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Silica origin and solubility in groundwater from the weathered zone of sedimentary rocks of the Intra-Sudetic Basin, SW Poland

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ABSTRACT:

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The groundwaters studied in the Intra-Sudetic Basin, SW Poland, occur in the regolith and in the fissured bedrock. Silica concentration in groundwaters ranges from 0.7 to 24.1 mg/L SiO_2. Mineral phases that are the source of silica solute were pointed out on bedrock mineralogy and saturation state analysis. Interpretation of aqueous chemistry in terms of mineral stability confirms that partial geochemical equilibrium is maintained. In groundwater with pH values below 4.8 from the fissured aquifer in Carboniferous siliciclastic rocks, kaolinite controls silica solubility. Congruent dissolution of the allophane phase and/or incongruent reaction between the $Al(OH)_3$ form and kaolinite/halloysite or allophane can be responsible for silica activity in groundwater, with pH values between 5.5 and 6.7, from the regolith on Carboniferous rocks and from the fissured aquifer in Cretaceous mudstones. Groundwaters with pH values above 6.7 occur in the Permian and Cretaceous fissured aquifers which contain calcite/dolomite minerals. Silica and aluminium concentrations in these aquifers are clearly maintained by equilibrium with the hydroxyaluminosilicate HAS_B. The solubility constant of HAS_B estimated on groundwater chemistry is lgK HAS_B = -44.88 (±0.48), which is lower than the recently published experimental value (SCHNEIDER & *al*. 2004). In groundwater with pH values between 4.8 and 5.5 from the regolith sampled during snow melt, equilibrium, even with reversible secondary aluminosilicates, is not maintained. Silicon and aluminium concentrations result from kinetics or steady-state between weathering release and hydrological removal.

Key words: Groundwater geochemistry, Silica, Allophanes, Hydroxyaluminosilicates (HAS), The Sudetes Mts., Poland.

INTRODUCTION

Silica dissolved in natural waters is considered to be a good indicator of weathering and water circulation conditions. In the near-surface environments, silica concentration can afford useful information on water turn-over, and is used to estimate outflow components (surface, subsurface, and groundwater) (WELS & *al*. 1991, HINTON & *al*. 1994, SCANLON & *al*. 2001, ASANO & *al*. 2003). The amount of silica released into the water is conditioned by different factors, such as water saturation deficit of the aeration zone, seasonal fluctuations of precipitation and temperature, bedrock reactivity, and mineral stability. Hydrolytic decay of primary silicate minerals is commonly regarded as the main source of silica dissolved in groundwater. Silica activity in waters can be controlled by different processes, including the solubility of secondary solid phases. Geochemical analysis indicates that equilibrium with metastable amorphous aluminosilicate phases can be responsible for controlling silica activity in soil water and groundwater in the regolith (Asano & *al.* 2003, Dobrzyński 2005). Researches into aluminosilicate solid and solute forms are focused mainly on soils and surface waters because of environmental concerns, e.g. soil fertility, aluminium toxicity to plants and fishes.

Groundwater chemistry has been investigated in three small headwater catchments composed of different sedimentary rocks. The areas studied are located in the central part of the Sudetes Mts. (SW Poland). The main subject of research comprised the relationships between bedrock and groundwater chemistry. The paper deals with conditions affecting silica concentration in groundwater, and is focused especially on silica solubility in terms of the stability of allophanes and hydroxyaluminosilicates (HAS).

METHODS

The groundwaters studied occur in different sedimentary rocks of Carboniferous, Permian, and Cretaceous ages, in the short turn-over time zone of the hydrogeological system. Groundwaters were sampled only in perennial and ephemeral springs because of the lack of other sampling points, such as intakes or wells. Water samples were filtered by cellulose-nitrate 0.45μm membranes, and stored in LDPE bottles. In total, 83 groundwater samples were examined from Carboniferous, 52 samples from Permian, and 66 samples from Cretaceous rocks. Silica was determined by the spectrophotometric silicomolybdate method, and aluminium by the ETA AAS method. Aqueous species calculation was provided by the PHREEQC code (Parkhurst & Appelo 1999). Solubility curves were constructed on the present thermochemical data.

GEOLOGY AND HYDROGEOLOGY OF THE AREAS STUDIED

Groundwaters were investigated in three areas (Text-fig. 1) located in the Intra-Sudetic Basin (the Sudetes Mts., SW Poland). Area 1 is composed of Lower Carboniferous clastic rocks, and is located in the Trójgarb Massif (part of the Wałbrzyskie Mts. range). Area 2 is situated in the Krzeszów Hills. The bedrocks of this area comprise a sedimentary complex (conglomerates, sandstones, mudstones, siltstones, tuffites, dolomites) of Early Permian age. Area 3, located in the Zawory Mts., is composed of Upper Cretaceous sandstones and mudstones.

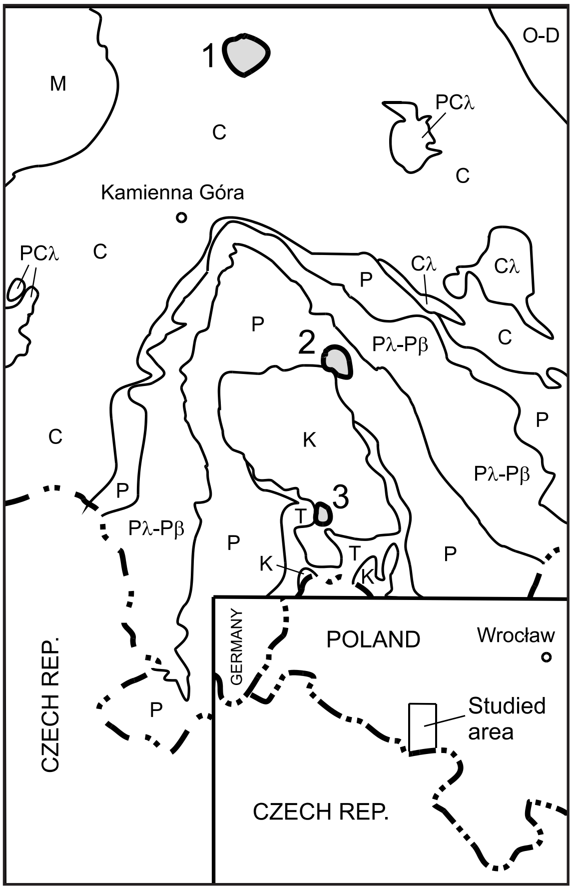

Fig. 1. Geological sketch and location of the areas studied. Explanations: 1, 2, 3 – number of area; M – metamorphic country rocks of the Karkonosze granitoid massif; O-D – Ordovician-Devonian; C – Carboniferous; P – Permian; T – Triassic; K – Cretaceous; Cλ, PCλ, Pλ-Pβ – volcanics of Carboniferous and/or Permian age respectively

The Lower Carboniferous rocks (mainly conglomerates and sandstones) are composed of various clasts (Tab. 1). The rocks of older cyclothems in the northern part of Area 1 contain 15-40 % of so-called Caledonian material (greenstones, paleobasalts, diabases, hornstones, phyllites, conglomerates) and chlorite cement (Teisseyre 1966, 1972). The rocks of younger cyclothems in the southern part of the area are composed mainly of quartzites, lydites and quartz, with only a small percentage of Caledonian material. The Lower Carboniferous rocks generally show low reactivity. Silification and kaolinisation of the bedrock (Teisseyre 1972, 1975; Dziedzic & Teisseyre 1990) brought about decay of the feldspars and the formation of quartz-kaolinite cements. These processes seriously influenced the hydrogeological conditions. The Lower Carboniferous rocks are usually massive and slightly fractured. The thin regolith (below 1 m thick) and the shallow zone of weathering fractures result in a low water retention capacity.

Lower Carboniferous conglomerates and sandstones with mudstones (after Teisseyre 1966, 1972) – area no. 1		
Clastic composition	mica schists, quartzites, volcanites, greywackes and conglomerates, greenstones, paleobasalts, diabases, lydites, hornstones, phyllites; secondary: marbles, gneisses, granites, cataclasites, jaspers	
Cement /matrix	In older cyclotems: chlorite, chlorite-quartz, chlorite-hematite. In the younger cyclotems (mainly): quartz-kaolinite, quartz-kaolinite-hematite, partly sericite	
Lower Permian sedimentary rocks (after Grocholski 1973, Don & *al.* 1981) – area no. 2		
	Tuffaceous conglomerates and sandstones with siltstones and dolomites (upper part of the eruptive complex, the Middle Rothliegendes)	Conglomerates, fanglomerates, sandstones (over-eruptive complex, the Upper Rothliegendes)
Clastic composition	volcanites (ignimbrites, tuffs, tuffites, andesitoides, rhyolites); secondary: quartz, quartzite schists, sandstones. Interbeddings of dolomites, dolomite conglomerates and tuffogenic siltstones	porphyres, quartz, feldspars; secondary: granites, gneisses, greywackes, quartzites, chlorite-mica schists, amphibolites
Cement /matrix	sandy-tuffaceous arkose matrix with sericite, biotite, chlorite and volcanic ash; in some layers carbonate cement with hematite	effusive rocks; in the upper layers: hematite, carbonate-quartz, quartz cements
Upper Cretaceous sedimentary rocks (after Jerzykiewicz 1971, Don & *al.* 1981) – area no. 3		
	Calcareous sandstones	Siliceous mudstones
Clastic composition	quartz, siliceous rocks; secondary: feldspars, micas, glauconite, heavy minerals	quartz, siliceous rocks; secondary: feldspars, micas, heavy minerals
Cement /matrix	calcium carbonate, secondary: clay minerals, iron oxides, rarely chalcedony (ca. 30 % by vol.)	chalcedony, secondary: micas, clay minerals, iron oxides (ca. 80 % by vol.)

Table. 1. Petrographic composition of sedimentary rocks in the areas studied

As a consequence, only ephemeral springs occur in the area. The only perennial spring discharges in the dislocation zone of the Domanów-Sędzisław fault. In terms of water chemistry, this spring is interesting in that its water is more acid than the water retained in the regolith, which is an uncommon phenomenon.

The petrographic composition of the Lower Permian rocks varies significantly (Tab. 1). The presence of dolomites, carbonate cement and tuffogenic material in bedrocks is very important from the point of view of groundwater chemistry. The rock components mentioned above are composed of readily reactive mineral phases. They strongly affect neutralisation of the recharge water and release most of the solutes into groundwater.

Area 2 abuts the Cretaceous Krzeszów Trough. Groundwaters occur in the fissured aquifer, as well as in the porous-fissured regolith. Perennial, ascending springs discharge from the Permian fissured aquifer underlying the Cretaceous rocks of the Krzeszów Trough, whereas ephemeral, descending springs discharge from the regolith of the Permian bedrocks. The regolith is usually less than one metre thick.

Area 3 is situated in the southern part of the Krzeszów Trough and is composed of Upper Cretaceous sandstones and mudstones. The perennial and ephemeral springs are related to two kinds of rocks: calcareous sandstones and siliceous mudstones. Calcite cement in the sandstones and silica solid phases in the mudstones (Tab. 1) are the main features of the composition of the bedrock. The water chemistry of the perennial springs does not differ significantly from that of the ephemeral ones.

Generally, groundwaters discharged in perennial springs derive from the fissured aquifer in the bedrock, whereas waters discharged in ephemeral springs derive from the regolith aquifer. Seasonally, both spring groups also discharge some shallower or deeper outflow components (Dobrzyński 1997). In the Sudetes Mts., three water-bearing depth zones were usually distinguished (Kowalski 1992). In the first, shallow zone, groundwaters occur within the regolith and in weathering fissures tens of metres deep in the bedrock. Water recharge in the zone depends mainly on the hydro-meteorological conditions. The second water-bearing zone is about hundreds metres deep in the network of syngenetic and/or tectonic fractures. The conditions of groundwater turn-over are affected by lithological, structural and sedimentological factors. Groundwaters within deep tectonic dislocations form the third zone. The most studied groundwaters occur in the first zone. Only waters discharged from Carboniferous and Permian bedrocks in perennial springs are related to deeper circulation in the second zone.

BEDROCK CONTRIBUTION TO GROUNDWATER CHEMISTRY. SILICA SOURCES

The groundwaters studied are only slightly mineralised. Their total dissolved solids (TDS) usually do not exceed 300 mg/L (Tab. 2). The anions are predominantly sulphate and bicarbonate ions, whereas the cations are predominantly calcium ions. Groundwater pH values range widely, from 3.94 to 8.39. Generally, groundwaters from Carboniferous rocks have the lowest pH values, whereas waters from Cretaceous rocks have the highest ones.

Silica concentrations in the groundwaters range from 0.7 mg/L to 24.1 mg/L SiO_2 (Tab. 2, Text-fig. 2). In the areas studied, the weighted mean silica content in wet atmospheric deposition is 0.227 mg/L SiO_2 (Dobrzyński 1997). At an estimated evapotranspiration coefficient of 2 (op.cit.), atmospheric-originated silica in groundwater will be about 0.45 mg/L SiO_2. Atmospheric-deposited silica can therefore be neglected in comparison to silica from lithogenic sources.

The highest average SiO_2 concentrations and the largest differences in SiO_2 content were found in the groundwaters of the Carboniferous rocks (Text-fig. 2). Lower silica concentrations were noted in groundwaters from Permian rocks, but groundwaters from the fissured aquifer contain more silica (on average 9.09 mg/L SiO_2) than groundwaters in the regolith (average 6.60 mg/L SiO_2) (Tab. 2). The lowest and the least varied silica concentrations occur in groundwaters from the Cretaceous rocks (Tab. 2, Text-fig. 2).

The average silica concentration in the groundwaters studied is lower than the average concentration in groundwater (17 mg/L SiO_2) given by Hem (1989), as well as in shallow groundwater of temperate climate (13.3 mg/L SiO_2) and in groundwater of mountain areas (15.2 mg/L SiO_2) after Svarcev (1998). The silica concentrations in the groundwaters studied are also lower than concentrations in groundwaters of volcanogenic rocks in this part of the Sudetes Mts. In groundwaters from rhyolitic tuffs and trachyandesites in the Intra-

	Conglomerates, sandstones with mudstones (C_1)			Conglomerates, sandstones, siltstones, dolomites (P_1)		Calcareous sandstones (K_2)	Siliceous mudstones (K_2)
	fissured aquifer	regolith aquifer		fissured aquifer	regolith aquifer	fissured and regolith aquifers	
		S part	N part				
TDS	119.9[1] 83-166[2]	127.3 100-184	179.1 117-258	305.7 185-351	137.8 93-244	198.0 113-294	134.3 96-174
pH	4.33 4.05-4.78	5.22 4.16-6.74	5.54 4.74-6.95	6.90 5.11-8.00	4.71 3.94-5.66	7.24 6.7-8.39	6.44 5.83-6.85
T (°C)	7.19 4.8-9.8	6.70 2.2-11	6.54 2.6-14.5	7.15 1.2-12.5	6.40 1.2-14.3	7.14 3.7-12	7.10 3.5-10.9
SiO_2	8.39 6.2-17.3	9.65 7.6-17.5	10.64 4.9-24.1	9.09 0.7-12.7	6.60 4.7-8.5	7.29 5.1-9.4	7.12 4.7-8.4
Al	1831.3 216-3800	236.1 6-1500	352.1 8-2300	21.6 2.1-520	689.2 15-4600	31.9 1-270	15 3-41
Ca	18.6 14.3-25	24.6 17.8-39.6	38.8 28.4-46.8	52.4 23.9-74.2	22.1 16.8-31.4	47.5 32.8-72.4	31.2 17.1-39.9
Mg	8.96 2.5-18	5.91 0.1-12.3	8.05 1-30.3	17.27 4.3-25.9	8.52 3.5-16.7	2.44 0.1-8.6	2.22 0.3-9.2
Na	2.65 1.4-4.6	3.23 1.6-5.6	4.94 2.2-8.5	3.14 1.3-5.8	3.08 1.4-6.4	3.38 1.5-5.2	3.76 2.6-5.9
K	2.81 1.1-4.3	2.14 0.7-16.8	1.96 0.2-12.3	2.58 1.1-5.7	3.61 0.7-15	2.85 1.1-12.7	2.47 1.4-7.5
HCO_3	4.2 0.6-9.2	13.3 1-45.2	22.4 0.5-65	153.7 14.6-199	8.2 0.5-14.6	66.7 2.2-148.3	22.3 1.2-44.6
SO_4	53.8 28.1-109.7	49.5 16.2-109.7	75.1 31.9-181.7	52.9 20-107.1	69.7 27.6-121.7	56.1 13.9-110.5	48.0 14.2-110.5
Cl	12.40 6.4-17.7	11.81 5.8-21.3	13.60 8.9-22.3	11.7 6-20.3	10.4 5.5-15.6	9.6 4.2-17	10.2 6.4-14.5
F	0.16 0.00-0.43	0.23 0.03-0.44	0.38 0.01-0.92	0.15 0.00-0.34	0.20 0.00-0.34	0.23 0.05-0.83	0.09 0.00-0.23
PO_4	0.05 0.00-0.15	0.08 0.02-0.18	0.06 0.02-0.16	0.24 0.02-0.63	0.07 0.00-0.31	0.07 0.00-0.45	0.07 0.00-0.54

Concentrations in mg/L (except Al, in μg/L). 1 - arithmetic mean, 2 - range.

Table. 2. Physico-chemical characteristics of groundwater in sedimentary rocks (after Dobrzyński 1997, updated)

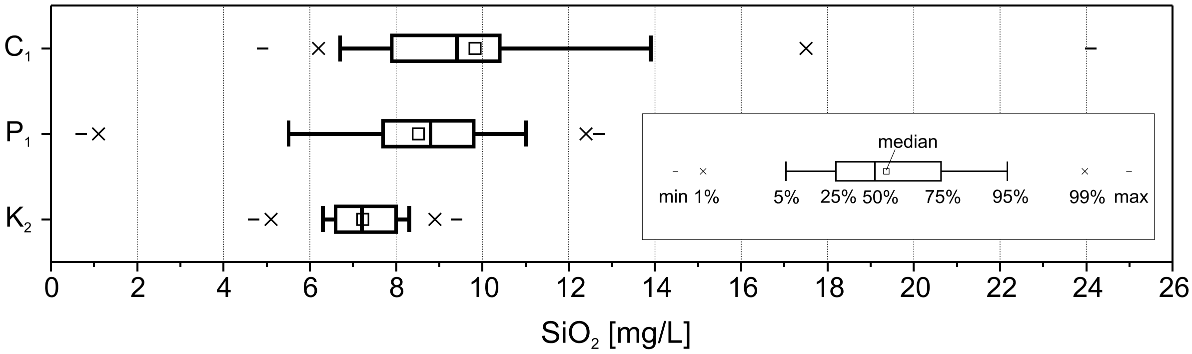

Fig. 2. Box charts of silica concentration in groundwater from sedimentary rocks (C_1 – Lower Carboniferous, P_1 – Lower Permian, K_2 – Upper Cretaceous). Explanations: min – minimum value; max – maximum value; 1% - 99% – percentiles

Sudetic Basin average concentrations between 12.00 and 17.05 mg/L SiO_2 have been found (DOBRZYŃSKI 2005). The silica concentration in groundwater from sedimentary rocks is typically lower than in groundwater from crystalline rocks (MACIOSZCZYK & DOBRZYŃSKI 2002). This is because of the lower content of reactive primary silicate phases in the sedimentary rocks.

The contributions of weathering to groundwater chemistry have been quantified. Calculations were based on the wet deposition chemistry (DOBRZYŃSKI 1997) and the groundwater composition data, and on the assumption that the lithogenic source of chlorides was negligible. The differences found in the weathering contributions are shown in Tab. 3.

Disequilibrium between the groundwaters and the bedrocks is corroborated by saturation indices (Tab. 4). Groundwaters are undersaturated with respect to the main primary silicates, and oversaturated or in equilibrium with some secondary phases.

Because of the varied petrographic composition of the Carboniferous rocks, especially the clastic composition of the conglomerates, it is difficult to indicate precisely the mineral phases that are a source of dissolved silica. Most compounds (including silica) dissolved in groundwater from the Carboniferous bedrocks could have originated from the weathering of a wide assemblage of reactive minerals contained in greenstone, palaeobasalt, diabase, phyllite, marble, mica schist, and greywacke clastics. The regolith aquifer in the northern part of Area 1 is the most contributed by Ca, Na, HCO_3, and SO_4 ions because of the presence of reactive components in Caledonian material. Bicarbonate ions originate from carbonate minerals that occur in the marble and greenstone clasts, whereas sulphate ions are released during oxidation of pyrite dispersed in the greenstones.

The chemistry of groundwater from the fissured aquifer in the Permian rocks differs significantly from that of the groundwater of the regolith aquifer (Tab. 2). The groundwater from the regolith aquifer also has average TDS values more than twice as small as those in groundwaters from the fissured aquifer. Of all the groundwaters studied, the highest contributions of Ca, Mg and HCO_3 were found in the fissured aquifer (Tab. 3). The fundamental source of these components is dolomite dissolution. Some amounts of calcium and magnesium might also derive from plagioclase and from biotite/chlorite respectively. The groundwaters of the fissured aquifer are therefore less acid (mean pH 6.90) than those of the regolith (mean pH 4.71). The former waters are completely neutralised due to carbonate mineral solubility and long-term water-rock interactions.

	Conglomerates, sandstones with mudstones (C_1)			Conglomerates, sandstones, siltstones, dolomites (P_1)		Calcareous sandstones (K_2)	Siliceous mudstones (K_2)
	fissured aquifer	regolith aquifer		fissured aquifer	regolith aquifer	fissured and regolith aquifers	
		S part	N part				
Na	0.09	0.11	0.18	0.11	0.11	0.12	0.14
K	0.02			0.03	0.05	0.04	0.02
Ca	0.38	0.54	0.88	1.23	0.48	1.12	0.71
Mg	0.31	0.19	0.27	0.65	0.30	0.05	0.04
HCO_3		0.08	0.21	2.34		0.98	0.25
SO_4	0.38	0.34	0.58	0.39	0.57	0.44	0.35

Table. 3. Weathering contributions to chemical composition of groundwater from sedimentary rocks. Concentrations in mmol/L

	Conglomerates, sandstones with mudstones (C_1)			Conglomerates, sandstones, siltstones, dolomites (P_1)		Calcareous sandstones (K_2)	Siliceous mudstones (K_2)
	fissured aquifer	regolith aquifer		fissured aquifer	regolith aquifer	fissured and regolith aquifers	
		S part	N part				
Forsterite	*-23.91*	*-19.61*	*-17.95*	*-10.60*	*-20.12*	*-13.53*	*-17.26*
Diopside	*-18.54*	*-13.76*	*-11.97*	*-4.97*	*-14.67*	*-7.08*	*-10.88*
Chlorite	*-43.92*	*-31.23*	*-25.57*	*-6.28*	*-32.78*	*-12.82*	*-22.60*
Anorthite	*-14.68*	*-10.13*	*-7.72*	*-3.33*	*-11.11*	*-3.27*	*-5.62*
Albite	*-8.20*	*-5.73*	*-4.38*	*-2.66*	*-6.56*	*-2.68*	*-3.78*
K-feldspar	*-5.63*	*-3.44*	*-2.42*	-0.23	*-4.22*	-0.28	*-1.43*
K-mica	*-1.67*	**2.41**	**4.89**	**8.13**	**1.43**	**8.84**	**7.27**
Illite	*-6.66*	*-3.07*	-0.96	2.00	*-4.03*	**2.17**	0.63
Beidellite-Ca	*-3.47*	-0.55	1.42	**2.85**	-1.45	**3.44**	**2.59**
Pyrophyllite	0,26	**2.43**	**3.96**	**4,79**	1,50	**5,24**	**4,82**
Kaolinite	-0.04	**2.02**	**3.55**	**4.38**	**1.49**	**5.05**	**4.59**
Halloysite	*-5.32*	*-3.26*	*-1.74*	*-0.89*	*-3.80*	-0.24	*-0.69*
$SiO_{2(a)}$	*-1.01*	*-0.93*	*-0.90*	*-0.99*	*-1.09*	*-1.05*	*-1.06*
Chalcedony	-0.10	-0.02	0.01	-0.09	*-0.18*	-0.14	-0.16
Quartz	**0.39**	**0.47**	**0.50**	**0.40**	**0.31**	**0.35**	**0.33**
$Al(OH)_{3(a)}$	*-3.65*	*-2.70*	*-1.97*	*-1.44*	*-2.81*	*-1.06*	*-1.27*
$Gibbsite_{(c)}$	*-0.78*	0.17	**0.90**	**1.42**	0.07	**1.81**	**1.59**
Dolomite	*-11.01*	*-7.88*	*-6.56*	-0.79	*-8.40*	*-3.02*	*-5.96*
Calcite	*-5.39*	*-3.63*	*-2.93*	-0.15	*-4.01*	*-0.84*	*-2.33*
Gypsum	*-2.39*	*-2.26*	*-1.92*	*-2.02*	*-2.18*	*-1.99*	*-2.14*
Jurbanite	*-0.70*	*-2.12*	*-1.95*	*-5.03*	*-1.72*	*-4.05*	*-2.50*

Explanations: Italic values indicate under-saturation (SI< -5% |lgK|); bolded values indicate over-saturation (SI> +5% |lgK|); shadowed cells refer to SI values in the assumed equilibrium range (±5%lgK).

Table. 4. Arithmetic mean saturation indices (SI) of groundwater in sedimentary rocks with respect to selected mineral phases (after DOBRZYŃSKI 1997, updated)

The regolith is actually depleted in carbonates and other more readily reactive solids, and is unable to neutralise acid atmospheric deposition. The contributions of Na and K are similar in both aquifers (Tab. 3). Potassium enrichment in the fissured aquifer is surprisingly low on account of the high content of K-feldspars in the clastics and in the arkose matrix. Groundwaters acquire nearly neutral pH due to carbonate solubility. This leads to a saturation of the water with respect to K-feldspar (Tab. 4). This equilibrium prevents a further increase in potassium concentration. Groundwaters in the regolith are enriched in potassium at the same level as waters of the fissured aquifer; nevertheless, the former have a much lower pH and are readily undersaturated with K-feldspar (Tab. 4). This is probably because of the very short time of water transit in the regolith. Groundwaters from the regolith show a higher sulphate contribution (0.57 mmol/L) due to decomposition of soil organic matter.

The Permian bedrocks abound in phases that can release silica into groundwater. The tuffaceous arkose matrix, components of tuffogenic siltstones, and the feldspars are considered to be the most important source phases. The silica in regolith groundwater probably originated mainly from clasts of porphyry and feldspar.

The groundwater chemistry of the Cretaceous rocks – both the calcareous sandstones and the siliceous mudstones – presents similar patterns. They differ from each other mainly in terms of the contributions of calcium and bicarbonate (Tab. 3). Groundwater in calcareous sandstones is more enriched in solutes originated from the dissolution of calcite cement (Tab. 1). The waters from the Cretaceous aquifers have the lowest magnesium contribution (only 0.04-0.05 mmol/L) compared to the other groundwaters. Cretaceous rocks deposited in shallow marine basins are depleted in Mg-bearing, readily reactive primary silicate minerals. In fact, the contributions of potassium, sodium and sulphate do not differ significantly from those in groundwaters of the Carboniferous and Permian aquifers. Feldspars, and also perhaps glauconite, were probable silica source-phases in the Cretaceous rocks.

The silica/basic cation molar ratio in groundwaters (Text-fig. 3) suggests that, during weathering, calcium and magnesium are usually released into water more

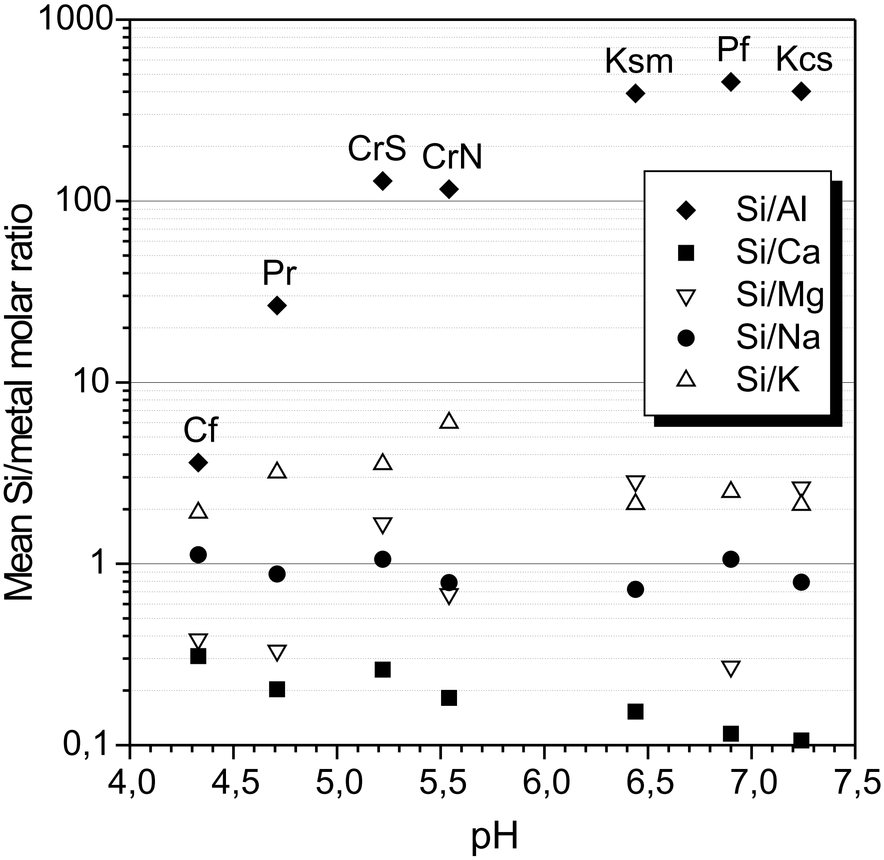

Fig. 3. Mean Si/metal molar ratio vs. pH of groundwater in sedimentary rocks. Explanations: Cf – Carboniferous, groundwater of fissured aquifer; Cr – Carboniferous, groundwater of regolith aquifer, in southern (S) and northern (N) parts respectively; Pf – Permian, groundwater of fissured aquifer; Pr – Permian, groundwater of regolith aquifer; Kcs – Cretaceous, groundwater in calcareous sandstones; Ksm – Cretaceous, groundwater in siliceous mudstones

readily than silica (molar ratio < 1). Sodium and silica are released at similar rates, whereas potassium is released much less readily than silica. The molar ratios found result from the mineral resistance to weathering and predominant irreversible incongruent reactions. A small amount of silica is also mobilised during weathering. The Si/Al molar ratio ranges widely, from 3.6 to 453.3, and depends on pH (Text-fig. 3) – the main variable that governs Al solubility in natural waters.

ALUMINOSILICATE PHASES STABILITY. DISCUSSION

During the weathering of primary silicates, numerous secondary mineral phases are formed. Weathering reactions involve thermodynamically unstable solid phases that can exist due to the equilibrium in partial geochemical systems. These phases may undergo ageing and crystallisation to form secondary metastable solids and, finally, thermodynamically stable secondary minerals. The chemical composition of groundwater feedbacks the stability of the secondary solid phases and influences the silicon concentration in the groundwater.

The silicon and/or aluminium concentrations observed in natural waters have been explained by a proposed equilibrium between the solution and different secondary mineral phases, such as kaolinite, halloysite, gibbsite, microcrystalline gibbsite, allophanes and imogolite.

Phases of amorphous and/or short-range ordered aluminosilicate are generally called allophanes. This is the term usually applied to a group of naturally occurring short-range ordered hydrous aluminosilicates with a Al/Si molar ratio typically of 1.0 to 2.0, and composition of $(Al_2O_3)\cdot(SiO_2)_{1\text{-}2}\cdot(H_2O)_{2.5\text{-}3.0}$ (WADA 1989). Allophanes with Al/Si ratios below 1.0 and above 2.0 are also noted. The chemical composition of allophanes varies in the range necessary to maintain a predominance of Si-O-Al bonds. Imogolite has an Al/Si molar ratio of 2.0 and a composition, $(Al_2O_3)\cdot(SiO_2)\cdot 2.5(H_2O)$, similar to allophanes.

Allophane/imogolite minerals are found worldwide in soils and regoliths developed on volcanic tuffs, but also

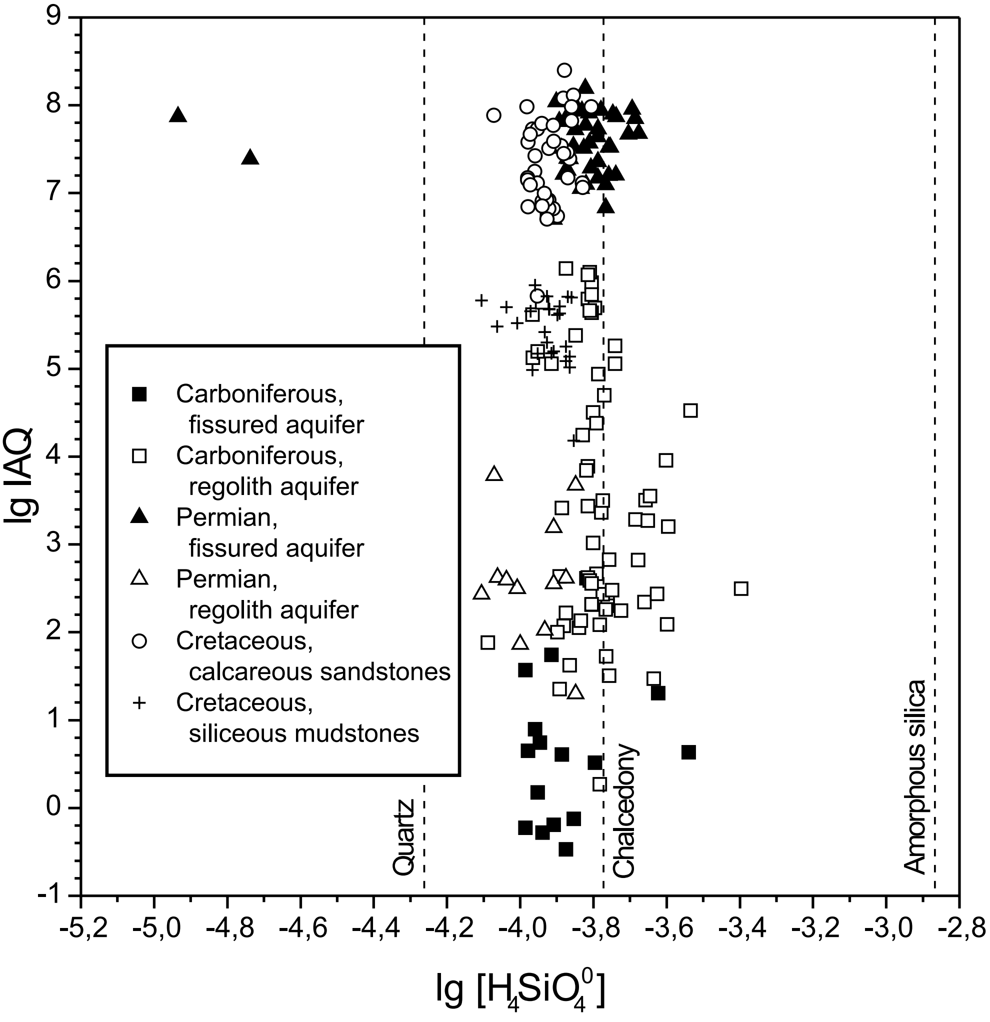

Fig. 4. Ion activity quotient of Pačes-concept allophane vs. silica activity in groundwater from sedimentary rocks. Solubility lines of silica forms for 7°C

in those developed on other bedrocks. The formation of allophane/imogolite phases requires sufficiently high aluminium and silicon activities. Both elements usually occur in soil and vadose zone waters in higher concentrations than in shallow groundwaters.

In the discussion on silicon and aluminium solubility in groundwater, PAČES (1973, 1978) proposed an allophane of varied composition $[Al(OH)_3]_{(1-x)}[SiO_2]_x$, depending on pH according to the formula, x = 1.24 - 0.135 pH. Its composition varies linearly between the pure amorphous silica end-member (at pH 1.8 – PZC of $SiO_{2(a)}$) and the amorphous alumina one (at pH 9.2 – PZC of $Al(OH)_{3(a)}$). PAČES gave lgK for two allophanes, a theoretical and an empirical one. The equilibrium constant of the theoretical allophane calculated using the equilibrium constants of amorphous silica and amorphous alumina was $lgK_{25} = -5.7 + 1.68$ pH (PAČES 1973). Field and experimental groundwater chemistry data allowed quantification of the equilibrium constant for the so-called „field" allophane as lgK equals -5.89 + 1.59 pH (PAČES 1978). The latter phase agreed well with Si and Al activities in cold and thermal groundwater of albite-rich granite massifs. Both hypothetical allophanes can be considered as reversible metastable phases forming during the weathering of primary silicates. Under favourable conditions, these allophanes can transform into the next phases, e.g. halloysite, kaolinite. Silicon and aluminium activities in cold groundwater from Permian trachyandesites in the Intra-Sudetic Basin (SW Poland) were consistent with the solubility of the allophane proposed by PAČES (DOBRZYŃSKI 2005).

Because at the solubility reaction of $Al_2O_3{\cdot}(SiO_2)_{1\text{-}2}$ allophane the amount of H^+ ions is three times greater than Al^{+3} ions, and three to six times (depending on the allophane composition) greater than silica activity the ion activity quotient of allophane depends mainly on water pH. Hydrogen activity is also the main variable that governs Al^{+3} activity in solution.

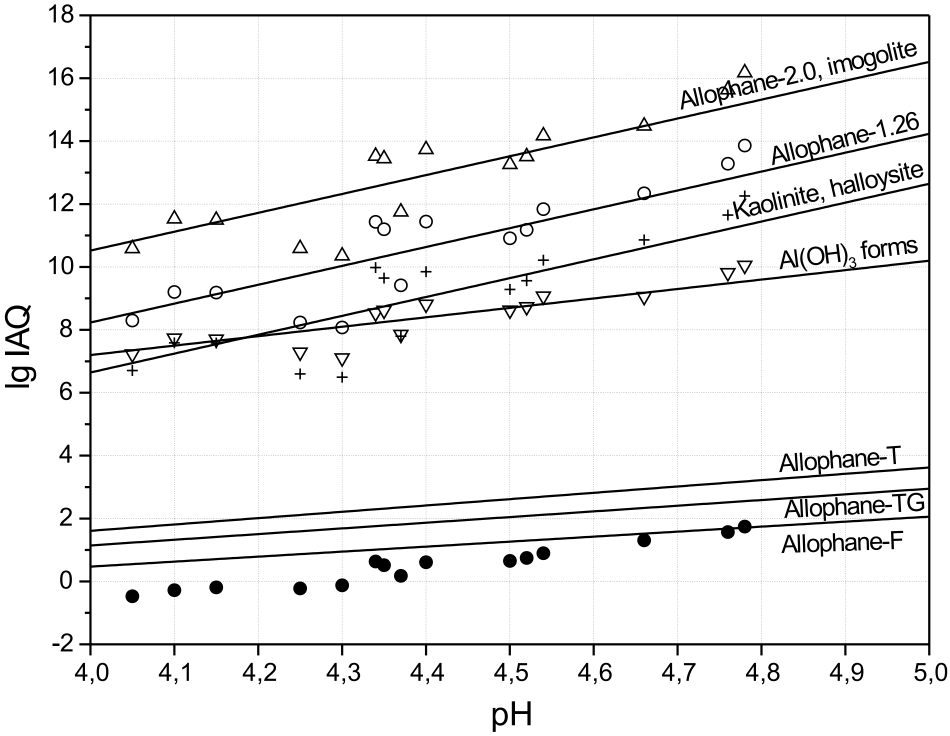

Fig. 5. Ion activity quotients of allophanes, kaolinite/halloysite and $Al(OH)_3$ forms in groundwater from Carboniferous sedimentary rocks.
Fig. 5a. Fissured aquifer. Allophanes of 2.0 and 1.26 after Su & Harsh (1998).
Explanations: Allophanes -F, -TG, and -T refer to phases of composition consistent with the Pačes-concept (1973, 1978): allophane-F – "field" allophane (Pačes 1978); allophane-T – allophane of theoretical composition calculated from amorphous silica and amorphous alumina as end-members (Dobrzyński 2005); allophane-TG – allophane of theoretical composition calculated from amorphous silica and microcrystalline gibbsite as end-members (Dobrzyński 2005).
Δ – Allophane-2.0, imogolite; ○ – Allophane-1.26; ∇ – $Al(OH)_3$ forms; + – Kaolinite, halloysite; ● – Pačes-concept allophanes

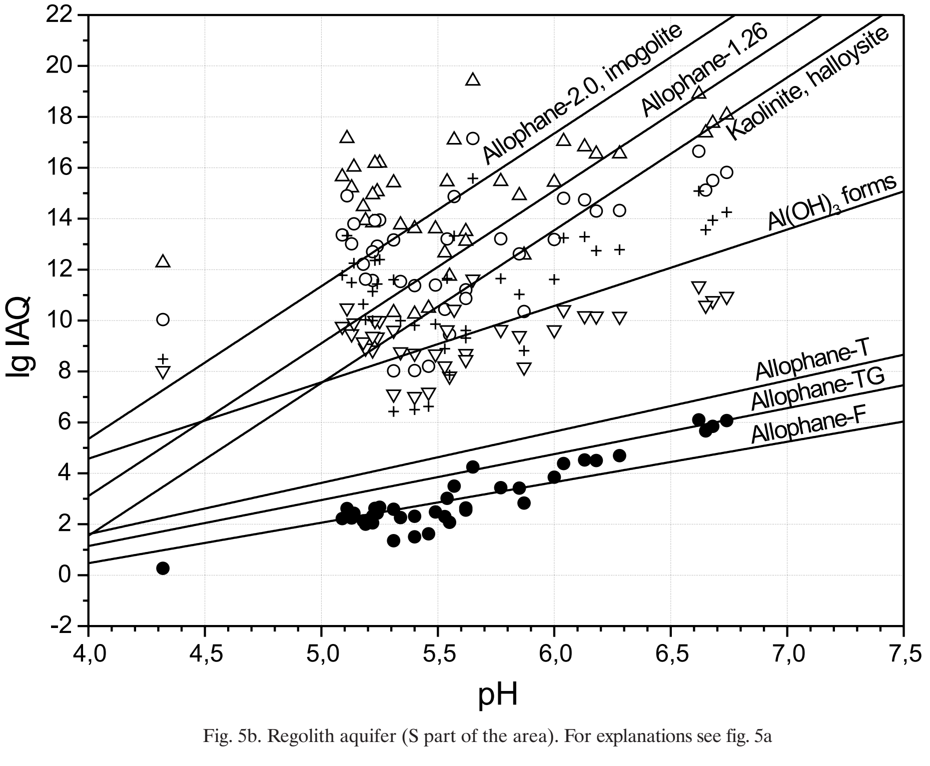

Fig. 5b. Regolith aquifer (S part of the area). For explanations see fig. 5a

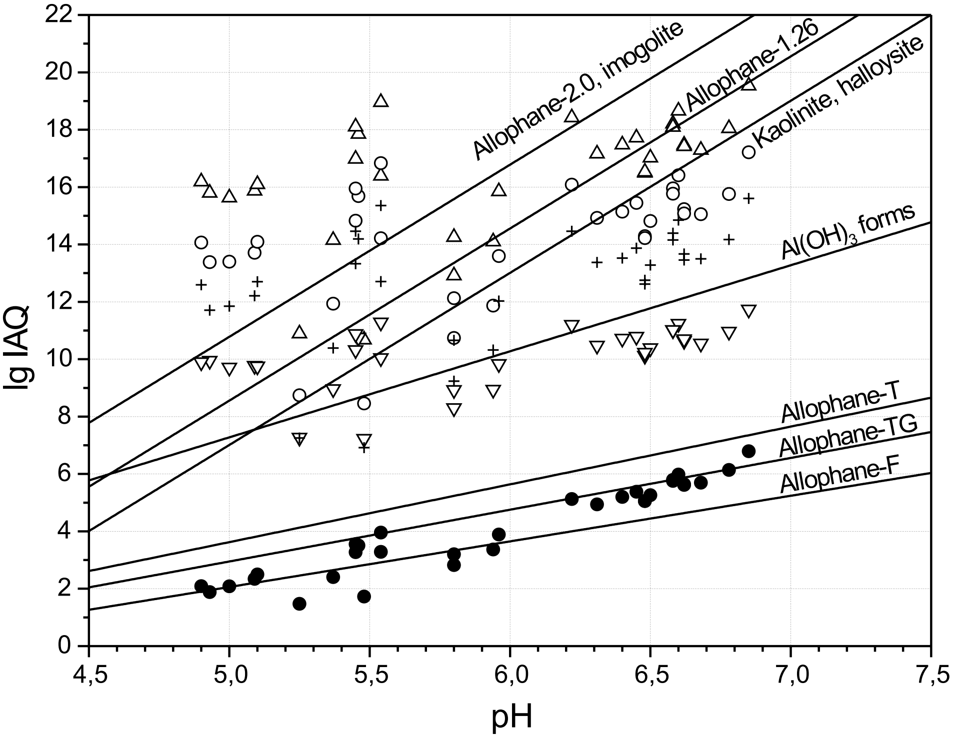

Fig. 5c. Regolith aquifer (N part of the area). For explanations see fig. 5a

Silica activity in groundwaters remains at a similar level, close to chalcedony solubility (Text-fig. 4). Two water samples of distinctly lower silica concentration ($lg[H_2SiO_4^0]$ ca - 4.9) came from the beginning of the snow melt, and show chemistries resulting from the mixing of groundwater with water released from snow retention.

Groundwater chemistry data were analysed in terms of the ion activity quotient for different secondary solids that potentially control Si and/or Al solubility. Analysis of solute activity for allophane phases consistent with PAČES proposal (1978) was used as an auxiliary method for the interpretation of hydrochemical data. Reaction quotients of these allophanes are affected by the artefact of the assumed mathematical relationship between the Al/Si ratio and pH. Solubility curves (Text-figs 5, 6) were prepared for arithmetic mean product (Al^{+3}, $H_2SiO_4^0$) activities in groundwaters from particular sedimentary bedrocks. Due to the same Al/Si molar ratio value, 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 relate to the composition of gibbsite, microcrystalline gibbsite or amorphous aluminium hydroxide. Cited data on the following allophane phases: (1) "field" allophane (allophane-F) (PAČES 1978); (2) allophanes after SU & HARSH (1998) of Al/Si molar ratio = 1.26 (allophane-1.26), and Al/Si = 2.0 (allophane-2.0), were considered. Data were also used for two allophanes with compositions consistent with Pačes' concept. The equilibrium constant of the allophane of theoretical composition (allophane-T) were re-calculated using present thermochemical data for amorphous silica and amorphous alumina (DOBRZYŃSKI 2005). The equilibrium constant for another theoretical phase – "aged" allophane – was calculated on amorphous silica end-member solubility and microcrystalline gibbsite end-member solubility instead of amorphous $Al(OH)_3$ (allophane-TG) (op.cit). The equilibrium constants of the above-mentioned allophane phases are given in Table 5. Reaction quotients vs. pH indicate that solute activities are close to the solubility of allophane-TG, allophane-F and, in some groundwaters, also to that of kaolinite/halloysite and/or $Al(OH)_3$ forms (Text-figs 5, 6).

The groundwaters studied present a wide range of pH and chemistry. The Pačes-concept allophane IAQ pattern (Text-fig. 7) allows four geochemical environments to be distinguished with respect to pH value. These are: groundwaters of (1) pH below 4.8; (2) pH 4.8-5.5; (3) pH 5.5-6.7; and (4) pH above 6.7. Silica solubility will be discussed in the order of these ranges (Text-fig. 8). The ion activity quotient of allophanes is a function of pH. Therefore, the good linear correlation in the diagrams of lgIAQ vs. pH can reflect mathematical relationships only and not the equilibrium state. In order to document whether equilibrium conditions are maintained, the deviations from the IAQ correlation line vs. pH were plotted (Text-fig. 9).

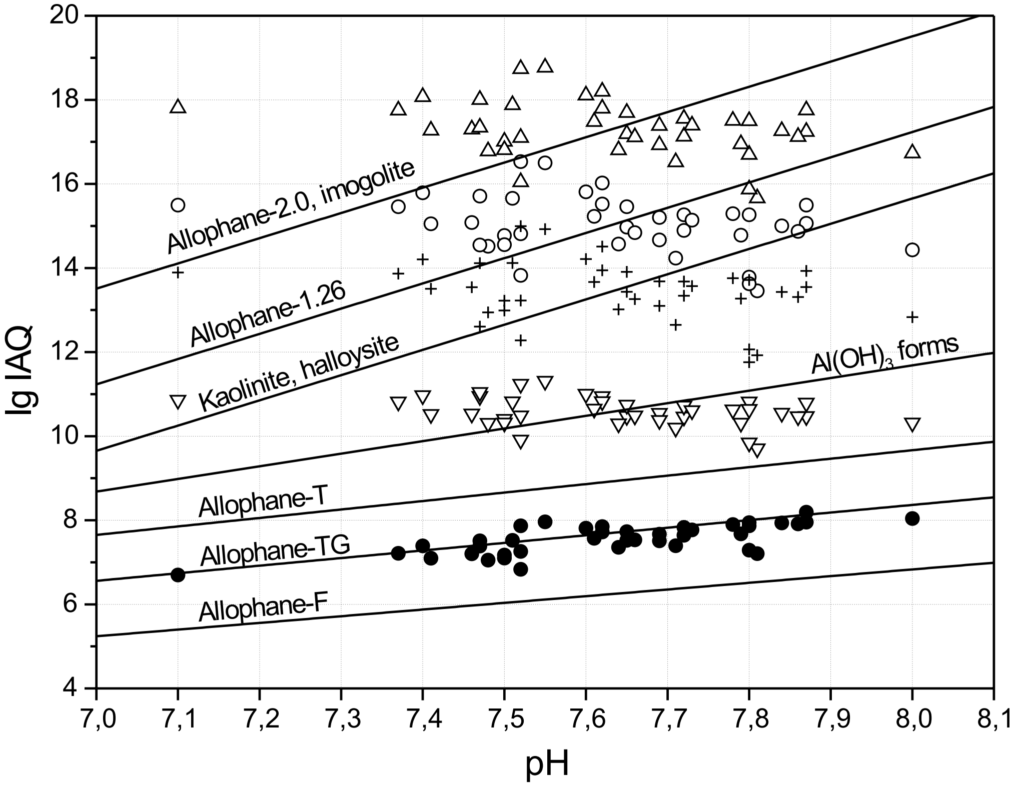

Fig. 6. Ion activity quotients of allophanes, kaolinite/halloysite and Al(OH)$_3$ forms in groundwater from Permian and Cretaceous sedimentary rocks.
Fig. 6a. Permian – fissured aquifer. Explanations as in Fig. 5

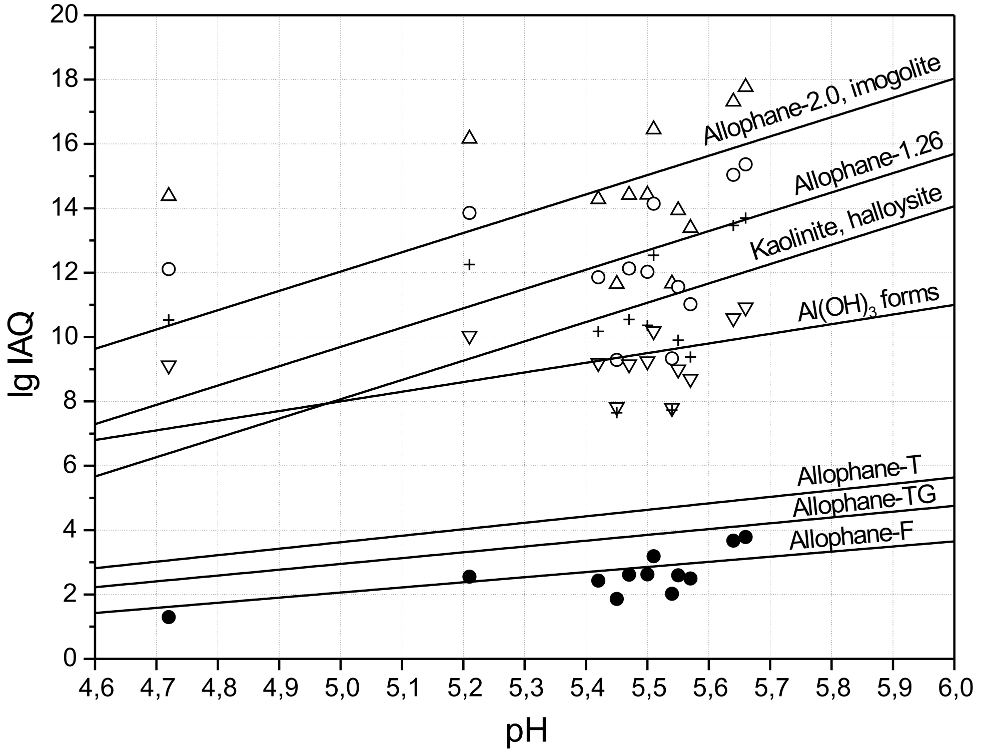

Fig. 6b. Permian – regolith aquifer. Explanations as in Fig. 5

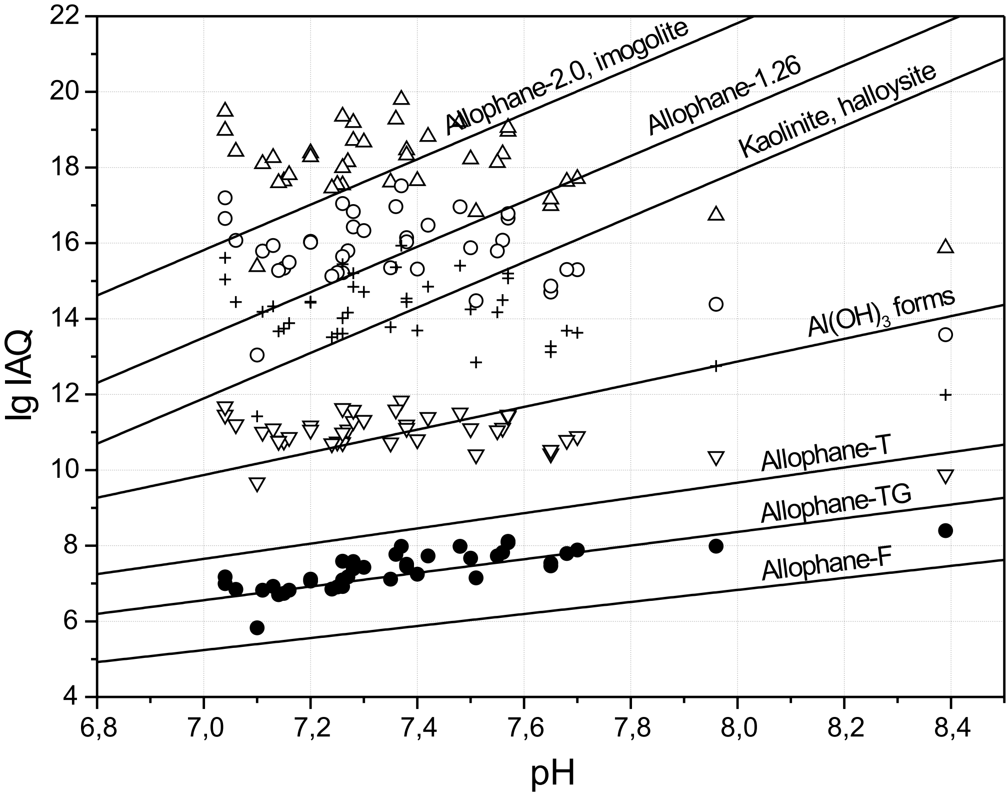

Fig. 6c. Cretaceous – calcareous sandstones. Explanations as in Fig. 5

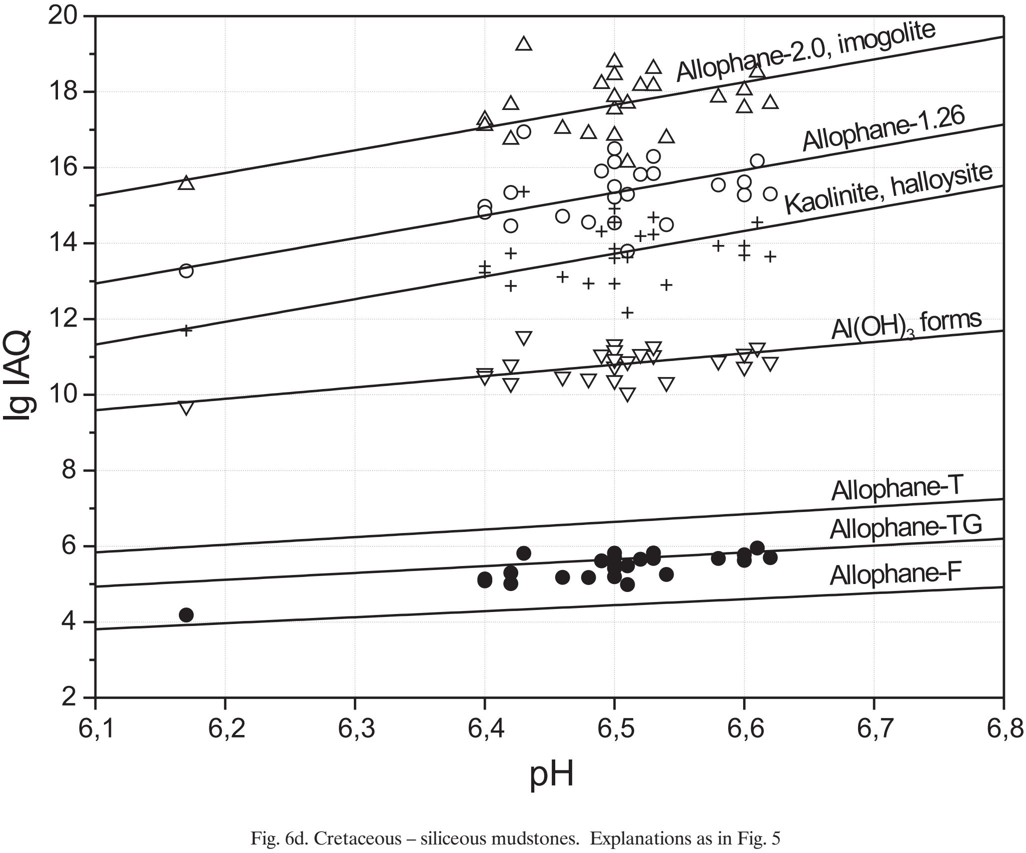

Fig. 6d. Cretaceous – siliceous mudstones. Explanations as in Fig. 5

Allophane phase	Formula	$\lg K_{25}{}^{1}$	Source
Allophane-2.0	$Al_2O_3 \cdot SiO_2 \cdot 2.53H_2O$	14.20±0.93	a
Allophane-1.26	$Al_2O_3 \cdot 1.59SiO_2 \cdot 2.63H_2O$	11.27±1.07	a
Allophane-T	$[Al(OH)_3]_{(1-x)}[SiO_2]_x$	-5.95 + 1.82 pH	b
Allophane-TG	$[Al(OH)_3]_{(1-x)}[SiO_2]_x$	-5.36 + 1.63 pH	b
Allophane-F	$[Al(OH)_3]_{(1-x)}[SiO_2]_x$	-5.89 + 1.59 pH	c
Allophane-FV	$Al(OH)_3 \cdot (SiO_2)_{0.5\text{-}1.0}$	-13.59(±0.75) + 2.92(±0.12) pH	b
Allophane-FS	$Al(OH)_3 \cdot (SiO_2)_{0.5\text{-}1.0}$	-12.39(±0.71) + 2.74(±0.11) pH	this text

1- lgK for hypothetical allophane-FV and allophane-FS at ≈ 7°C, mean temperature of studied groundwaters. a - SU & HARSH (1998), b - DOBRZYŃSKI (2005), c - PAČES (1978)

Table. 5. Equilibrium constants of allophane phases

Analysis of aluminium activity in waters of different geochemical environments has shown that waters with pH values below 5 do not tend to equilibrate with gibbsite and/or kaolinite, and, when pH values drop below 4.5, the waters become undersaturated with respect to these phases (NORDSTROM 1982). NORDSTROM & BALL (1986) proposed the presence of a transition zone at pH 4.6-4.9, within which aluminium changes solubility independently of site localisation, ion strength, and sulphate concentration. This transition zone corresponds fairly well to the pK for the first hydrolysis constant of aqueous aluminium ion, that is of pK_1=5.00(±0.04), at 298.15 K and I=0 (NORDSTROM & MAY 1996). Aluminium concentration in waters of pH <4.9 is usually lower than is needed to obtain equilibrium with aluminosilicates (e.g. kaolinite) or $Al(OH)_3$ forms and, at pH <4.5, could be controlled by sulphate phases, such as jurbanite, $Al(SO_4)OH{\cdot}5H_2O$, alunite, $KAl_3(SO_4)_2(OH)_6$, or basaluminite, $Al_4(SO_4)(OH)_{10}{\cdot}5H_2O$ (ERIKSSON 1981, NORDSTROM 1982).

Only the groundwater from the Carboniferous fissured aquifer has pH values of <4.8 (Text-fig. 7). However, these waters have sulphate concentrations that are too low to reach saturation with respect to jurbanite (Tab. 4). In contrast to published data, groundwaters with pH values of <4.8 are in equilibrium with respect to kaolinite (Tab. 4, Text-fig. 5a). This mineral commonly occurs in the cement of the Carboniferous conglomerates (TEISSEYRE 1972), and can control silica solubility in the groundwater. The patterns of the allophane and $Al(OH)_3$ IAQs (Text-fig. 5a) result from Al^{+3} and H^+ activities controlled by kaolinite.

The Al/Si molar ratio ranges from 1 to 2 in allophane of the composition $(Al_2O_3)(SiO_2)_{1\text{-}2}(H_2O)_{2.5\text{-}3.0}$ whereas in the reversible metastable allophane phase, $[Al(OH)_3]_{(1-x)}[SiO_2]_x$, proposed by PAČES (1973, 1978), this molar ratio depends on pH. PAČES allophane reaches an Al/Si ratio of 1 at a pH 5.50, and 2 at pH 6.73. Analyses of allophane phase solubility in groundwaters from volcanic rocks show that, at the same limits (pH 5.5 and pH

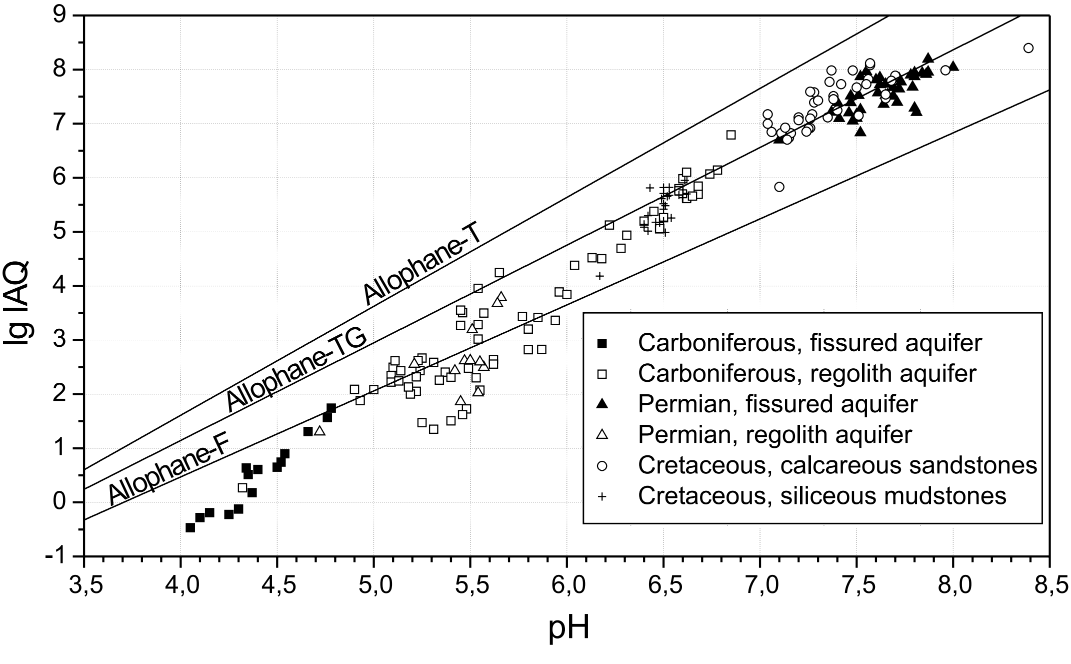

Fig. 7. Ion activity quotients of Paães-concept allophanes in groundwater from different sedimentary rocks

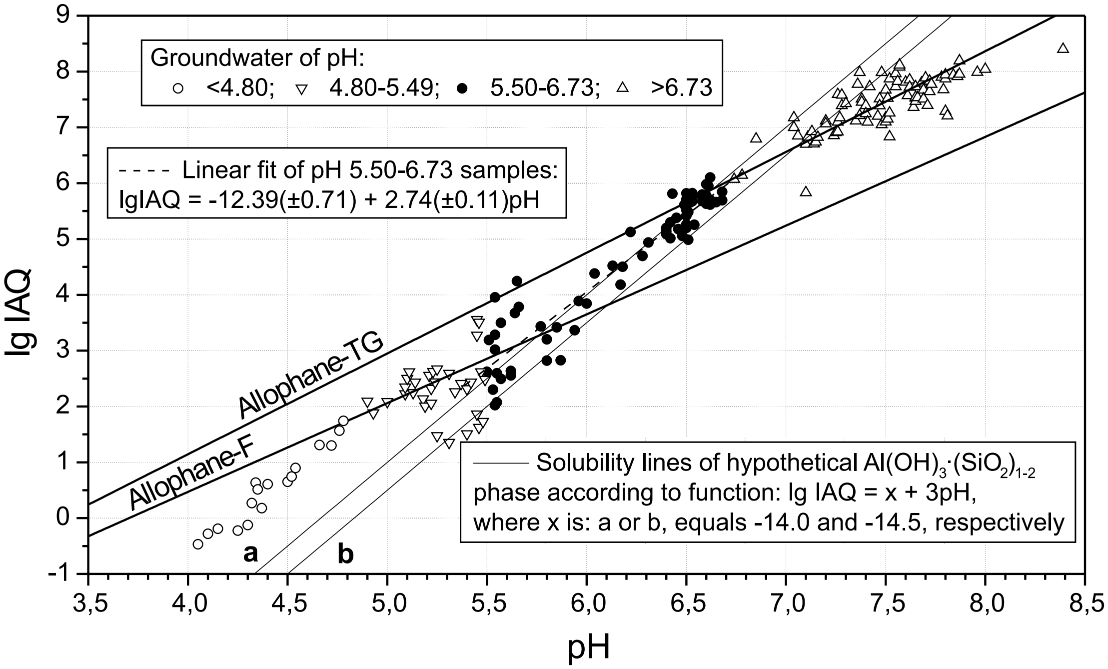

Fig. 8. Ion activity quotients of Paães-concept allophanes in the groundwaters studied , divided into pH value groups

6.7), silica solubility is readily changed (DOBRZYŃSKI 2005). The pattern of IAQs (Text-fig. 7) shows similar relationships within the same range. This was the basis for taking pH 5.5 and pH 6.7 as "border" values.

Groundwaters with pH values ranging between 4.8 and 5.5 are discharged from the Permian and Carboniferous rocks in ephemeral springs after snow melt. Groundwaters of Carboniferous rocks originate mainly from the southern part Area 1, where poorly reactive conglomerates with quartz and quartz-kaolinite cements predominate. The IAQs show no regular pattern (Text-figs 5b, 5c, 7) and it is therefore difficult to indicate the phase(s) that control the silica concentrations. Regoliths developed on Permian and Carboniferous bedrocks are thin, with low reactivity. Therefore, groundwaters of ephemeral springs are not efficiently neutralised. These waters show that chemical non-equilibrium conditions commonly obtain during and after the snowmelt in shallow groundwater and surface water, especially in mountain areas developed on poorly reactive bedrock. Chemical non-equilibrium conditions are caused by the simultaneous action of several factors, e.g. rapid water flow, lower temperatures, low reaction rates at lower temperatures (CAMBELL & *al.* 1986). Silica and aluminium concentrations in the above-mentioned aquifers result from kinetics or steady-state between weathering release and hydrological removal.

Groundwaters from Cretaceous siliceous mudstones and from part of the Carboniferous regolith show pH values ranging from 5.5 to 6.7 (Text-fig. 7). Allophane IAQs in this pH range can be fitted by the line of regression function (Text-fig. 8) lgK = -12.39(±0.71) + 2.74(±0.11) pH (R=0.95; N=69). The regression found could relate to solubility of the hypothetical allophane phase with composition close to $Al(OH)_3·(SiO_2)_{0.5\text{-}1.0}$. A similar regression was noted in the same pH range in groundwater from volcanic rocks by DOBRZYŃSKI (2005) for the hypothetical phase named allophane-FV (Tab. 5). The strength of the correlation is weakened by a few water samples of lg IAQ >3 at pH values of 5.5 to 5.7 (Text-fig. 8). These samples come mainly from the regolith on Carboniferous bedrocks in the southern part of Area 1, and were taken during snow melt. The regression function suggests that the precipitation of the solid uses three protons. This can correspond to the reaction $Al(OH)_3·(SiO_2)_x + 3\ H^+ = Al^{+3} + x\ H_2SiO_4^0 + (3\text{-}2x)\ H_2O$, and yields equilibrium function lgK = lg $[Al^{+3}]$ + x lg $[H_2SiO_4^0]$ + 3 pH. In fact, the sum of "lg $[Al^{+3}]$" and "x lg $[H_2SiO_4^0]$" varies between -14 and -14.5 (Text-fig. 8). The results indicate that silica could be controlled by an allophane-like metastable reversible phase (farther called allophane-FS) of lgK = -12.39(±0.71) + 2.74(±0.11) pH (Tab. 5). This hypothetical solid phase can be interpreted as a precursor of potentially forming allophane/imogolite minerals that are widely identified in both weathered volcanic rocks and in clastic rocks (e.g. FARMER & *al.* 1980, GUSTAFSSON & *al.* 1998, 1999). However, the regular IAQ pattern of allophane-FS found might also be an artefact of mathematical relationships.

Ion activity quotients (Text-figs 6d, 7) also support

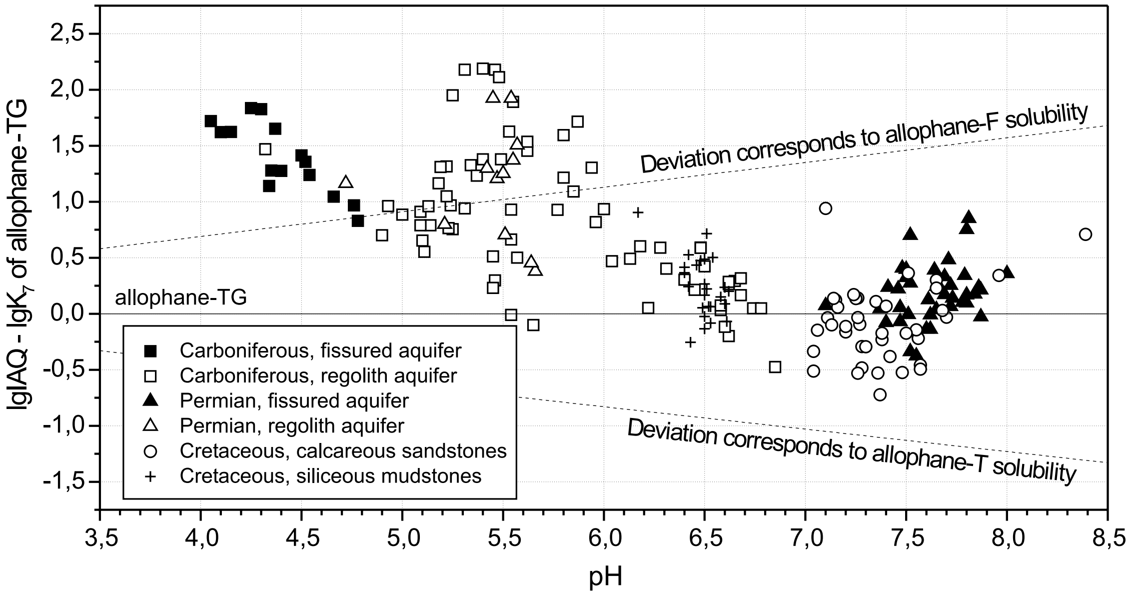

Fig. 9. Deviation of lg IAQ value for allophane of composition proposed by PAČES (1978) from allophane-TG solubility vs. pH

the possibility of simultaneous equilibrium between Al(OH)$_3$ phase and allophane or kaolinite/halloysite. This equilibrium can control Al concentration and consequently influence aqueous silica activity in groundwater from the Cretaceous siliceous mudstones. Examples of the coexistence of allophane/imogolite and Al(OH)$_3$ phases have been documented in soils of different bedrocks and climates (GUSTAFSSON & *al.* 1998, 1999, NDAYIRAGIJE & DELVAUX 2003). The lack of appropriate mineralogical data makes interpretation of aqueous chemistry difficult. Secondary aluminosilicate phases have not yet been investigated in the areas studied.

Groundwaters that react sufficiently long with rock-forming minerals in the fissured Permian and Cretaceous aquifers reach pH values higher than 6.7. An increase in pH is caused by dissolution either of dolomite in the Permian conglomerates or calcite in the Cretaceous calcareous sandstones (Tab. 2). Ion activity quotients of PAČES's allophane plot around the solubility line of allophane-TG (Text-figs 6a, 6c, 7). This solid phase has a molar ratio Al/Si slightly above 2.0. The occurrence of allophanes with Al/Si ratios > 2.0 was reported by WADA (1989) and supports the hypothesis that the concentration of dissolved silica in groundwater might be controlled by a chemical equilibrium with the metastable secondary aluminosilicate. An important role in the formation of amorphous/short-range ordered aluminosilicate minerals can be played by the hydroxyaluminosilicate (HAS) colloids (e.g. FARMER & LUMSDON 1994, LUMSDON & FARMER 1995). These are formed by the reaction of silicic acid with aluminium. In many soils, the so-called proto-imogolite sol (HO)$_3$Al$_2$O$_3$SiOH, which probably plays important role in soil formation (FARMER & *al.* 1980, FARMER & FRASER 1982, GUSTAFSSON & *al.* 1998), has been identified. The formation and structure of two kinds of HAS, named HAS$_A$ and HAS$_B$, have been documented in detail (DOUCET & *al.* 2001, EXLEY & *al.* 2002). These two HAS types have compositions identical to those of proto-imogolite or allophane/imogolite minerals, and have idealised Si/Al molar ratio of 0.5 and 1.0 respectively. The formation of HAS phases is also of environmental significance in that they reduce aluminium toxicity (e.g. EXLEY & *al.* 1997).

It is conceivable that aluminium as well as silicon activity in the groundwaters studied can be controlled by hydroxyaluminosilicates (HAS). HAS colloids can form even at low aluminium concentration as it was found in groundwaters studied. Researches on HAS equilibrium constants are still in progress. The most recent investigation by SCHNEIDER & *al.* (2004) provided the solubility constant of synthetic HAS$_B$, Al$_2$Si$_2$O$_5$(OH)$_4$, estimated experimentally. The calculation scheme proposed by those authors was applied to quantify HAS$_B$ ion activity products in groundwaters. The reaction quotient was calculated for the reaction HAS$_B$ − Al$^{+3}_{(aq)}$ + 2H$_2$SiO$^0_{4(aq)}$ + 6OH$^-$.

The ion activity quotients of HAS$_B$ plotted vs. pH and Al^{+3} activity show very regular patterns (Text-figs 10, 11). Equilibrium with HAS$_B$ is maintained over a wide range of aqueous chemistry, mainly in groundwaters from the Permian and Cretaceous fissured aquifers. In fact, the IAQ of HAS$_B$ is constant for lg[Al^{+3}] values below -9.5 and for pH values above 6.7. The arithmetic mean lgIAQ$_{HAS-B}$ value in water samples of lg[Al^{+3}] < -9.5 is

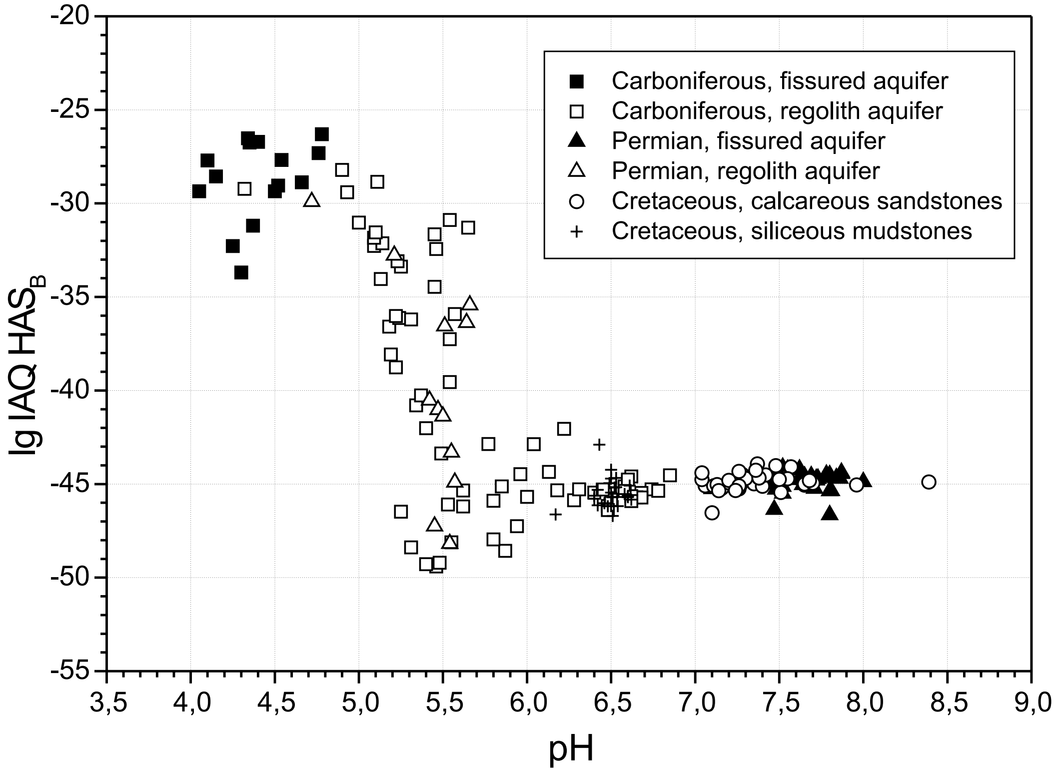

Fig. 10. Ion activity quotient of hydroxyaluminosilicate HAS_B vs. pH

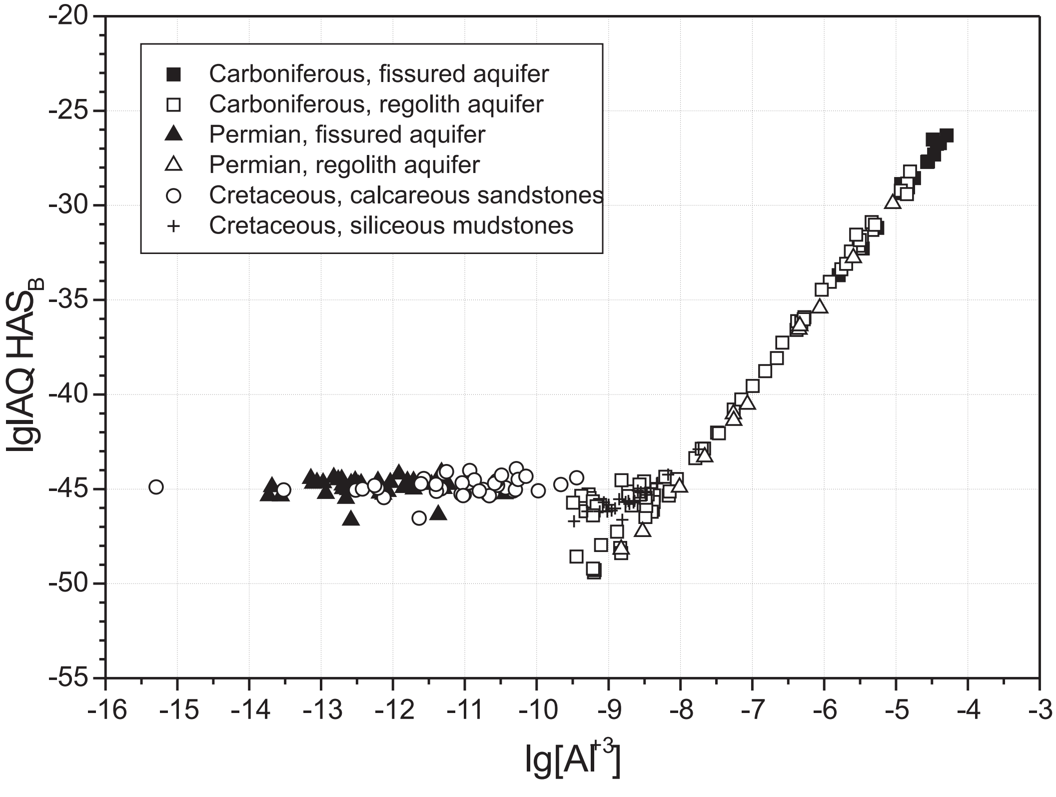

Fig. 11. Ion activity quotient of hydroxyaluminosilicate HAS_B vs. Al^{+3} activity in groundwater

–44.882 (SD=0.486, N=79), whereas in samples of pH>6.7 it is -44.882 (SD=0.483, N=83). These values are very similar to the $\lg IAQ_{HAS\text{-}B}$ = -44.74 (±0.52) value found in groundwaters from Permian volcanic rocks in the same part the Sudetes Mts. (DOBRZYŃSKI 2005).

The published value $\lg K_{HAS\text{-}B}$ = -40.6 (±0.15) (SCHNEIDER & *al*. 2004) is higher than values found in the present investigation. There are several possible explanations for this difference. $K_{HAS\text{-}B}$ is likely to have been overestimated if fast-reacting aluminium $[Al_r]$ instead of $[Al^{+3}]$ was used by SCHNEIDER & *al*. (2004) in their calculation. The laboratory experiment (op.cit.) took place at a temperature of 20°C, while the mean temperature of the groundwaters studied was about 7°C (Tab. 2). However, $\lg K_{HAS\text{-}B}$ can also be slightly overestimated in groundwaters. Aluminium forms stable complexes with different ligands, such as hydroxyl, sulphate, fluoride or organic groups. In the groundwaters analysed dissolved organic carbon usually occurred below the detection limit, 0.5 mg/L C_{org}. Therefore, Al^{+3} activity calculated by the geochemical code can be overestimated. The hydrochemical data point to the occurrence of HAS colloids in the groundwater, which is conducive to the formation of allophane phases.

CONCLUSIONS

The groundwaters studied occur in regolith and fissured bedrocks. They represent the zone of short turnover time in the hydrogeological system and non-equilibrium chemical conditions. Nevertheless, equilibrium was found in some partial geochemical systems with secondary phases, mainly with aluminosilicates. Part of the silica released during weathering might be immobilised in secondary aluminosilicate phases such as allophanes, halloysite and kaolinite. Interpretation of the aqueous chemistry in terms of mineral stability indicates phases that probably control silica concentration in groundwater from different sedimentary rocks. Data analysis corroborates the existence of a state of partial metastable equilibrium in the water-rock system. The concentration of dissolved silica can be controlled by reactions in these partial geochemical systems.

Ion activity quotients allow four hydrogeochemical environments to be distinguished in the sedimentary rocks. In three of them partial chemical equilibrium is probably maintained. Silica activity in groundwaters with pH values below 4.8 – which occur in the Carboniferous conglomerates fissured aquifer – is controlled by equilibrium with kaolinite (Text-figs 5a, 9). Groundwaters from the regolith on Carboniferous bedrock and from the Cretaceous siliceous mudstones, which have pH values between 5.5 and 6.7, represent different conditions (Text-figs 5b, 5c, 6d, 9). Silica dissolved in these groundwaters can be controlled by the equilibrium of the incongruent reaction between kaolinite/halloysite or allophane and $Al(OH)_3$ forms. In groundwaters (of pH above 6.7) from the Permian fissured aquifer and from the Cretaceous calcareous sandstones, the hydroxyaluminosilicate HAS_B is certainly responsible for the control of silicon and aluminium activity. The role of allophanes with the composition proposed by PAČES (1978) is less probable because regular IAQ patterns can be an artefact of mathematical relationships. It is difficult to indicate the phase(s) that might control the silica concentrations in groundwaters with pH values between 4.8 and 5.5. These groundwaters represent non-equilibrium conditions that occurred in the regolith during snow melt. Silicon and aluminium concentrations in those groundwaters are affected by kinetics or steady-state between weathering release and hydrological removal.

Partial chemical equilibrium with aluminosilicate phases is proved by the hydrochemical data. Hydroxyaluminosilicate (HAS) colloids can also play an important role in the formation of secondary reversible aluminosilicate minerals. These have compositions and Al/Si molar ratios similar to those of allophane/imogolite minerals. It is conceivable that the activities of aluminium and silicon in groundwaters can be controlled by HASs. Ion activity quotients of HAS_B in groundwaters, calculated according to the scheme given by SCHNEIDER & *al*. (2004), prove that equilibrium with HAS_B can be maintained in groundwaters that have $\lg[Al^{+3}]$ values below -9.5 and pH values above 6.7. The HAS_B solubility value in the groundwaters studied is $\lg K_{HAS\text{-}B}$ = -44.88 (±0.48), which is lower than that obtained ($\lg K_{HAS\text{-}B}$ = -40.6 ±0.15) experimentally (op.cit.). The role of hydroxyaluminosilicates in aluminium and silicon geochemistry in natural waters appears to be a promising subject for future investigation.

The role of aluminosilicate minerals in the control of silica solubility in the groundwaters studied should be ascertained by mineralogical investigations of secondary phases, especially of amorphous/short-range ordered aluminosilicates (allophanes). This is important, because processes other than solid phase solubility, such as adsorption onto solids or kinetics, can be responsible for silica activity in groundwaters. The hydrochemical results for sedimentary rocks in the Sudetes Mts., as well as for volcanic rocks in the same area (DOBRZYŃSKI 2005), suggest that allophanes and hydroxyaluminosilicates play an important role in the control of silica and aluminium activity in groundwater from the weathered zone. Allophane phases should be taken into account in the analysis and geochemical modelling of the weathering reactions of silicate rocks.

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