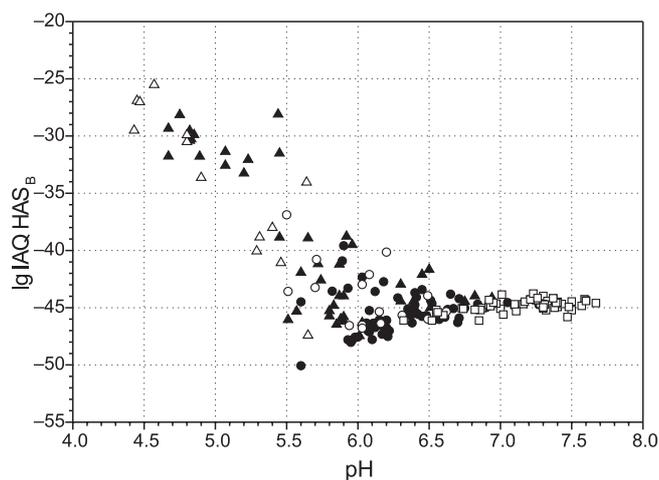


Fig. 6. Ion activity quotient of hydroxyaluminosilicate HAS_B vs. pH in groundwater

Explanations as in Figure 4

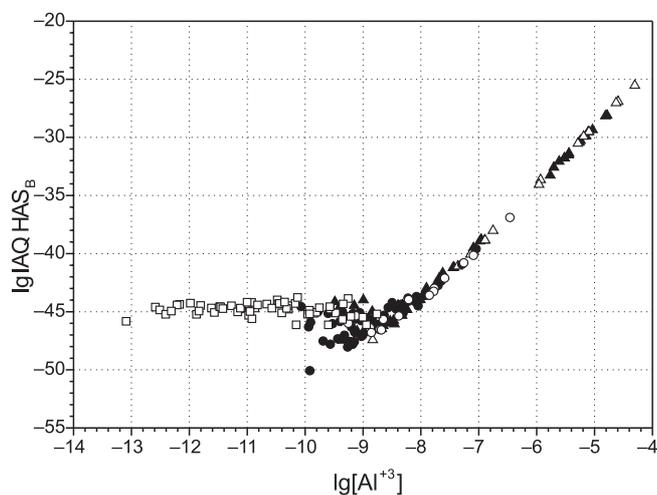


Fig. 7. Ion activity quotient of hydroxyaluminosilicate HAS_B vs. Al^{+3} activity in groundwater

Explanations as in Figure 4

$[Al^{+3}]$ was used in calculation by Schneider *et al.* (2004). The $[Al_r]$ refers to “fast reacting” aluminium estimated by the fluorescent morin-Al complex method (Browne *et al.*, 1990). Another reason is the laboratory experiment (Schneider *et al.*, 2004) was carried out at a temperature of 20°C while the mean temperature of groundwater is near 7°C (Table 1).

The hydrochemical data point to the occurrence of HAS colloids in the groundwater, which is conducive to the formation of allophane-like phases in the geochemical system studied.

DISCUSSION

Groundwater chemistry plotted in a co-ordinates (two-ion parameter, “ $lg[Al^{+3}] + 3pH$ ” vs. silica) system shows that in groundwater from B-trachyandesites (Fig. 2C) conditions are closer to equilibrium. The chemistry of groundwater from rhyolitic tuffs (Fig. 2A) and from SW-trachyandesites (Fig. 2B) shows a significant (local and/or temporal) diversity.

Stoichiometric weathering reactions indicate that mobilization of silica is higher than concentrations found in groundwater (Table 4). Calculation is based on the concentration of alkali (K, Na, Ca, Mg) elements in groundwater, and on the assumption that hydrolytic decay of primary silicates is the only source of compounds released into water. Part of the alkali elements can also originate from the biodegradation of biomass (mainly litter) and/or from cation exchange in the real geochemical systems of soil and regolith. It is probable that part of the silica released from the primary silicate minerals during weathering is immobilized in the structure of secondary reversible aluminosilicate solids, such as allophanes or hydroxyaluminosilicates.

The ion activity quotient for different aluminosilicate secondary phases indicates that in some of the groundwater studied a partial chemical equilibrium with solid phases might be maintained.

GROUNDWATER WITH PH BETWEEN 4.4 AND 5.5

Groundwaters with pH within this range discharge from the SW-trachyandesites. The main source of dissolved silica is the dissolution of Na-rich plagioclases and devitrified volcanic glass. Low pH values are caused by the lack of the solids that can efficiently neutralize the acidified recharging water. Wet atmospheric deposition had weighted average pH of 4.79 in the area studied (Dobrzyński, 1997). The groundwater from the regolith aquifer and from the fissured aquifer in the SW-trachyandesites has mean pHs 4.80 and pH 5.29, respectively (Table 2). Silicon and aluminium activities are consistent with the solubility of allophane (allophane-F) proposed by Pačes (1978; Fig. 4). However, chemical equilibrium probably does not occur (Fig. 5), and the pattern for allophane-F (Fig. 4) is a mathematical artefact. The chemical composition of water in the SW-trachyandesites likely resulted from steady-state conditions between processes such as weathering release, hydrological removal and precipitation of secondary phases.

GROUNDWATER WITH PH BETWEEN 5.5 AND 6.7

Groundwater from the rhyolitic tuffs has pH mainly within the above range (Table 6). The main source of dissolved silica is the groundmass of the rhyolitic tuffs. This is predominantly composed of devitrified, re-crystallised glass shards. The ion activity quotient for allophane-FV and pH correlate (Fig. 4). The composition of the allophane-FV is very similar to that of allophane/imogolite minerals, and it might be regarded as their hypothetical precursor. However, the IAQ pattern for allophane-FV is an artefact of the mathematical relation between pH and IAQ. Therefore, this phase should be considered as a hypothetical one only. Correlation between the IAQ for proto-imogolite and for $Al(OH)_3$ forms, and pH (Fig. 3A) might indicate equilibrium. The proto-imogolite has an Al/Si molar ratio of 2.0 and a composition of $(HO)_3Al_2O_3SiOH$, similar to that of the hydroxyaluminosilicate HAS_A (Doucet *et al.*, 2001; Exley *et al.*, 2002). The role of proto-imogolite (or HAS_A) in groundwater from the rhyolitic tuffs is likely doubtful because they can form in a solution of Al/Si ratio about 1.0. Whereas, in the groundwaters studied aluminium activities are

too low to fulfil this condition. The aluminium concentration in groundwater from the rhyolitic tuffs is probably controlled by dissolution of $\text{Al}(\text{OH})_3$ forms.

Allophane/imogolite phases are abundant in soils and regoliths developed on volcanic rocks of different geochemistry, especially on tuffs (Wada, 1989). They form preferentially in the lower horizons of soil and regolith developed on pyroclastic rocks rich in alkali, at pH values above 5.0 (Ugolini and Dahlgren, 1991). The large proportion of allophane, predominantly of Al/Si ratio of about 2.0, are found in soils developed on volcanic ash when the pH of associated soil and groundwater is within the range 5.5 to 6.8 (Parfitt and Kimble, 1989). Allophanes are formed from the dissolution of volcanic glass rather than feldspar, probably because the pH is above 5.5.

The mineral and chemical composition of rhyolitic tuffs is conducive to forming secondary aluminosilicate solids, such as allophanes. However, field hydrochemical data in this group do not show equilibrium with allophane minerals. Non-equilibrium conditions are caused by the short turn-over time of groundwater in the system and the poor neutralisation capacity of the rhyolitic tuffs.

GROUNDWATER WITH PH BETWEEN 6.7 AND 7.7

Groundwater from the B-trachyandesites dominates within this group. This groundwater has the highest pH (Table 2). The main source of dissolved silica is andesine-labradorite plagioclases. Within this pH range a state closer to the equilibrium with Pačes' concept of allophanes is maintained (Figs. 2C and 5). Two phases may be considered as responsible for the silica solubility control, proposed hypothetical "aged" allophane-TG and hydroxyaluminosilicate HAS_B .

Allophane-TG has a composition as defined by Pačes (1978) for "field" allophane (allophane-F), but it has a higher solubility and less ordered structure than the latter one.

The HAS_B is formed when molar ratio of silicic acid to aluminium in water is greater than 2.0 (Doucet *et al.*, 2001; Exley *et al.*, 2002). All the groundwaters studied fulfil this condition. However, the HAS_B manifests equilibrium only in groundwater from the B-trachyandesites (Figs. 6 and 7). The HAS_B seems to be stable at pHs above 6.7 and $[\text{Al}^{+3}]$ lower than 10^{-10} , with silica activity between $10^{-4.00}$ and $10^{-3.55}$. Hydrogeochemical conditions in the B-trachyandesites are conducive to equilibrium with secondary aluminosilicate solids, and support the thesis that HAS_B might be present in B-trachyandesites.

CONCLUSIONS

The groundwaters studied occur in the regolith and fissured volcanic bedrock. The main dissolved silica source phases are devitrified volcanic glass, feldspars, and chlorites. The calculated stoichiometric amount of silica re-

leased during weathering is higher than the analytical silica concentration in groundwater. It indicates that part of silica is immobilised in metastable hydroxyaluminosilicates.

Bedrock chemistry and reactivity affect groundwater chemistry and pH. Many solids, such as silicates, dissolve and form by reactions depending on H^+ activity in the solution. This is shown also in the groundwater studied. The chemical equilibrium state with secondary aluminosilicates is related to the pH of the groundwaters. In groundwater with pH between 4.4 and 5.5 that occurs in the least reactive bedrock (SW-trachyandesites), chemical equilibrium is not established. The silica content in these waters depends upon steady-state conditions between weathering release, hydrological removal and precipitation of secondary sink phases. A partial chemical equilibrium is reached in groundwater with pH above 5.5. Aluminium activity in groundwater with pH between 5.5 and 6.7 from the rhyolitic tuffs might be controlled by the solubility of the $\text{Al}(\text{OH})_3$ form. The hydroxyaluminosilicate HAS_A does not play this role because it forms when the Al/Si molar ratio in solution is about 1.0, whereas the studied groundwater has a much lower Al/Si ratio.

The content of Si and Al is controlled by equilibrium with the hydroxyaluminosilicate HAS_B in groundwater from the B-trachyandesites with pH above 6.7. This "field" hydroxyaluminosilicate HAS_B has a solubility lower than its synthetic equivalent. The solubility constant ($\lg K_{\text{HAS-B}} = -44.744 \pm 0.515$) estimated here from the ion activity products in groundwater with pH above 6.7 is lower than the value ($\lg K_{\text{HAS-B}} = -40.6 \pm 0.15$) obtained experimentally by Schneider *et al.* (2004).

Hydroxyaluminosilicates (HAS), especially HAS_B , probably exist in the volcanic aquifers investigated. The HAS_B can form even at low total aluminium concentrations as it was found in the groundwater studied. Hydroxyaluminosilicates might be considered as precursors of potentially forming allophane/imogolite minerals. The chemical composition of groundwater indicates that secondary metastable aluminosilicate phases may be formed in the weathered volcanic rocks studied. These phases have not been ascertained mineralogically yet, and this requires further investigation. A confirmation of the presence of those phases is important because adsorption onto solids and kinetics might be responsible for the silica activity in the groundwaters rather than an assumed equilibrium with aluminosilicates.

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