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ORIGINAL PAPER

Chemistry of Neutral and Alkaline Waters with Low Al^{3+} Activity Against Hydroxyaluminosilicate HAS_B Solubility. The Evidence from Ground and Surface Waters of the Sudetes Mts. (SW Poland)

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Abstract A wide set of aqueous chemistry data (574 water analyses) from natural environments has been used to testify and validate of the solubility of synthetic hydroxyaluminosilicate (HAS_B), $Al_2Si_2O_5(OH)_4$. The ground and surface waters represent regolith and/or fissure aquifers in various (magmatic, sedimentary and metamorphic) bedrocks in the Sudetes Mts. (SW Poland). The solubility of HAS_B in natural waters was calculated using the method proposed by Schneider et al. (Polyhedron 23:3185–3191, 2004). Results confirm usefulness and validity of this method. The HAS_B solubility obtained from the field data ($\log K_{sp} = -44.7 \pm 0.58$) is lower than it was estimated ($\log K_{sp} = -40.6 \pm 0.15$) experimentally (Schneider et al. Polyhedron 23:3185–3191, 2004). In the waters studied the equilibrium with HAS_B is maintained at pH above 6.7 and at $[Al^{3+}] \leq 10^{-10}$. Silicon activity ($\log[H_4SiO_4]$) ranges between –4.2 and –3.4. Due to the calculation method used, the K_{sp} mentioned above cannot be considered as a classical solubility constant. However, it can be used in the interpretation of aluminium solubility in natural waters. The HAS_B has solubility lower than amorphous $Al(OH)_3$, and higher than proto-imogolite. From water samples that are in equilibrium with respect to HAS_B, the solubility product described by the reaction, $Al_2Si_2O_5(OH)_4 + 6H^+ \leftrightarrow 2Al^{3+} + 2H_4SiO_4 + H_2O$ is calculated to be $\log K_{sp} = 14.0$ (±0.7) at 7°C.

Keywords Hydroxyaluminosilicate · Water chemistry · Natural water · The Sudetes Mts. · Poland

1 Introduction

Silicon and aluminium are—besides oxygen—the most abundant elements of the continental lithosphere (Si—27.7%, Al—8.1%). Aqueous geochemistry of both elements differs, and in most natural waters, like in low-temperature fresh ground water or surface

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water, silicon concentration considerably exceeds that of aluminium. In ground water, silicon concentration is usually 10^{-4} –10^{-3} mol/l, whereas aluminium is 10^{-7}–10^{-5} mol/l (Hem 1989; Svarcev 1998). In near-surface environments, research into aluminium geochemistry focuses mainly on soils, and soil and surface waters due to environmental concerns, e.g., acidification effects, aluminium toxicity to plants and aqueous organisms, or soil fertility. Investigations on silicon usually deal with hydrological or weathering problems. Dissolved silicon is considered as a good measure of weathering processes and water circulation conditions. Its concentration can afford useful information on water turnover, and is used to estimate outflow components.

Different factors and processes—like equilibrium with solid phases, adsorption onto solids, kinetics of reactions, steady state between weathering release and hydrological removal—can control Al and Si concentrations in shallow ground water and surface water. The role of different phases, like halloysite and/or microcrystalline gibbsite (Hem et al. 1973), metastable aluminosilicates (Pačes 1973, 1978; Neal et al. 1986; Neal and Williams 1988), $Al(OH)_3$ forms (Sullivan and Cosby 1998), or mixed phase amorphous $Al(OH)_3$ and aluminosilicate (Gustafsson et al. 1998) was proposed to explain aluminium and/or silicon activity in water.

Amorphous and/or short-range ordered phases, like hydroxyaluminosilicate colloids or allophane/imogolite minerals play an important role during weathering transformation of primary silicates. The former ones can also affect the chemistry of natural water. For instance, activity of dissolved silicon affects formation of hydroxyaluminosilicate solute and solid species, and reduces aluminium toxicity (e.g., Exley et al. 1994, 1997). Hydroxyaluminosilicates (HAS) are formed by the reaction of silicic acid (H_4SiO_4) with $Al(OH)_{3(s)}$ (Exley and Birchall 1992, 1993). Amongst hydroxyaluminosilicates, initially proto-imogolite, $(HO)_3Al_2O_3SiOH$ was recognised. Formation of proto-imogolite and its role in the soil was presented in numerous works (e.g., Farmer et al. 1977, 1979, 1980; Farmer and Fraser 1982; Farmer and Lumsdon 1994). The solubility of proto-imogolite was given by Lumsdon and Farmer (1995) and Pokrovsky et al. (1996). Two types of hydroxyaluminosilicates, named HAS_A and HAS_B, of Al/Si ratio of 2:1 and 1:1, respectively, were described (Doucet et al. 2001b). The HAS_A can form in solutions in which $[Al] \geq [H_4SiO_4]$ and HAS_B only when Si concentration exceeds the Al one. The hydroxyaluminosilicate HAS_A refers to proto-imogolite. The formation, stoichiometry, structure and methods of identification of both HASs were documented by Doucet et al. (2001a, b), Exley et al. (2002), Strekopytov and Exley (2006) and Strekopytov et al. (2006). The investigation by Schneider et al. (2004) provided the solubility constant of synthetic HAS_B, estimated experimentally. It might be important in the prediction of aluminium and silicon activity, because the Si/Al ratio in most natural waters favours the formation of hydroxyaluminosilicate HAS_B.

The chemistry of ground and surface waters from area composed of various bedrocks in the Sudetes Mts. (SW Poland) has been investigated. The waters studied mainly occur in rocks composed of low-reactive mineral phases, and are affected by acid atmospheric deposition. In Poland, the Sudetes Mts. is one of the areas with the highest acid deposition loads. Field hydrochemical data were used to demonstrate whether the HAS_B solubility estimated experimentally (Schneider et al. 2004) corresponds to that found in natural environments.

2 Methods

The natural waters were sampled at headwater mountainous catchments in central and eastern parts of the Sudetes Mts. (SW Poland) (Fig. 1). Different (magmatic, sedimentary,

Fig. 1 Location of the areas studied. Explanation: 1—areas of ground and surface water investigations

and metamorphic) bedrocks occur in the areas studied (Table 1). Ground water samples were mainly taken in springs, partly also in shallow piezometers installed in the regolith. In total, 574 chemical analyses of waters are presented, 525 analyses after investigations by the author and 49 analyses after Przychodzka (2004).

Field measurements included pH, temperature and specific electric conductivity. All water samples were filtered in the field by 0.45 μm cellulose-nitrate membranes and stored in LDPE (Nalge) bottles. Chemical composition of water was determined by ICP–AES (Ca, Mg, Na, K, Fe, Mn, Sr, Ba), spectrophotometric (SO_4, F, PO_4, NO_3, DOC) and volumetric (HCO_3, Cl) methods. Silicon concentration was determined by the classical silicomolybdate spectrophotometric method and aluminium usually was determined by the ETA–AAS method. The detection limit of the ETA–AAS method used for aluminium determination was 1 μg/l, with the precision (RSD%), for samples of Al concentration below 50 μg/l and above 50 μg/l, being better than 2% and 1%, respectively. Aluminium in about fifty samples was determined using ICP–AES. The detection limit of silicon method is 0.01 mg/l SiO_2 with a standard deviation ±0.45 mg/l SiO_2. Concentration of dissolved organic carbon (DOC) usually was below the detection limit (DL = 0.5 mg/l) of the analytical method that was used. Actually, only in a few samples the DOC

Table 1 Bedrock lithology and amount of water samples

Bedrock	Lithology	Amount of samples	
		Ground water	Surface water
Plutonic rocks	Granodiorites, granites with syenodiorites, monzonites, tonalites	33	–
Volcanic rocks	Rhyolites, rhyolitic tuffs, trachyandesites	197	46
Sedimentary rocks	Greywackes, conglomerates, sandstones, siltstones, mudstones, clay shales	248	28
Metamorphic rocks	Mainly gneisses, with mica schists, graphite schists, quartzites, migmatites, hornfelses, mylonites	22	–
	Total	500	74

concentration was slightly above the detection limit. Consequently, organic carbon was not included in the speciation calculating.

The PHREEQC code (Parkhurst and Appelo 1999) was used for speciation calculation. Amongst Al-silicate complexes, well recognised reaction of $AlH_3SiO_4^{2+}$ complex formation ($Al^{3+} + H_4SiO_4^0 = AlH_3SiO_4^{2+} + H^+$) was included, with $\log K_{25} = -2.30$ (Spadini et al. 2005) and $\Delta H_r^o = 66.6$ kJ/mol (Pokrovsky et al. 1996).

Chemical analyses of ground and surface waters have been used for studying hydroxyaluminosilicate HAS_B solubility, experimentally obtained by Schneider et al. (2004). Species (H^+, Al^{3+}, H_4SiO_4) activities were used for calculating ion activity quotient (IAQ) of the hydroxyaluminosilicate (HAS_B) according to the method that was proposed by Schneider et al. (2004).

3 Outline of Ground and Surface Water Chemical Composition

The ground waters represent regolith and/or fissure aquifers in the short turnover time zone of the hydrogeological system. Ground and surface waters are mineralized slightly. Their total dissolved solids (TDS) usually do not exceed 300 mg/l. Surface waters show chemical features similar to ground water that occur in the area composed of the same bedrock. Mineral reactivity results in differences of water chemistry and the wide range of pH (between 4.05 and 8.39; Table 2). Sulphate, bicarbonate, calcium and magnesium ions dominate in the chemical composition.

Aluminium concentration in waters between 3.7×10^{-8} mol (1 μg/l) and 1.37×10^{-4} mol (3.7 mg/l) was found. Usually, it ranges between 10^{-7} mol/l and 10^{-5} mol/l

Table 2 Characteristics of ground and surface water chemistry (after Dobrzyński 1997; Przychodzka 2004, and unpublished data). Concentrations in mg/l. Size—574 samples

Parameter	Arithmetic mean	Median	Standard deviation	Minimum	Maximum
pH	5.56[a]	6.51[a]	8.34E–06[b]	4.05	8.39
T [°C]	6.92	6.50	2.717	0.2	21.8
SiO_2	11.79	11.5	3.990	3.7	26.9
Ca	28.32	23.5	14.298	4.06	74.2
Mg	6.61	5.5	4.674	0.1	37.03
Na	4.75	4.4	2.242	1.7	30.02
K	3.59	2.2	3.546	0.2	21.2
Al	0.133	0.019	0.410	0.001	3.70
Fe	0.06	0.02	0.184	<0.01	2.74
Mn	0.082	0.0131	0.356	<0.001	3.66
HCO_3	43.55	23.00	48.333	0.05	238.26
SO_4	43.24	39.00	20.905	7.00	209.9
Cl	10.54	10.30	3.863	0.50	50.7
F	0.19	0.17	0.145	0.01	1.46
PO_4	0.22	0.07	0.861	<0.01	13.72
NO_3	17.02	16.38	10.311	0.89	113.83

[a] pH calculated as a –log of the mean and median [H^+] molar concentration, respectively

[b] Molar concentration

(Fig. 2). Silicon concentration shows smaller differences, from 6.16×10^{-5} mol/l (3.7 mg/l SiO_2) to 4.48×10^{-4} (26.9 mg/l SiO_2), usually between 1×10^{-4} mol/l and 3×10^{-4} mol/l.

4 Results

Speciation calculations included complexes of aluminium with different ligands, like hydroxyl, fluoride, sulphate, and silicate groups. In waters studied Al–OH and Al–F complexes dominate. Their role strongly depends on water pH. The amount of Al–OH and Al–F complexes changes from near 1% to above 99% of total aluminium. Al–OH complexes present a minimum concentration at pH 5.5–6.0, and the maximum one at pH above 8.0. Al–F complexes behave inversely. The amount of Al–silicate complexes does not exceed 1% of total aluminium, and is the highest at pH between 5.0 and 6.5. Al–sulphate complexes range from 20 to 40% at pH between 4 and 5, to 10^{-6}% at pH near 8.

The formation of hydroxyaluminosilicates needs the prior formation of $Al(OH)_3$ solid. In the waters studied, formation of $Al(OH)_3$ solids appears greatest at pH above 6.0 (Fig. 3). Schneider et al. (2004) tried to determine the solubility of $HAS_{B(s)}$ to compare it with other solid phases that could control Al solubility, like $Al(OH)_3$ forms. Aluminium solubility in equilibrium with the HAS_B relates to $[H_4SiO_4]$, and reduces at higher H_4SiO_4 concentrations. Dissolution of the HAS_B was found to be non-congruent with actually no Al being released, and HAS_B turned out to be less soluble than $Al(OH)_{3(s)}$. To take into account this fact and non-stoichiometric dissolution of HAS_B, Schneider et al. (2004) proposed an unconventional method and solubility expression. The HAS_B was treated as a hydroxide of aluminosilicate with the following hypothetical dissolution equation:

$$Al_2Si_2O_5(OH)_4 \leftrightarrow Al_2O^{4+} + 2SiO_2 + 4OH^- \quad (1)$$

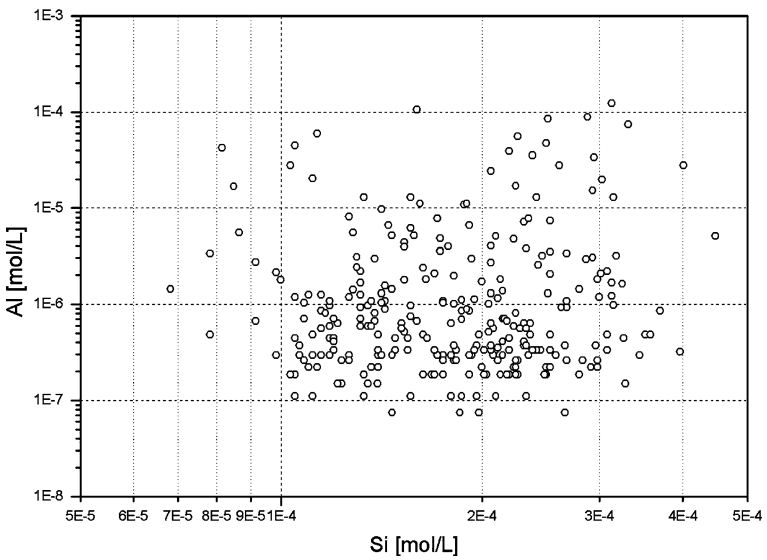

Fig. 2 Aluminium concentration versus silicon concentration in water. Size—574 samples

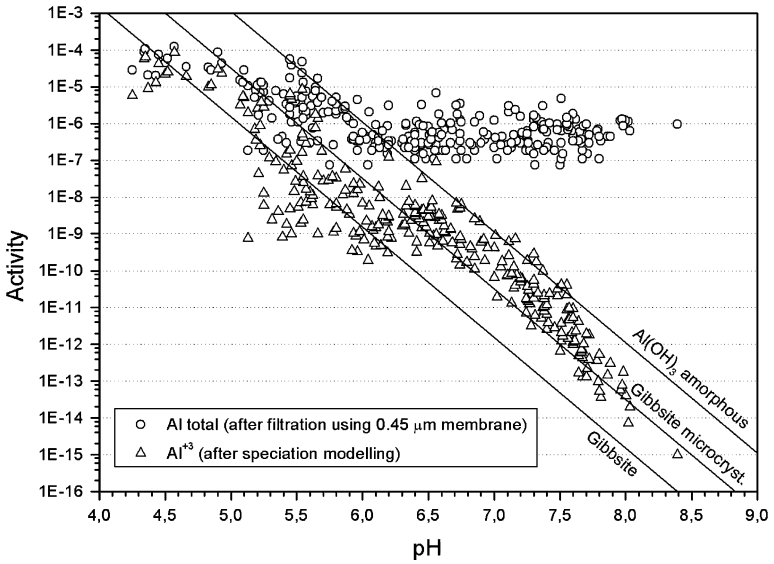

Fig. 3 Activity of Al total and Al^{3+} versus pH in water compared with the solubility of $Al(OH)_3$ forms, at 7°C. Solubility curves for $Al(OH)_3$ forms plotted after solubility constant for gibbsite ($logK_{25}$ = 8.11), microcrystalline gibbsite ($logK_{25}$ = 9.35), $Al(OH)_3$(a) ($logK_{25}$ = 10.8) (after Nordstrom et al. 1990), calculated using the van't Hoff equation

and the HAS_B solubility expression could be written as:

$$K_{sp}HAS_B = [Al_r]^2[H_4SiO_4]^2[OH^-]^4 \quad (2)$$

where, Al_r is the so-called fast reacting aluminium estimated by the fluorescent morin–Al complex method (Browne et al. 1990). Fast reacting Al corresponds to monomeric and other rapidly equilibrating species of Al that are biologically available (e.g., Exley and Birchall 1996). Theoretical dissolution products were substituted by dissolution products measured experimentally. This attempt has been validated by the application of results of quasi-equilibrium solubility lab experiments carried out at different H_4SiO_4 concentrations (from 0 μmol/l to 2000 μmol/l). Thereafter, the solubility of HAS_B was estimated on $logK_{sp}HAS_B$ = –40.6 (±0.15), at 20°C and I = 0.1 mol/l (Schneider et al. 2004).

This non-standard calculation was used to testify validity of the estimation to explain Al and Si geochemistry in the natural waters studied. Calculation of the ion activity quotient (IAQ) of hydroxyaluminosilicate HAS_B was based on species (Al^{3+}, H_4SiO_4) activities and water pH measured in the field.

The IAQ of HAS_B calculated varies within a wide range, however, logIAQ values between –44.0 and –45.5 prevail. The logIAQ value plotted versus pH and Al^{3+} activity shows regular patterns (Figs. 4, 5). The steep part of both plots probably is an artefact of the mathematical relation between the IAQ and products activity. The artefact effect is more easily visible in Fig. 5 than in Fig. 4 because Al^{3+} activity is mainly governed by pH, and hydrolysis of each Al^{3+} ion uses three protons. The flat parts of patterns show that in some geochemical environments IAQ actually remains quasi-constant. It indicates that the equilibrium with HAS_B might be maintained. Waters from different (magmatic, sedimentary or metamorphic) bedrocks present the same IAQ pattern. Solubility product for

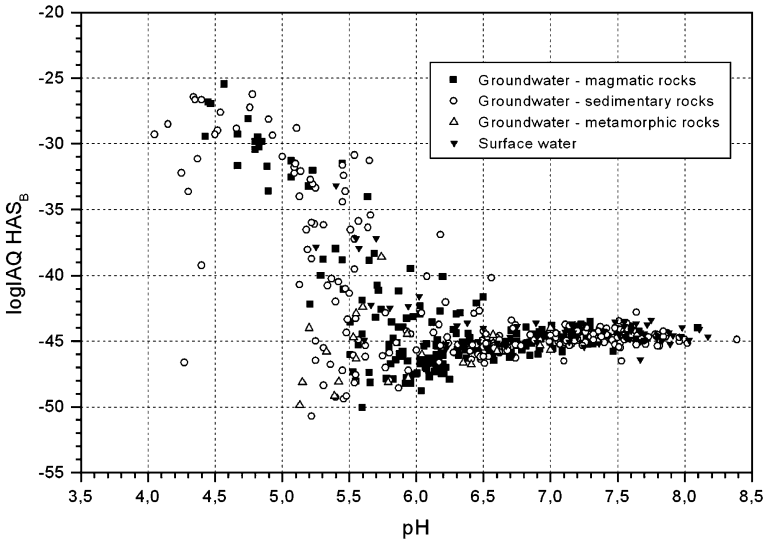

Fig. 4 Ion activity quotient of HAS_B versus pH

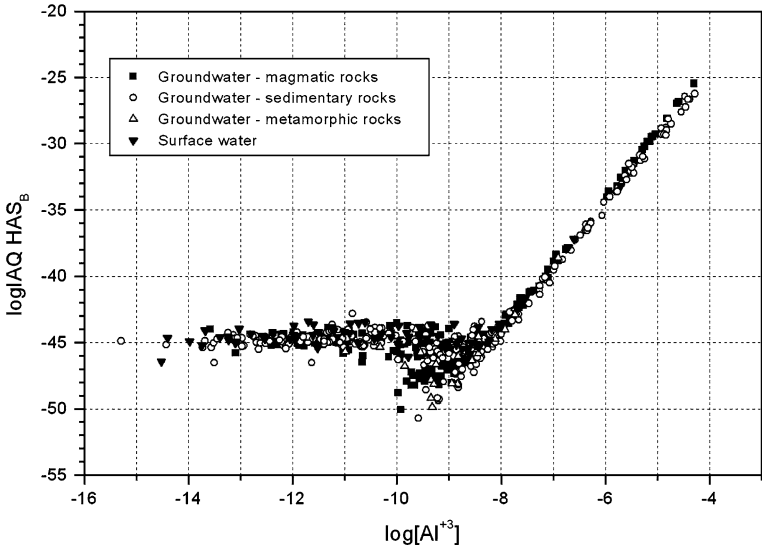

Fig. 5 Ion activity quotient of HAS_B versus Al^{3+} activity

HAS_B is quasi-constant at pH above 6.7 (Fig. 4) and $\log[Al^{3+}] \leq -10$ (Fig. 5). Exley and Birchall (1993) indicated that minimum solubility of HAS is at pH near 5.5, i.e. around one unit lower than solubility of $Al(OH)_{3(s)}$. A similar pattern with the minimum HAS solubility at pH $\approx$ 5.5 was found in waters studied (Fig. 4). About 188 water samples of the total 574 studied have $\log[Al^{3+}] \leq -10$. Waters with $\log[Al^{3+}] \leq -10$ also are of pH $\geq$ 6.7. Only one of 188 samples has pH slightly lower (pH = 6.58) than 6.7. It was assumed that

chemistry of this sub-population (188 water samples) reflects the conditions of equilibrium with hydroxyaluminosilicate HAS_B.

Differences in Al solubility control between waters with pH below 6.7 and waters with pH above 6.7 result from Al species distribution. Al–OH complexes dominate at pH above 6.7. The change in solubility control of metastable aluminosilicate phases at pH around 6.7 was noted by Dobrzyński (2005, 2006b) in ground water from different sedimentary and volcanic bedrocks. Probably, the pH 6.7 can be regarded as an important transition point of aluminium solubility control.

The IAQ of samples with $\log[Al^{3+}] \leq -10$ plotted versus $[H_4SiO_4]$ also shows a regular pattern (Fig. 6). The set of water samples with $\log[Al^{3+}] \leq -10$ shows a wide data range for logIAQ HAS_B from –46.5 to –43 (usually between –45.5 and –44), while $\log[H_4SiO_4]$ ranges less than an order of magnitude (from –4.2 to –3.4). The scatter of data for logIAQ HAS_B is probably caused by: (1) cumulating effects of analytical uncertainties, and (2) partial equilibration of some waters with respect to the HAS_B.

5 Discussion

The K_{sp} of HAS_B given by Schneider et al. (2004) cannot be treated as a conventional solubility constant, but it can be used to identify aluminium solubility control in natural environments.

The arithmetic mean of logIAQ HAS_B for water samples with $\log[Al^{3+}] \leq -10.0$ equals –44.73 (SD = 0.58; N = 188). Linear fit for waters that are assumed to be in equilibrium with respect to the HAS_B is slightly slanted (Fig. 7).

The solubility of HAS_B found in natural waters (logIAQ HAS_B = –44.73 ± 0.58) is lower than it was estimated experimentally by Schneider et al. (2004) ($\log K_{sp}$ HAS_B = –40.6 ± 0.15). There can be a few reasons for this difference. Solubility products (K_{sp}) referenced are surely overestimated because the fast-reacting aluminium [Al_r] instead of [Al^{3+}] was used in calculations. Another reason is that the laboratory experiment (op. cit.)

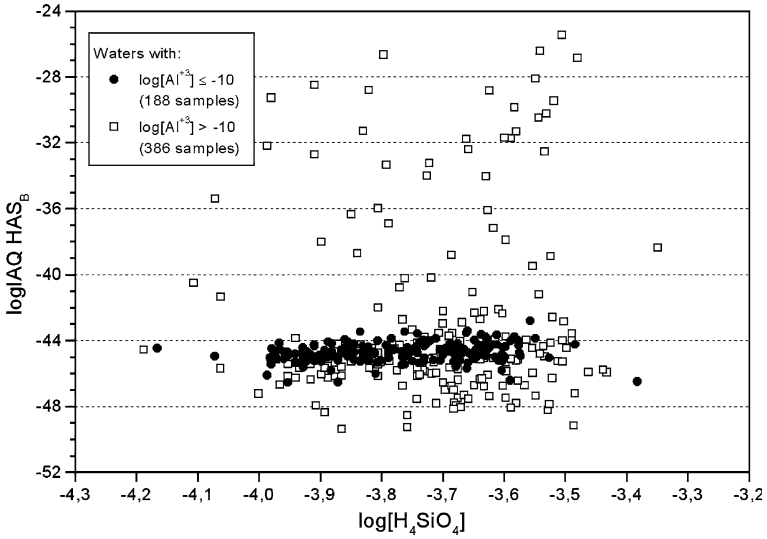

Fig. 6 Ion activity quotient of HAS_B versus H_4SiO_4 activity

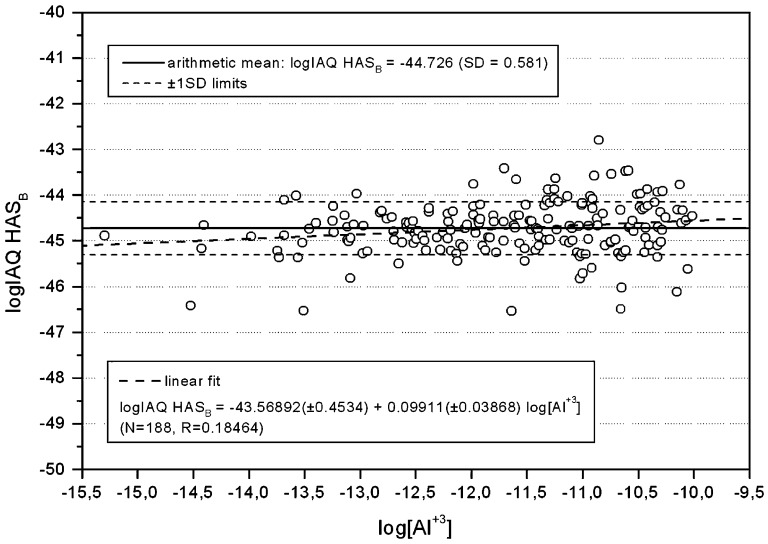

Fig. 7 Ion activity quotient of HAS_B versus Al^{3+} activity in waters with $\log[Al^{3+}] \leq -10$

was carried out at the temperature of 20°C while the mean temperature of the natural waters was nearly 7°C (Table 2).

Actually, it is likely that logIAQ HAS_B in the waters studied might also be slightly overestimated. Distribution of aluminium species is governed by water pH, the ligands present and the formation of complexes. Aluminium forms stable complexes with different ligands, like hydroxyl, sulphate, fluoride or organic groups. Dissolved organic carbon (DOC) was below the detection limit and was not included in speciation model, which led to the increased $[Al^{3+}]$ and thus influenced solubility products estimated. On the other hand, filtering by 0.45 μm membrane filters could leave some part of Al species in the filter, and lead to underestimation of Al solute concentration and solubility products. Amongst reasons mentioned above, probably the most important is the effect of the difference between $[Al_r]$ and $[Al^{3+}]$.

Results indicate that conditions of equilibrium with hydroxyaluminosilicate HAS_B existed in waters studied. The equilibrium with the HAS_B is likely to be maintained within a wide range of aqueous chemistry, i.e., at Al^{3+} activity below 10^{-10} and at pH above 6.7. In "equilibrium" water samples $[Al^{3+}]$ vary between 10^{-15} and 10^{-10}, and silicic acid, between $\log[H_4SiO_4] = -4.2$ and $\log[H_4SiO_4] = -3.4$.

The dissolution equation of HAS_B could be written as

$$Al_2Si_2O_5(OH)_4 + 6H^+ \leftrightarrow 2Al^{3+} + 2H_4SiO_4^0 + H_2O \quad (3)$$

The solubility expression from this equation is

$$\log K_{sp}\ HAS_B = 2\log\left[Al^{3+}\right] + 2\log\left[H_4SiO_4^0\right] + 6pH \quad (4)$$

and relation between $[Al^{3+}]$ and pH is

$$\log\left[Al^{3+}\right] = 0.5\log K_{sp}\ HAS_B - \log\left[H_4SiO_4^0\right] - 3pH \quad (5)$$

The IAQ of HAS_B in waters with $\log[Al^{3+}] \leq -10$ (188 samples) shows a regular pattern if it is plotted versus activity of products—pH, Al^{3+}, H_4SiO_4 (Figs. 4–6). Equilibrium with HAS_B should also give regular pattern for $[Al^{3+}]$ versus pH (Fig. 8). A linear fit of the scatter plot gives the function of $\log[Al^{3+}] = 13.16(\pm1.09) - 3.32(\pm0.15)$ pH ($R = -0.85854$, $N = 188$). The solubility line of HAS_B should have a gradient of –3 (Eq. 5). Within the 99% confidence limits function of $\log[Al^{3+}] = x - 3$ pH with x parameter varied between 10.7 and 10.8 is included. At the average x value ($x = 10.75$), hypothetical solubility line of HAS_B is $\log[Al^{3+}] = 10.75 - 3$ pH.

Comparing HAS_B solubility with the solubility of $Al(OH)_3$ it appears that HAS_B controls $[Al^{3+}]$ lower than amorphous $Al(OH)_3$ and higher than gibbsite. A scatter plot suggests that Al^{3+} activity might also be controlled by $Al(OH)_3$ solid solubility near microcrystalline gibbsite. It could be the case if the IAQ of HAS_B did not show regularity when plotted versus $[H_4SiO_4]$ (Fig. 6). However, the pattern in Fig. 8 is clearly coincidental—the HAS_B may control $[Al^{3+}]$ slightly higher than microcrystalline gibbsite (plotted after solubility data given by Nordstrom et al. 1990).

Assuming that HAS_B controls aluminium activity, the solubility constant $\log K_{sp}$ of HAS_B equals $21.5 + 2\log[H_4SiO_4]$ (see Eq. 4). The value of 21.5 was obtained from Eq. 4 and from value of $x = \log[Al^{3+}] + 3\text{pH} = 10.75$ (see Fig. 8). Silicic acid activity in waters with $\log[Al^{3+}] \leq -10$ ranges between $10^{-4.17}$ and $10^{-3.38}$ (Fig. 6), and the mean value is $10^{-3.77}$. Then, $\log K_{sp,7}$ HAS_B for the Eq. 4 equals 14.0 (±0.7). This rough estimation has semi-quantitative character and should be verified by the followed experiments. Solubility of HAS_B depends on pH, $[Al^{3+}]$ and $[H_4SiO_4]$. Experiments described by Schneider et al. (2004) have shown that aluminium activity at the equilibrium state also depends on $[H_4SiO_4]$. It yields difficulty in HAS_B solubility estimation.

On the basis of solubility curves (Fig. 9), it is shown that hydroxyaluminosilicate HAS_B is more soluble than proto-imogolite, which is a HAS_A type colloid. The estimated solubility of HAS_B ($\log K_{sp} \approx 14.0$ at 7°C) is higher than that of proto-imogolite. For the

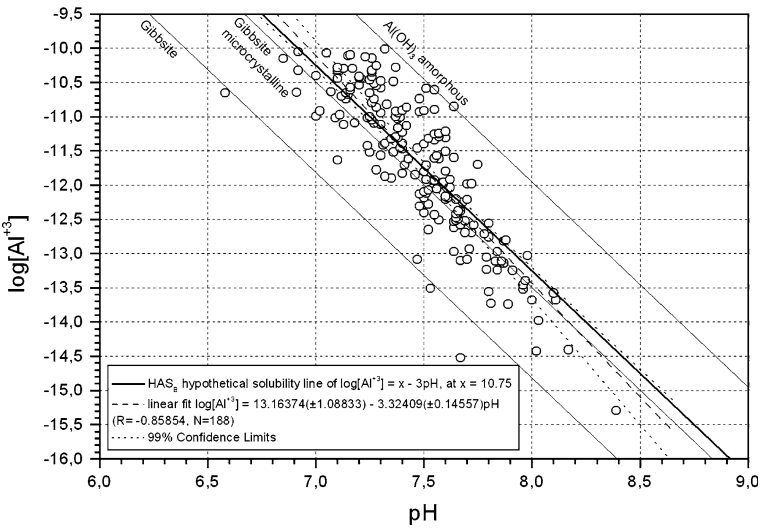

Fig. 8 Activity of Al^{3+} versus pH in waters of $\log[Al^{3+}] \leq -10$ compared to solubility of $Al(OH)_3$ forms, at 7°C. Solubility curves for $Al(OH)_3$ forms plotted as in Fig. 3

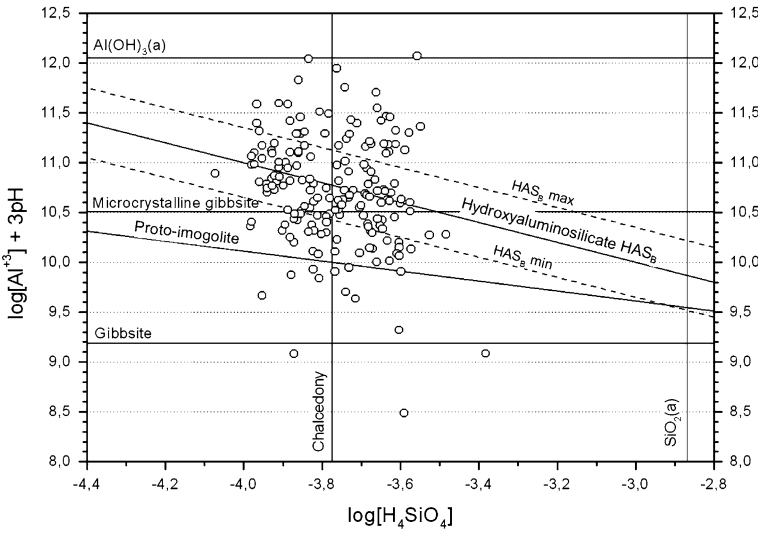

Fig. 9 Two-ion parameter $\log[Al^{3+}] + 3pH$ versus $\log [H_4SiO_4]$ in waters with $\log[Al^{3+}] \leq -10$ (size—188 samples). Solubility lines for $Al(OH)_3$ and SiO_2 forms plotted at 7°C, after solubility constant for gibbsite ($\log K_{25} = 8.11$), microcrystalline gibbsite ($\log K_{25} = 9.35$), and $Al(OH)_3(a)$ ($\log K_{25} = 10.8$) calculated using the van't Hoff equation. Solubility constant, $\log K_7$ for chalcedony and amorphous SiO_2 calculated using the analytical expression after Nordstrom et al. (1990). Proto-imogolite solubility line at 7°C plotted for the reaction $0.5Al_2SiO_3(OH)_4 + 3H^+ = Al^{3+} + 0.5H_4SiO_4^0 + 1.5H_2O$ ($\log K_{25} = 7.02$, $\Delta H_r^o = -96.8$ kJ/mol) after Lumsdon and Farmer (1995). HAS_B solubility line for the reaction $Al_2Si_2O_5(OH)_4 + 6H^+ = 2Al^{3+} + 2H_4SiO_4^0 + H_2O$ ($\log K_7 = 14.0 \pm 0.7$) with uncertainty of solubility plotted

reaction concerning the proto-imogolite ($0.5Al_2SiO_3(OH)_4 + 3H^+ = Al^{3+} + 0.5\ H_4SiO_4^0 + 1.5H_2O$) solubility constant, $\log K_{sp}$ equals 8.109 at 7°C (calculated using the van't Hoff equation after data ($\log K_{25} = 7.02$, $\Delta H_r^o = -96.8$ kJ/mol) by Lumsdon and Farmer 1995). In most natural waters that present assumed equilibrium with HAS_B, this solid should be more stable than amorphous $Al(OH)_3$. This is in agreement with a study by Schneider et al. (2004). The HAS_B is metastable with respect to crystalline gibbsite in all waters, and microcrystalline gibbsite at $[H_4SiO_4] < 10^{-3.5}$ (Fig. 9). Both gibbsite forms might control Al concentration lower than HAS_B. However, hydroxyaluminosilicates dissolve incongruently by forming amorphous $Al(OH)_3$ precipitate (op. cit.), and initially, aluminium concentration in a solution will be much higher than saturation state with respect to gibbsite. The crystalline gibbsite can be formed as a result of ageing of $Al(OH)_3$ precipitates only at the conditions of permanent deficiency of silicic acid in an aqueous environment.

In low-temperature ground and surface waters, dissolved silicon commonly occurs at concentrations close to the solubility of chalcedony, even when the mineral is absent in the bedrock. This also found in the waters studied (Fig. 9). Solubility of the HAS_B may affect silicon activity in waters, and it is conceivable that commonly noted equilibrium with chalcedony could be the chance convergence. Silicon activity in many natural waters might be controlled by the equilibrium of incongruent dissolution of HAS_B by $Al(OH)_{3(s)}$ formation. The reaction was noted by Schneider et al. (2004) during lab experiments. Effects of incongruent reaction between aluminosilicates and $Al(OH)_3$ forms on the silicon activity in natural waters were suggested by Dobrzyński (2006a).

Formation of hydroxyaluminosilicate HAS_B demands silicon concentrations to exceed aluminium one in the solution. All waters studied fulfil the condition, but only about 33% of samples (188 samples) showed equilibrium with respect to the HAS_B. It is clear that pH of the water plays the crucial role.

6 Conclusions

Interpretation of a wide set of natural water chemistry data from the hydroxyaluminosilicate HAS_B solubility viewpoint indicates its importance for controlling aqueous aluminium activity. Results also confirm the usefulness of the method proposed by Schneider et al. (2004) for the estimation of HAS_B solubility.

The HAS_B can form only in solutions in which silicon concentration exceeds the aluminium. These conditions are common in natural waters. However, results suggest that equilibrium with HAS_B could be maintained only in waters with pH ≥ 6.7 at low Al^{3+} activity ($<10^{-10}$).

Incongruent dissolution of HAS_B with formation of $Al(OH)_{3(s)}$ noted during lab experiments (Schneider et al. 2004) is also likely in natural environments. Equilibrium of the reaction between HAS_B and $Al(OH)_{3(s)}$ forms might be responsible for controlling silicic acid activity in natural waters.

The hydroxyaluminosilicate HAS_B has a composition similar to allophane minerals but surely cannot be considered as their precursor phase. The equilibrium with HAS_B was found in natural waters with pH above 6.7. Allophanes form preferentially in regoliths at pH between 5.0 (5.5) and 6.8 (Parfitt and Kimble 1989; Wada 1989; Ugolini and Dahlgren 1991). The HAS_B controls aluminium activity in waters studied at pH higher than that needed for formation and stability of allophanes.

The presence of HAS_B in natural waters should be the subject of further research, because of the role that hydroxyaluminosilicates are likely to play in controlling of Al and Si in natural waters.

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