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Reversible control of aqueous aluminum and silica during the irreversible evolution of natural waters

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Abstract—Primary aluminosilicates are transformed at low temperature into a sequence of metastable and thermodynamically stable secondary minerals by an irreversible process. The aqueous concentrations in the associated solution may continuously change during the process or they may be maintained constant through hydrodynamic or chemical steady-state mechanisms or through chemical equilibrium with a reversible metastable solid.

Disequilibrium indices calculated for 152 natural waters and experimental solutions show that the solutions are unsaturated with amorphous aluminum hydroxide, microcrystalline gibbsite, amorphous silica and amorphous aluminosilicate, and they are supersaturated with gibbsite and kaolinite. The disequilibrium index for halloysite varies widely from unsaturation to supersaturation.

Only the index for the reversible metastable cryptocrystalline aluminosilicate whose composition is pH dependent is very close to zero indicating saturation. The index varies in a narrow range. This, supported by electron micrographs and the results of X-ray fluorescence spectroscopy presented by other authors, suggests that this metastable solid, and not the secondary aluminosilicate minerals, controls the concentrations of alumina and silica in natural waters.

INTRODUCTION

IT HAS BEEN PROPOSED that the concentrations of dissolved alumina and silica in natural waters are controlled by partial equilibria between solution and clay minerals and/or gibbsite (e.g. HELGESON, 1968; HELGESON *et al.*, 1969; FRITZ and TARDY, 1974, 1976; FRITZ, 1975; MICHARD and FOULLAC, 1974; FOULLAC *et al.*, 1977) or by equilibrium between solution and halloysite and/or microcrystalline gibbsite (HEM *et al.*, 1973). However, when the compositions of cold natural waters are compared with their calculated equilibrium compositions with respect to the minerals, significant departures from the equilibria are apparent (PAČES, 1970, 1972, 1973). Another possible controlling mechanism may be the adsorption of dissolved silica and aluminum on silica or silicate surfaces (BECKWITH and REEVE, 1963; MCKEAGUE and CLINE, 1963; STÖBER, 1967; ILER, 1973). However, the adsorption of aluminum is probably not very effective in controlling the aqueous concentration because of the high affinity of hydroxyl ions towards Al^{3+} ion and a rapid polymerization to form hydroxocomplexes (SMITH and HEM, 1972). While both the equilibrium with respect to well defined minerals and adsorption operate in $Al_2O_3-SiO_2-H_2O$ system under favorable conditions, it is proposed here, that a reversible equilibrium between solution and a metastable cryptocrystalline aluminosilicate of varied composition explains best the observed concentration of alumina and silica in natural waters at low temperatures (0–25°C). This reversible mechanism operates during the irreversible dissolution of primary minerals and the irreversible formation of thermodynamically

stable secondary minerals. The secondary minerals may have reached different stages of crystallinity (PETROVIC 1976, Fig. 1) and morphology (HENMI and WADA, 1976). The experimental studies of the effect of adsorbed aluminum on the solubility of amorphous silica in water (ILER, 1973) supports the hypothesis that silica and aluminum in solution combine to form a metastable aluminosilicate that is less soluble than either oxide alone. This solid behaves reversibly. Part of the aluminum and silicon are removed from solution irreversibility, because they are fixed in newly formed minerals.

THEORY

An example of a typical irreversible process at low temperatures, such as rock weathering, is illustrated in Fig. 1. During this process a primary mineral whose mass in moles is M_p dissolves and M_r moles of a reversible metastable mineraloid, M_r , moles of an irreversible metastable secondary mineral and M_s moles of a thermodynamically stable secondary mineral are produced. The portions of the chemical components remaining in the water are m_1, m_2, \dots, m_n . The total irreversible process consists of a sequence of reactions whose rate constants are k_1, \dots, k_6 . In general, the molarities in solution change during the irreversible process in which $dM_p/dt < 0$ and $dM_s/dt > 0$. However, concentrations of some components can be maintained constant due to a hydrodynamic steady state, chemical steady state and chemical thermodynamic equilibrium.

Let us consider a general sequence of reactions in Fig. 1. The rates of the reactions are controlled by

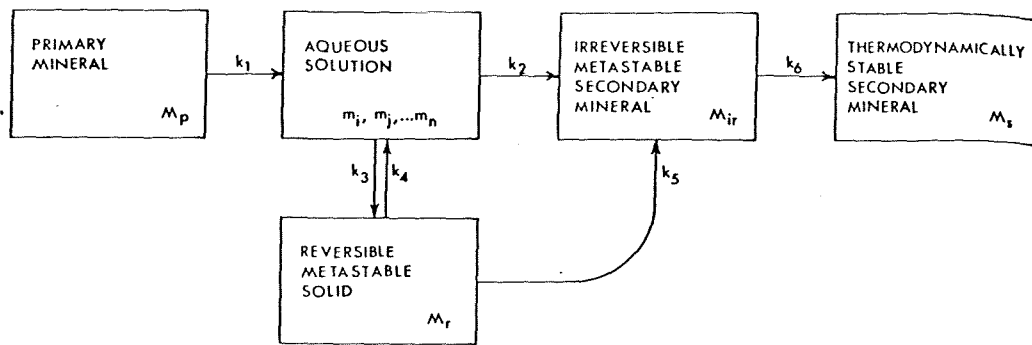


Fig. 1. Irreversible transformation of a primary mineral into secondary minerals and the position of a reversible metastable solid in a natural water system. M_p , M_r , M_{tr} , M_s are the extensive masses of the primary mineral and the reversible, irreversible metastable and thermodynamically stable secondary phases respectively. m_i , m_j , m_n are molarities of participating chemical components in aqueous solution.

the concentrations in solution. Their kinetic orders with respect to a dissolved species i are $\alpha_{1,i} \dots \alpha_{4,i}$.

The general rate law of reaction r with respect to the aqueous species i is

$$R_{r,i} = \left(\frac{dm_i}{dt} \right)_r = k_r \prod_{j=1,i}^n m_j^{\alpha_{r,j}} \quad (1)$$

where $j = 1, 2 \dots i \dots n$ includes all the aqueous species participating in the reaction r .

The hydrodynamic steady state is defined by the condition

$$\frac{\partial m_i}{\partial t} = 0 = R_{1,i} + R_{4,i} - R_{2,i} - R_{3,i} - \nabla v m_i \quad (2)$$

The hydrodynamic dispersion and diffusion are neglected in eq. (2), v is the mean linear velocity of water in the x , y and z directions and ∇ is space-gradient operator

$$\frac{\partial}{\partial x} + \frac{\partial}{\partial y} + \frac{\partial}{\partial z}$$

The chemical steady state is maintained under the following conditions

$$v = 0 \quad (3)$$

$$\frac{dm_i}{dt} = 0 = R_{1,i} - R_{2,i} \quad (4)$$

and

$$R_{4,i} > R_{3,i} \quad (5)$$

or

$$R_{4,i} < R_{3,i} \text{ and } R_{5,i} > R_{3,i} - R_{4,i} \quad (6)$$

so that

$$M_r = 0 \quad (7)$$

The equilibrium concentration of a component i in solution is maintained under the following conditions

$$R_{1,i} \ll R_{4,i} \text{ and } R_{2,i} \ll R_{3,i} \quad (8)$$

$$\frac{dm_i}{dt} = 0 = R_{4,i} - R_{3,i}; \quad (9)$$

for a reversible process

$$\frac{R_{3,i}}{R_{4,i}} = 1 \quad (10)$$

and after substituting eq. (1) into eq. (10)

$$\prod_{j=1,i}^n m_j^{(\alpha_3 - \alpha_4)_j} = \frac{k_4}{k_3} = K, \quad (11)$$

here $(\alpha_3 - \alpha_4)_j$ is the stoichiometric coefficient of the component j in the reaction between the solution and the reversible metastable solid; K is the equilibrium molarity product identical to the equilibrium constant for ideal behavior.

The equilibrium control by the reversible metastable phase during an irreversible process permits changes in the molar quantities of the solid phases as follows:

$$\frac{dM_p}{dt} = -v_{1,i} R_{1,i} \quad (12)$$

$$\frac{dM_r}{dt} = v_{1,i} R_{1,i} - v_{2,i} R_{2,i} - v_{5,i} R_{5,i} \quad (13)$$

$$\frac{dM_{tr}}{dt} = v_{2,i} R_{2,i} + v_{5,i} R_{5,i} - v_{6,i} R_{6,i} \quad (14)$$

$$\frac{dM_s}{dt} = v_{6,i} R_{6,i} \quad (15)$$

where $v_{r,i}$ are the stoichiometric coefficients of a component i in the r th reaction.

The natural system can reach a steady state in which the irreversible process continues while both the aqueous concentrations and the molar quantities of the metastable phases are maintained constant.

In a closed system this steady-state condition is expressed by means of eq. (13) and (14)

$$v_{1,i} R_{1,i} - v_{2,i} R_{2,i} - v_{5,i} R_{5,i} = 0 \quad (16)$$

$$v_{2,i} R_{2,i} + v_{5,i} R_{5,i} - v_{6,i} R_{6,i} = 0 \quad (17)$$

from which

$$v_{1,i} R_{1,i} - v_{6,i} R_{6,i} = 0 \quad (18)$$

or

$$\frac{dM_s}{dt} = -\frac{dM_p}{dt} = v_{6,i} R_{6,i} = v_{1,i} R_{1,i} \quad (19)$$

The steady state in an open system is expressed by means of eq. (2)

$$R_{1,i} + R_{4,i} - R_{2,i} - R_{3,i} - \nabla v m_i = 0 \quad (20)$$

in combination with eqs. (16) and (17)

$$R_{1,i}(1 - v_{1,i}) - R_{2,i} + v_{6,i}R_{6,i} + R_{4,i} - R_{3,i} - \nabla v m_i = 0. \quad (21)$$

Since $R_{3,i} = R_{4,i}$ for the reversible process and $R_{2,i} = R_{1,i}$, providing that the steady-state composition has been reached, eq. (21) has the form

$$v_{6,i}R_{6,i} - v_{1,i}R_{1,i} - \nabla v m_i = 0. \quad (22)$$

After substitution of eqs. (12) and (15) into eq. (22)

$$\frac{dM_s}{dt} = \nabla v m_i - \frac{dM_p}{dt} = \nabla v m_i + v_{1,i}R_{1,i} \quad (23)$$

and

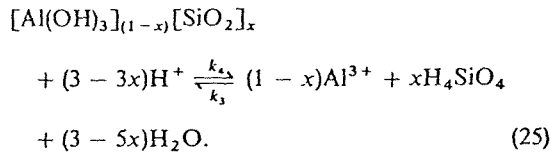
$$\frac{dM_p}{dt} = \nabla v m_i - \frac{dM_s}{dt} = \nabla v m_i - v_{6,i}R_{6,i}. \quad (24)$$

This formal treatment of the irreversible process leads to several conclusions. First, the formation of a thermodynamically stable phase does not necessarily control the concentration of a dissolved component in natural water through a chemical equilibrium. The controlling mechanisms may be the hydrodynamic steady state (eq. 2), the chemical steady-state (eq. 4) and a chemical equilibrium with a reversible metastable solid (eqs. 8, 9, 10, 11). Second, the control of the solution composition by a reversible reaction with a metastable phase does not preclude the formation and existence of irreversible metastable or stable mineral phases in the system. Third, the formation of the secondary solids can proceed independently of the equilibrium composition of the solution. Consequently, it cannot be assumed a priori that the evolution of the chemical composition of a natural solution can be calculated from the data on primary and secondary solids using the stoichiometry of reactions and their equilibrium constants (HELGESON 1968; FRITZ, 1975) unless it is proved that all the secondary solids behave reversibly and the rates of the irreversible dissolution are proportional to the masses of the primary solids. The evolution of the system is time dependent and the composition of the solution depends on the percolation velocity of water and the rate constants of the irreversible reactions as well as on the equilibrium constants of the reversible reactions.

The reliable data required to make the model represented by Fig. 1 quantitative are scarce. This paper is a partial contribution to the quantitative problem and deals with the reversible metastable solid which apparently controls the concentrations of aluminum and silica in natural waters during their irreversible evolution.

NATURE OF THE METASTABLE ALUMINOSILICATE

Early experiments by MATTSON (1928) and further elaboration by PARKS (1967) showed that the X-ray amorphous aluminosilicates which precipitate from aqueous solutions containing aluminum and silica have a neutral surface at given pH of the solution. This pH is called the point of zero charge (PZC). The PZC of pure hydrous alumina is at pH 9.2 and the PZC of pure silica is at pH 1.8 (PARKS, 1967). The compositions of the aluminosilicate which precipitated at various pH in the Mattson's experiments varied roughly linearly between pure silica at pH 1.8 and pure hydrous alumina at pH 9.2. This led PAČES (1973) to an assumption, that the reaction which controls the concentration of silica and alumina in cold waters is



The straight line in a plot x vs pH between the end points $(x, \text{pH}) = (0, 9.2)$ and $(1, 1.8)$ correlates reasonably well with Mattson's experimental points (PARKS, 1967, Fig. 10), hence

$$x = 1.24 - 0.135 \text{ pH}. \quad (26)$$

The activity quotient of the reaction (25) is

$$Q_{as} = \frac{a_{Al^{3+}}^{(1-x)} a_{H_4SiO_4}^x}{a_{H^+}^{(3-3x)}}; \quad (27)$$

assuming that a reversible equilibrium is maintained between the solution and the aluminosilicate, $Q_{as} = K_{as}$, where K_{as} is the equilibrium constant of reaction (25).

Table 1. Regression lines and correlation coefficients between pH of solutions and logarithms of the activity quotient of reaction (25): $\log Q_{as} = a + b \text{ pH}$

Data set	n	r	a	b	log Q_{as}	
					pH=1.8	pH=9.2
Synthetic solutions ¹	56	0.997	-6.251	1.671	-3.24	9.13
Natural waters from granitic rocks ²	37	0.957	-3.268	1.203	-1.10	7.80
Natural waters from granites ³	23	0.946	-9.117	2.058	-5.41	9.82
Natural waters from gneisses ⁴	23	0.936	-4.070	1.343	-1.65	8.29
Solutions of feldspars ⁵	13	0.880	-10.400	2.473	-5.95	12.35
11 samples	152	0.984	-5.891	1.588	-3.03	8.72
Linear plot between the solubility products of amorphous alumina and silica			-5.7	1.68	-2.7	9.7

¹HEM *et al.*, 1973; ²FETH *et al.*, 1964; ³FOUILLAC *et al.*, 1976; ⁴PAČES *et al.*, in prep.; ⁵BUSENBERG and CLEMENCY, 1967; BUSENBERG, written communication.

EQUILIBRIUM CONSTANT OF THE DISSOLUTION OF THE METASTABLE ALUMINOSILICATE

If the amorphous aluminosilicate were an ideal solid solution of amorphous silica and alumina, the equilibrium constant would be a combination of solubility products of silica ($K_s = a_{H_4SiO_4} = 10^{-2.7}$, KRAUSKOPF, 1956) and alumina ($K_a = a_{Al^{3+}} \cdot a_{H^+}^3 = 10^{9.7}$, SILLÉN, 1964) with the solubility product of the aluminosilicate [eq. (27)]. At equilibrium

$$Q_{as} = K_{as} = \frac{a_{Al^{3+}}^{(1-x)} \cdot a_{H_4SiO_4}^x}{a_{H^+}^{(3-3x)}} = K_s^x K_a^{(1-x)} = 10^{9.7-12.4x} \quad (28)$$

Substituting eq. (26) into eq. (28)

$$K_{as} = 10^{-5.7 + 1.68 \text{ pH}} \quad (29)$$

Six sets of experimental laboratory and field data on total aqueous aluminum, silica, pH, ionic strength and temperature were selected to calculate the values of Q_{as} given by eq. (27). They include 36 acid and 20 basic synthetic solutions of silica and aluminum aged from a few months to longer than four years (HEM *et al.*, 1973, Tables 3, 4), 37 filtered natural waters from granitic rocks in the Sierra Nevada, USA (FETH *et al.*, 1964, Table 1), 23 filtered natural waters from the granitic rocks in the Truyera River Basin, France (FOUILLAC *et al.*, 1976), 23 filtered natural waters from gneisses in the Trnávka River Basin, Czechoslovakia (PAČES *et al.*, in prep.) and 13 final solutions resulting from the dissolution of 9 feldspars in various initial solutions (BUSENBERG and CLEMENCY, 1976; BUSENBERG, 1976, written communication). The data are tabulated and entered into the files of NAPS*. All the samples were filtered through 0.1 μm membrane (FETH *et al.* (1964) used a 0.45 μm filter) prior to aluminum analysis and the pH of the natural waters was measured in the field. The activity of silica was assumed to be equal to its molarity. The activity of Al^{3+} was calculated using the equations in the Appendix. The calculated activities of Al^{3+} are included in the NAPS Document.

The base 10 logarithms of the activity quotients, $\log Q_{as}$, calculated for all the data are plotted against the pH of the solutions in Fig. 2. The regression lines and correlation coefficients for the individual data sets and for all data are given in Table 1. The values of $\log Q_{as}$ for the PZC of the end members i.e. for pH 1.8 and 9.2 are included in Table 1. These values should correspond to the activity products of silica and alumina respectively under the conditions of the individual sets of data.

The $\log Q_{as}$ -pH lines for the sets of experimental and field data deviate from the line connecting the

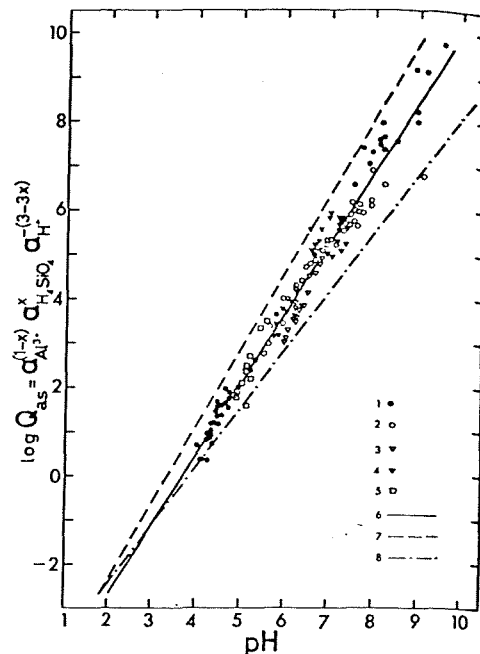
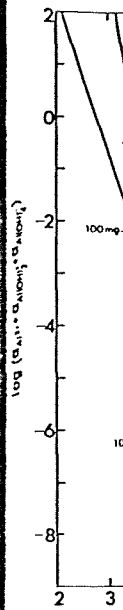


Fig. 2. The linear correlation between pH and logarithm of activity product $a_{Al^{3+}}^{(1-x)} \cdot a_{H_4SiO_4}^x / a_{H^+}^{(3-3x)}$ in experimental solutions and natural water samples. 1, Aged synthetic solutions of alumina and silica (HEM *et al.*, 1973); 2, subsurface water from granitic rocks in Sierra Nevada, U.S.A. (FETH *et al.*, 1964); 3, surface and subsurface water from gneisses in the Bohemian Massif, Czechoslovakia (PAČES *et al.*, in prep.); 4, subsurface and surface waters from granitic rocks of the Margaride Massif, France (FOUILLAC *et al.*, 1976); 5, final solutions resulting from the experimental dissolution of feldspars (BUSENBERG and CLEMENCY, 1976; BUSENBERG, written communication); 6, regression line for all the data points; 7, linear plot between the solubility products of amorphous alumina and silica at the pH values of their points of zero charge; 8, linear plot between the solubility products of microcrystalline gibbsite and amorphous silica at the pH values of their points of zero charge (PZC of microcrystalline gibbsite is at pH 11, SMITH, 1969).

solubility product of amorphous silica ($10^{-2.7}$) and alumina ($10^{9.7}$). This deviation may be explained by a hypothesis that the aluminum atoms after random precipitation assume coordinated positions during aging while silicon atoms maintain their random distribution (PAČES, 1973). Therefore, the solubility of the alumina end member in the aluminosilicate can vary while the solubility of the silica end member should remain similar to those of amorphous silica. The present results indicate that the solubility product of alumina decreases from theoretical $10^{9.7}$ down to $10^{9.13}$ in aged synthetic solutions, $10^{8.29}$ and $10^{7.80}$ in natural waters but increases in the solutions resulting from the feldspars. The decrease may be caused by the incomplete octahedral and/or tetrahedral arrangements of aluminum observed with X-ray fluorescence spectroscopy by HENMI and WADA (1976) in natural allophane and by HEM *et al.* (1973) in electron micrographs of aged laboratory precipitates.

The solubility product of the silica end member increases in two data sets from the theoretical value $10^{-2.7}$ up to $10^{-1.1}$ and decreases in three data sets



3. The equilibrium species whose composition is given in Fig. 2. The solubility product of the end members is given in Table 1. The activity of Al^{3+} was calculated using the equations in the Appendix. The calculated activities of Al^{3+} are included in the NAPS Document.

This solubility product changes with the composition of the end members.

A solubility product in terms of $a_{Al^{3+}} \cdot a_{H^+}^3$ for 10, 50, and 100 mg/l. The solubility product is given in eq. (26), (27) and (28). $Q_{as} = K_{as}$.

The total activity of the end members in the aluminosilicate is given by

$$a_{Al^{3+}} \cdot a_{H^+}^3$$

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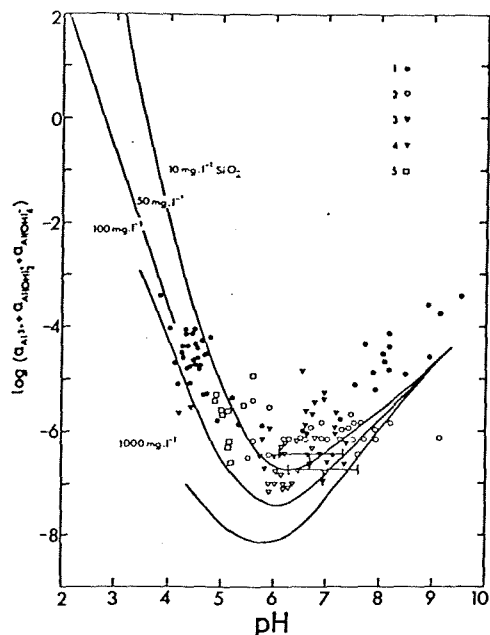


Fig. 3. The equilibrium sum of the activities of aluminum aqueous species with respect to the reversible aluminosilicate whose composition is determined by eq. (26) and its solubility product by eq. (30). The symbols are the same as given in Fig. 2. \bar{pH} represents mean pH and standard deviation for samples with aluminum concentrations below analytical sensitivity. The theoretical equilibrium curves for silica concentrations of 10, 50, 100 and 1000 mg.l⁻¹ are calculated using eqs. (31) and (32).

down to 10^{-5.95}. The increase in the product is difficult to explain but is probably caused by the scatter of the data which affect the regression lines. The decrease may be due to both the nonideal behavior of the solid and to substitution of iron for silica (McKYES *et al.*, 1974). In spite of all these uncertainties, the experimental and field data indicate that the concentration of silica and aluminum in natural waters may be controlled by a chemical equilibrium with a nonideal solid solution called here reversible aluminosilicate. Its mean solubility product given by the regression line for all the samples is

$$K_{ras} = 10^{-5.89 + 1.59 \text{ pH}} \quad (30)$$

This solubility product, however, should be expected to change during aging and by the content of impurities.

A solubility diagram of the reversible aluminosilicate in terms of the total active aluminum ($a_{Al(\text{Total})} = a_{Al^{3+}} + a_{Al(OH)_2} + a_{Al(OH)_4}$) vs pH is presented in Fig. 3 for 10, 50, 100 and 1000 mg.l⁻¹ of dissolved SiO₂. The solubility curves were calculated employing eqs. (26), (27) and (30) for the equilibrium condition $Q_{ras} = K_{ras}$. This yields

$$\log a_{Al^{3+}} = \frac{2.308 - \frac{5.891}{\text{pH}} - 0.41 \text{ pH} - \frac{1.24}{\text{pH}} - 0.138 \log a_{H_4SiO_4}}{0.135 - \frac{0.24}{\text{pH}}} \quad (31)$$

The total active aluminum is calculated using the constants in the Appendix

$$a_{Al(\text{Total})} = a_{Al^{3+}} \left(1 + \frac{10^{-9.76}}{a_{H^+}^2} + \frac{10^{-22.07}}{a_{H^+}^4} \right) \quad (32)$$

The experimental and field data on total dissolved aluminum were recalculated in the form of the total active aluminum and are plotted in Fig. 3. The major feature of the model is the minimum solubility which shifts slightly with the increasing concentrations of silica from pH 6.35 at 10 mg.l⁻¹ SiO₂ to pH 6.1 at 100 mg.l⁻¹ SiO₂. The experimental and field data are in majority higher than predicted by the model. This is caused by the independent assumption on the composition of the reversible aluminosilicate expressed by eq. (26). If the PZC of the alumina in the solid solution is higher than 9.2 the solubility curves will shift to lower total active aluminum. The higher PZC (~ 11 pH) was measured on microcrystalline gibbsite (Smith, 1969).

DEPARTURES FROM EQUILIBRIA WITH VARIOUS Al, Si MINERALS AND SOLIDS

If the suggested reversible aluminosilicate controls the concentrations of aluminum and silica in natural waters then the waters should be in chemical equilibrium with the solid. However, they may depart from equilibrium with other solids or minerals. This can be tested by comparing the disequilibrium indices

$$I_p = \log \frac{Q_p}{K_p}$$

for the solubility products of various solid phases p . An aqueous solution is supersaturated with p if $I_p > 0$, it is unsaturated if $I_p < 0$ and it is in chemical equilibrium if $I_p = 0$.

The solids which may control the aluminum and silica concentrations in natural waters, the expressions for their activity quotients and their equilibrium constants are given in table 2.

The arithmetic means of the disequilibrium indices for all the data sets are summarized in Table 3. The variation of the indices is expressed by their standard deviations in Table 4.

By studying Tables 3 and 4 it is obvious that all or the majority of the solutions are unsaturated with amorphous Al(OH)₃, microcrystalline gibbsite, amorphous SiO₂ and amorphous aluminosilicate [Al(OH)₃]_(1-x) [SiO₂]_(x). The solutions are supersaturated with gibbsite and kaolinite so that their precipitation is probable and will be irreversible. Some solutions are supersaturated and others are saturated or unsaturated with halloysite which was identified by HEM *et al.* (1973) in the secondary product during

the aging of their synthetic solutions. The disequilibrium indices for the postulated reversible aluminosilicate, I_{ras} , are close to zero in majority of data sets.

Table 2. Activity quotients, Q_p , and equilibrium constants, K_p , for 25°C for minerals and solids which may control the concentrations of Al and Si in natural waters

Solid	Symbol for P	Activity quotient Q_p	Equilibrium constant K_p /25°C/	Source
Amorphous Al(OH) ₃	aa	$\frac{a_{Al}^{3+}}{a_H^+}$	10 ^{9.7}	Sillén, 1964
Microcrystalline gibbsite	mg	ditto	10 ^{9.36}	Hem and Roberson, 1973
Gibbsite	g	ditto	10 ^{8.22}	Smith, 1971
Amorphous silica	s	$a_{H_4SiO_4}$	10 ^{2.7}	Krauskopf, 1956
Halloysite	h	$\frac{a_{Al}^{3+} a_{H_4SiO_4}^2}{a_{H^+}^6}$	10 ^{11.28}	Hem et al., 1973
Kaolinite	k	ditto	10 ^{6.74}	Robie and Waldbaum, 1968
Amorphous /ideal/ aluminosilicate Al(OH) ₃ /1-x/ SiO ₂ /x/ x	aas	$\frac{a_{Al}^{1-x} a_{H_4SiO_4}^x}{a_{H^+}^{3-3x}}$	10 ^{-5.7+1.68pH}	Pačes, 1973
Reversible /nonideal/ aluminosilicate Al(OH) ₃ /1-x/ SiO ₂ /x/	ras	ditto	10 ^{-5.89+1.59pH}	this paper

Table 3. Mean values of the disequilibrium indices with respect to the solids in Table 2

Data set	number of samples	I _{aa} amor- phous alumina	I _{mg} micro- crystal- line gibbsite	I _g gib- bsite	I _s amor- phous silica	I _h hal- loysite	I _k kaolin- ite	I _{aas} amor- phous aluminosilicate	I _{ras} rever- sible aluminosilicate
Acid synthetic solutions ¹	36	-0.98	-0.62	0.50	-0.42	-0.06	4.48	-0.59	0.01
Basic synthetic solutions ¹	20	-0.51	-0.17	0.97	-0.89	0.04	4.58	-0.61	0.32
Waters from Sierra Nevada ²	37	-0.91	-0.57	0.57	-0.76	-0.61	3.93	-0.95	-0.10
Waters from Truyere River Basin ³	23	-0.92	-0.58	0.56	-1.21	-1.52	3.02	-1.04	-0.27
Waters from Trnávka River Basin ⁴	23	-0.58	-0.24	0.90	-0.77	0.01	4.55	-0.68	0.13
Solutions of feldspars ⁵	13	-0.58	-0.24	0.90	-0.67	0.23	4.77	-0.63	0.03

¹HEM *et al.*, 1973; ²FETH *et al.*, 1973; ³FOUILLAC *et al.*, 1976; ⁴PAČES *et al.*, in prep.; ⁵BUSENBERG and CLEMENCY, 1973

The near zero values of I_{ras} are not an independent proof of the existence of the solid because they are predetermined by the fact that the equilibrium solubility product is pH dependent and was fitted to the selected data. On the other hand, the smallest scatter of I_{ras} together with its near-zero values is a more significant support for the reversible control. A direct indication that an amorphous solid precipitates very fast in such systems are the high resolution micrographs presented by JONES and VEHARA (1973). The micrographs show that such a solid exhibits a coat-of-paint effect on the crystalline aluminosilicate surfaces. BUSENBERG (written communication, 1977) found experimental evidence that the reversible aluminosili-

cate controls aluminum and silica at higher concentrations of silica while halloysite and microcrystalline gibbsite control aluminum concentration at low to moderate concentration of silica.

CONCLUSION

This paper does not offer a definitive proof that the aluminosilicate of variable composition does exist. Nevertheless, the hypothetical solid which interacts with water according to reaction (27), whose composition is pH dependent according to eq. (26) and whose activity product is given by eq. (30) has the best predictive power for the behavior of silica and aluminum in natural waters within the framework of the model.

Table 4. Standard deviations of the disequilibrium indices from the mean values in Table 3

Data set	I _{aa} , I _{mg} , I _g	I _s	I _h , I _k	I _{aas}	I _{ras}
Acid synthetic solutions	0.50	0.32	0.98	0.13	0.13
Basic synthetic solutions	0.43	0.33	1.10	0.37	0.37
Waters from Sierra Nevada	0.62	0.16	1.19	0.49	0.43
Waters from Truyere River Basin	0.31	0.12	0.60	0.19	0.20
Waters from Trnávka River Basin	0.64	0.10	1.38	0.45	0.44
Solutions of feldspars	0.39	0.49	1.18	0.31	0.32

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in Fig. 1 considering the common aluminosilicate minerals.

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APPENDIX

THE EQUATIONS for the solubility calculation:

$$m_{\text{Al(Total)}} = \frac{a_{\text{Al}^{3+}}}{\gamma_3} + \frac{a_{\text{Al(OH)}^2+}}{\gamma_2} + \frac{a_{\text{Al(OH)}_2^+}}{\gamma_1} + \frac{a_{\text{Al(OH)}_3^0}}{\gamma_1}$$

$$\frac{a_{\text{Al}^{3+}}}{a_{\text{Al(OH)}_2^+ \cdot a_{\text{H}^+}^2} = 10^{5.00} \quad \text{HEM et al. (1973)}$$

$$\frac{a_{\text{Al}^{3+}}}{a_{\text{Al(OH)}_2^+ \cdot a_{\text{H}^+}^2} = 10^{9.76} \quad \text{HEM et al. (1973)}$$

$$\frac{a_{\text{Al}^{3+}}}{a_{\text{Al(OH)}_3^0 \cdot a_{\text{H}^+}^3} = 10^{22.07} \quad \text{HEM et al. (1973)}$$

$$\log \gamma_z = -Az^2 \left(\frac{\sqrt{I}}{1 + \sqrt{I}} - 0.3I \right)$$

where a_i is activity of species i , $m_{\text{Al(Total)}}$ is total molarity of aluminum in solution, γ_z is the activity coefficient, z is the absolute value of the ionic charge, I is ionic strength, $A = 0.4883 + 7.38 \times 10^{-4}t + 2.723 \times 10^{-6}t^2$ where t is temperature in °C.