

# Monomeric versus mixed monomeric-polymeric models for aqueous aluminium species: Constraints from low-temperature natural waters in equilibrium with gibbsite under temperate and tropical climate

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(Accepted for publication April 13, 1989)

## Abstract

Bourrié, G., Grimaldi, C. and Régeard, A., 1989. Monomeric versus mixed monomeric-polymeric models for aqueous aluminium species: Constraints from low-temperature natural waters in equilibrium with gibbsite under temperate and tropical climate. In: K. Grönvold (Guest-Editor), Water-Rock Interaction. Chem. Geol., 76: 403-417.

Spring waters from Fougères (Armorican Massif), Margeride and Mont Lozère (Central Massif, France), groundwaters, flood waters and recession waters from Sinnamary (French Guyana) were collected in small watersheds on granitic or metamorphic rocks. Leaching experiments were also conducted on soils from Fougères. Waters were analyzed for major elements and Al, in order to check the control on dissolved Al by gibbsite, kaolinite, imogolite and other possible secondary minerals, and of different models concerning the speciation of Al in aqueous solution. The results show that: (1) the single monomeric model hitherto widely used leads to large supersaturations with respect to gibbsite, kaolinite and even in some cases to amorphous Al-hydroxide, and to a great scattering of data; (2) the polymeric-monomeric model leads to values of IAP (ionic activity product) in agreement with control by gibbsite; (3) total dissolved Al decreases at constant pH and temperature and gets closer to the solubility curve of gibbsite in deeper springs in Fougères and in recession waters in Guyana as contrary to shallower springs in Fougères and flood waters in Guyana. This allows us to propose a new reaction scheme for Al precipitation: as pH increases to > 5, in a first step a polymeric species forms, and in a second step gibbsite crystallization from monomeric species proceeds, coupled with depolymerization. This picture is consistent with classical data, if one considers no more polymerization to occur by an edge-to-edge mechanism, but by a face-to-face mechanism. The polymeric form thus appears to constitute a pool buffering Al activity. IAP of gibbsite is well correlated with temperature, but uncertainty on the solubility product of gibbsite is amplified by the polymer-monomer relationship, which limits the use of the relation obtained as a low-temperature geothermometer.

## 1. Introduction

Aluminium precipitation in surface conditions is usually dealt with in terms of solid/solution equilibria. As Al occurs in solution in a variety of species and as its solubility is very low in neutral conditions, studies are not very

numerous despite the importance of Al and its abundance. Data for the stability and the stoichiometry of Al species in waters are not sound, and the assumption is most often made that only monomeric hydroxo ions exist. However, in recent years an increasing number of studies has shown that polymeric species exist, and this

was previously used to compute IAP (ionic activity product) for gibbsite, imogolite, kaolinite and various 2:1 clay minerals (Bourrié, 1981).

The purpose of this paper is to check the validity of monomeric vs. monomeric-polymeric models for Al aqueous speciation in natural waters under different conditions of pH and temperature, both under temperate and tropical climate.

## 2. Aqueous species of aluminium

Aluminium aqueous species are still a matter of controversy. The aluminium aquo ion in acidic medium is octahedrally coordinated and thus can be written  $\text{Al}(\text{H}_2\text{O})_6^{3+}$ . The existence of a secondary hydration shell has even been demonstrated to account better for the total hydration energy of the  $\text{Al}^{3+}$  cation (Veillard, 1977, 1978); so that the hydration number 6 for the first hydration shell appears well established, as linear combination of atomic orbitals-molecular orbitals-self-consistent field (LCAO-MO-SCF) calculations show that (Veillard, 1977):

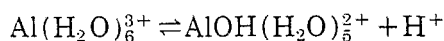
“when the hydration number exceeds 6, it is energetically more favorable for the additional water molecule to form a second hydration shell than to insert in the first shell”

Agreement is general as regards the dominance at  $\text{pH} > 5.0$  in standard conditions of the first hydrolyzed species,  $\text{AlOH}(\text{H}_2\text{O})_5^{2+}$  and the existence in basic conditions of the aluminate ion  $\text{Al}(\text{OH})_4^-$  that are in equilibrium with  $\text{Al}^{3+}$ . Stepwise hydrolysis conception led to considering  $\text{Al}(\text{OH})_2^+$  and  $\text{Al}(\text{OH})_3^0$  (omitting coordinated water molecules) as intermediate species. However, the very existence of those species is questionable as their consideration does not improve the fitting of the models to experimental data from gibbsite solubility measurements (Kittrick, 1966; Shih Singh, 1976; May et al., 1979; Sarazin, 1979) or from potentiometric titrations. Those species are thus either ignored for the sake of simplicity or con-

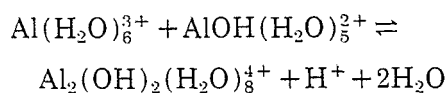
sidered for logical assumption of stepwise hydrolysis, this leading of course to slightly different sets of pK-values. For example, two different sets of data were shown by May et al. (1979) to fit their data equally well, according to the consideration of  $\text{Al}(\text{OH})_3^0$  or not. Sarazin (1979) stated that the existence of those intermediate species depends on the conditions of obtention of the solution:  $\text{AlOH}^{2+}$  would form when equilibrium is attained from supersaturation as pH increases, whereas  $\text{Al}(\text{OH})_2^+$  would form when equilibrium is attained from undersaturation. The strong tendency of  $\text{Al}(\text{OH})_2^+$  to polymerize, with formation of bridging OH-containing clusters (Hem and Roberson, 1967; Hem, 1970; Smith and Hem, 1972) is certainly responsible for the lack of accurate data concerning monomeric species. Though polymeric species were earlier considered (Johansson et al., 1960; Johansson, 1963), their stoichiometry and stability could not be established on the sole basis of solubility and potentiometric measurements and only monomeric species were considered in most studies (Michard et al., 1979; Sarazin, 1979; Grimaldi, 1981). This will be designated hereafter as the *monomeric model*.  $^{27}\text{Al}$  NMR (nuclear magnetic resonance) studies provide some evidence for the existence of a polymeric form such as  $\text{Al}_{13}\text{O}_4(\text{OH})_{24}(\text{H}_2\text{O})_{12}^{7+}$  (Akitt et al., 1972) or as  $\text{Al}_{13}\text{O}_4(\text{OH})_{28}(\text{H}_2\text{O})_8^{3+}$  (Bottero et al., 1980), along with a possible dimeric form  $\text{Al}_2(\text{OH})_2^{4+}$ . Because the consideration of the dimer was discouraged by Hsu (1977), as it would be unstable due to strong electrostatic repulsion between the two  $\text{Al}^{3+}$  ions, it was not considered in a previous work (Bourrié, 1981), and the polymeric form proposed by Bottero et al. (1980) was solely considered in addition to the monomeric ones, this constituting then the *monomeric-polymeric model*. Recent refinements of  $^{27}\text{Al}$  NMR studies (Akitt and Farthing, 1981a, b, c, d; Akitt et al., 1981, 1985; De Jong et al., 1983; Akitt and Gessner, 1984; Akitt and Milic, 1984; Akitt and Elders, 1985) more

firmly establish the existence of the polymeric form  $\text{Al}_{13}\text{O}_4(\text{OH})_{24}^{7+}$  and of the dimer  $\text{Al}_2(\text{OH})_2^{4+}$  (omitting coordinated water molecules). Akitt and Farthing (1981d) consider that hydrolysis equilibria are relatively quickly attained between  $\text{Al}^{3+}$ , the dimeric and polymeric forms, the latter form undergoing slow transformation in a variety of pathways. The following reaction scheme can be proposed from Akitt and coworkers' results; which consists of three main steps:

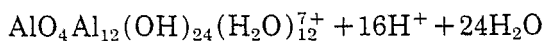
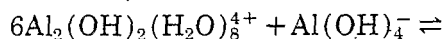
(1) Hydrolysis of  $\text{Al}^{3+}$ :



(2) Dimerization:



(3) Polymerization:



The two first steps can be considered as fast equilibrating reactions, whereas the third step is partly at least irreversible, as Akitt et al. (1981) observed that the polymeric form is not readily destroyed upon acidification of the solution. This could be due to the necessity of protonating the polymer up to 10  $\text{H}^+$ 's per molecule, in order to destroy simultaneously four bridging OH's, before extracting a single octahedrally coordinated Al. Formation of the polymer by direct nucleation of dimers on a central tetrahedrally coordinated Al, such as  $\text{Al}(\text{OH})_4^-$ , was suggested by Akitt and Farthing (1981, part 4). However, it must be noted that NMR distinguishes neither between different acid monomeric forms, nor between more or less protonated polymeric forms so that the proportion of OH's and coordinating water molecules in the polymer is not accurately known. It is not necessarily constant anyway, as proton transfer between the polymer and the surrounding water molecules is likely to be much faster than polymerization and depolymerization reac-

tions, so that it may be considered as a polyacid, which allowed Bottero et al. (1980, 1982) to modify the charge to fit their potentiometric data, though their fit was approximate. Moreover, as NMR is relatively very insensitive, all the experiments were conducted in concentrated solutions, so that this reaction scheme cannot be checked directly in dilute solutions with the present measurement techniques. Potentiometric titrations of Al were performed in 0.6 M NaCl in presence of gallic acid (Öhman and Sjöberg, 1981, 1982), carbonic acid (Öhman and Forsling, 1981), *o*-diquinones (Öhman et al., 1983), salicylic acid (Öhman and Sjöberg, 1983a), citric acid (Öhman and Sjöberg, 1983b) and pyrocatechol (Öhman and Sjöberg, 1983c). The existence of the dimer was confirmed by its ability to give ternary complexes with gallic acid and carbonate, but its concentration was very low even in the pure  $\text{Al}_2\text{O}_3\text{-H}_2\text{O}$  system, and Öhman and coworkers favored the consideration of the monomers, a trimer  $\text{Al}_3(\text{OH})_4^{5+}$  and the polymer  $\text{Al}_{13}\text{O}_4(\text{OH})_{24}^{7+}$ . The ternary complexes  $\text{Al}_2(\text{OH})_2\text{CO}_3^{2+}$  and  $\text{Al}_3(\text{OH})_4\text{HCO}_3^+$  were shown to give a better fit to potentiometric data, but their calculations led to the conclusion that they were negligible in dilute waters (alkalinity  $< 5 \text{ meq l}^{-1}$ ; pH 4–8;  $p_{\text{CO}_2} < 5 \text{ kPa}$ ), as are the conditions of our samples. However, as the thermodynamic data they derived are relative to 0.6 M NaCl, they should be corrected to zero ionic strength. This implies in turn the need to compute the activity coefficients of polymeric forms and to assign to them values for the closest approach parameter  $a^0$ , which was not made by Öhman and coworkers. As the electric charge proposed for the polymer by them is 7+, the activity coefficient is extremely low and its value is very sensitive to the value of  $a^0$  chosen: with the value of  $a^0$  proposed by Bottero et al. (1980),  $a^0 = 19.7$ , one obtains in 0.6 M NaCl  $\log \gamma = -3.19$ , using the Debye-Hückel extended law ( $A_\gamma = 0.5095$ ;  $B_\gamma = 0.3284$ ;  $C = 0.041$  for NaCl), whereas with  $a^0 B_\gamma = 1$  (Davies equa-

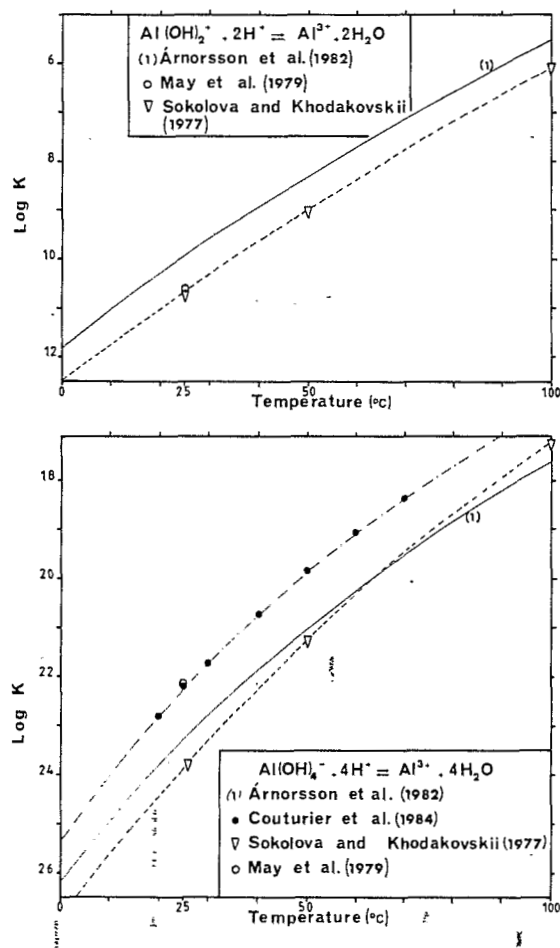
tion), one obtains  $\log \gamma = -10.9$ , for the complex written  $\text{Al}_{13}\text{O}_4(\text{OH})_{24}^{7+}$ . If we consider the complex as was proposed by Bottero et al. (1980),  $\text{Al}_{13}\text{O}_4(\text{OH})_{28}^{3+}$ , with  $a^0 = 19.7$  and  $Z = 3$ , we obtain  $\log \gamma = -0.57$  in 0.6 M NaCl. So it seems rather hazardous to correct thermodynamic data from Öhman and coworkers to zero ionic strength, by extrapolation in the absence of direct measurements in dilute solution. In summary, we can conclude that besides the monomeric species, the existence of the dimer is demonstrated, but that it is important as a kinetic intermediate in the process of polymerization, and is always present in negligible concentrations with respect to the other forms, so that it can be neglected in an equilibrium speciation model. Contrarily, the polymeric form is likely to be present in non-negligible amounts in solution, but its electric charge and its stability are not well established. As the electric charge  $7+$  leads to very low activity coefficients and parameter  $a^0$  is not known for the complex  $\text{Al}_{13}\text{O}_4(\text{OH})_{24}^{7+}$ , and as the electric charge is not well established and was proposed on the structural assumption that all the non-bridging vertices were occupied by water molecules, not knowing even if the Debye-Hückel extended law may be applied to cations with a charge as high as  $7+$ , as the highest charge for ions to which  $a^0$  data exist is  $4+$  (Whitfield, 1979), and the proton transfer between the polymer and the surrounding water molecules being very fast, the form  $\text{Al}_{13}\text{O}_4(\text{OH})_{28}^{3+}(\text{H}_2\text{O})_8^{3+}$ , with  $a^0 = 19.7$ , as proposed by Bottero et al. (1980, 1982), remains at present the only one that can be checked in a model at low ionic strength and will be used here as previously by Bourrié (1981).

### 3. Thermodynamic data

#### 3.1. Monomeric species

Few thermodynamic data are available at other temperatures than 25°C. For  $\text{Al}(\text{OH})_2^+$ ,  $\text{Al}(\text{OH})_3^0$  and  $\text{Al}(\text{OH})_4^-$ , agreement is good be-

tween data from May et al. (1979) at 25°C and from Sokolova and Khodakovskii (1977), but polynomials proposed by Arnórsson et al. (1982) give systematically higher values (Fig. 1). Although May et al.'s (1979) data can be at present considered as the best values for monomeric species, though restricted to 25°C, the values from Sokolova and Khodakovskii (1977) will be used here, through the polynomials fitted by Fritz (1981). Data for  $\text{Al}(\text{OH})_2^+$  proposed by Couturier et al. (1984) are in good agreement with the ones chosen (Fig. 1). As for  $\text{Al}(\text{OH})_4^-$ , there exists a discrepancy between Sokolova and Khodakovskii's data on one hand, and data from May et al. (1979) and Couturier et al. (1984) on the other; data from Arnórsson et al. (1982) are closer to the first set. This discrepancy is ultimately due to uncertainty on the



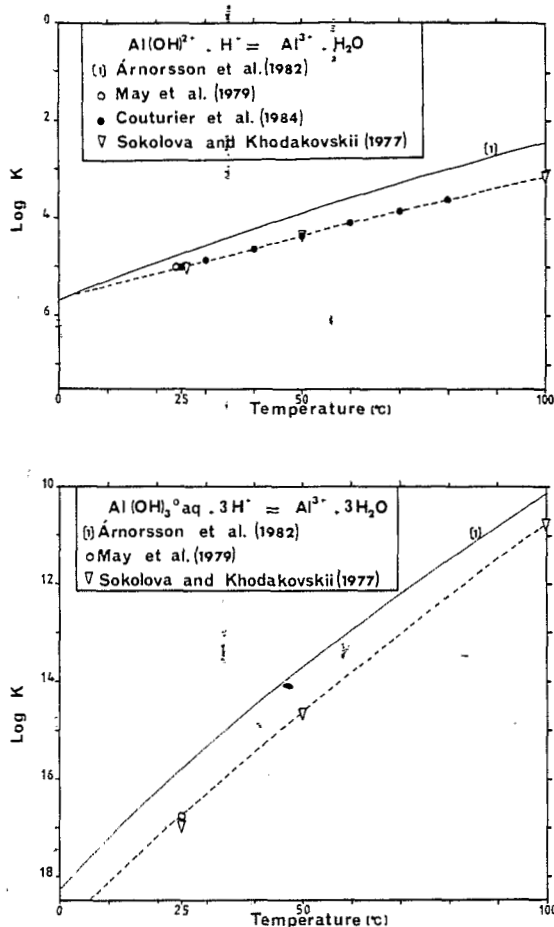


Fig. 1. Plot of  $\log K$  vs. temperature for hydroxo-monomeric species of Al.

nature of the phase that controls Al at high pH, as discussed by Couturier et al. (1984). In order to be consistent, values from Sokolova and Khodakovskii (1977) will be used here.

### 3.2. Polymeric species

The only thermodynamic value proposed for  $\text{Al}_{13}\text{O}_4(\text{OH})_{28}^{3+}$ , from Bottero et al. (1980), is restricted to 25°C, and must be considered as tentative. By lack of better experimental data, it will be used, and as a first approximation will be considered as constant throughout the range of temperatures of our samples (5–25°C).

### 3.3. Other aqueous species

All other data for aqueous species are polynomials fitted by Fritz (1981). All the calculations were made using the program EQUIL(T) (Fritz, 1981), a version of which was modified to provide for the existence of the polymeric species. Mass-balance and alkalinity equations were modified as previously stated (Bourrié, 1981).

### 3.4. Minerals

**3.4.1. Fixed composition minerals.** In the range 0–25°C, the  $\log K(T)$ -values computed from  $C_p^0(T)$  data and  $\log K(T_0=298.15\text{ K})$  fit very closely to a straight line. For gibbsite, a Maier-Kelley function was earlier fitted (Bourrié, 1981) to  $C_p^0$  data from Hemingway et al. (1977) and used together with  $\log K(T_0)=8.047$  from Hemingway et al. (1978). This latter value is very close to the value from May et al. (1979), i.e.  $\log K=8.102$  when considering  $\text{Al}(\text{OH})_3^0$  in the polynomial fitted by the authors. The variation of  $\log K(T)$  for amorphous  $\text{Al}(\text{OH})_3$  was supposed to follow a parallel dependence to that of gibbsite; the  $\log K(T_0)$ -value is from Sarazin (1979). Kaolinite solubility was linearly interpolated between  $\log K(0^\circ\text{C})=9.73$  and  $\log K(T_0)=7.43$  (Fritz, 1981). The variation obtained is practically the same as obtained using the  $C_p^0$  function from Hemingway et al. (1978). Natural samples of kaolinite present variations in solubility according to their origin, ranging from  $\log K(T_0)=7.02$  for “England” kaolinite to 8.02 for “Georgia” kaolinite (Kittrick, 1980), so that the selection is somewhat arbitrary. However, the value chosen leads to  $\log a_{\text{H}_4\text{SiO}_4}=-4.33$  at equilibrium between gibbsite and kaolinite, so that in this case gibbsite is unstable with respect to the quartz-kaolinite paragenesis. Quartz solubility and amorphous silica solubility are from Walther and Helgeson (1977).

Thermodynamic data for imogolite at 25°C are based on two sets of experimental data, im-

TABLE I

Solubility data in the system  $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-H}_2\text{O}$  at 1 bar, 0°, 10° and 25° C

Reaction	log K			Reference
	0° C	10° C	25° C	
$\text{Al}(\text{OH})_3 + 3\text{H}^+ \rightleftharpoons \text{Al}^{3+} + 3\text{H}_2\text{O}$ (amorphous)		11* <sup>1</sup>	10	[1]
$\text{Al}(\text{OH})_3 + 3\text{H}^+ \rightleftharpoons \text{Al}^{3+} + 3\text{H}_2\text{O}$ gibbsite	9.62	8.95	8.05	[2]
$\text{Si}_2\text{Al}_2\text{O}_5(\text{OH})_4 + 6\text{H}^+ \rightleftharpoons 2\text{Al}^{3+} + 2\text{H}_4\text{SiO}_4 + \text{H}_2\text{O}$ kaolinite	9.73	8.80* <sup>2</sup>	7.43	[3]
$\text{SiO}_2 + 2\text{H}_2\text{O} \rightleftharpoons \text{H}_4\text{SiO}_4$ quartz	-4.50	-4.28	-4.00	[4]
$\text{SiO}_2 + 2\text{H}_2\text{O} \rightleftharpoons \text{H}_4\text{SiO}_4$ (amorphous)	-2.99	-2.87	-2.71	[4]
$\text{SiAl}_2\text{O}_5(\text{OH})_4 + 6\text{H}^+ \rightleftharpoons 2\text{Al}^{3+} + \text{H}_4\text{SiO}_4 + 3\text{H}_2\text{O}$ imogolite	15.09	13.82	12.09	[5]

References: [1]=Sarazin (1979); [2]=Bourrié (1981); [3]=Fritz (1981); [4]=Walther and Helgeson (1977); [5]=Aurousseau et al. (1987).

\*<sup>1</sup>Extrapolated, assuming a parallel dependence to that of gibbsite.

\*<sup>2</sup>Linearly interpolated between 0 and 25° C.

ogolite-boehmite (Farmer et al., 1979) and imogolite-gibbsite (Farmer and Fraser, 1982) equilibria, leading to slightly different values. It was shown (Aurousseau et al., 1987) that the two sets of data can be reconciled when considering the more recent value for boehmite from Haas et al. (1981). This leads to  $\Delta G_f^0(T_0) = -2929.27 \text{ kJ mol}^{-1}$  and  $\Delta H_f^0(T_0) = -3193.64 \text{ kJ mol}^{-1}$ . These values allow to compute  $\log K(T)$  for imogolite between 0° and 25° C, assuming  $\Delta H_R^0(T) = \Delta H_R^0(T_0)$  in this interval.  $\Delta G_f^0$ - and  $\Delta H_f^0$ -values for  $\text{Al}^{3+}$  are from Hemingway and Robie (1977), Hemingway et al. (1978), for  $\text{H}_4\text{SiO}_4$  from Hemingway et al. (1978), and for water and boehmite from Haas et al. (1981). From these data (Table I), activity diagrams can be constructed at 25° C for waters from French Guyana and soil leachates, and at 10° C for waters under temperate climate.

3.4.2. Variable composition minerals. Alumino-silicate gels (allophanes) are known to occur,

especially in andosols and weathering products of volcanic rocks; in order to check the saturation of waters with respect to these gels, they can be considered as an ideal solid solution between amorphous  $\text{Al}(\text{OH})_3$  and amorphous silica. By writing one equation for each end-member and the condition for mole fractions (Bourrié, 1983); one obtains the following equation between the solution and the ideal solid solution:

$$\log a_{\text{Al}^{3+}} + 3\text{pH} = \log K_1 + \log [1 - (a_{\text{H}_4\text{SiO}_4}/K_2)] \quad (1)$$

where  $K_1$  and  $K_2$  stand for the solubility products of amorphous  $\text{Al}(\text{OH})_3$  and amorphous silica, respectively.

This formalism allows us to check the saturation of waters with respect to aluminosilicate gel, and to use the same diagram ( $\log a_{\text{Al}^{3+}} + 3\text{pH}$  vs.  $\log a_{\text{H}_4\text{SiO}_4}$ ) as for fixed compo-

sition minerals. Eq. 1 leads to a *curve* asymptotic to the two straight lines for end-members:

#### 4. Sites studied

Spring waters were collected in small experimental watersheds, in Fougères (Armorican Massif, Brittany, France) under humid temperate climate and in Sinnamary (French Guyana) under tropical climate.

A smaller number of spring waters were collected in the Central Massif, France (Mont Lozère and Margeride granitic massifs) and in Paimpont (Armorican Massif). Lysimeter experiments were also performed on soil columns from Fougères.

##### 4.1. Temperate climate

The Fougères watersheds lie on granodioritic rock (Vire-type granite), near the belt of metamorphic schists. It is localized on the cordierite and biotite facies of the granodiorite. It is entirely covered by a beech forest. Average annual rainfall is ~900 mm and average temperature is 10°C. Soils are developed in a silty loam which is partly eolian and partly derived from the weathering of granite. Due to oceanic influence, mineralization of organics is very slow, hence a thick mor-moder humus and a slight discontinuous surface micropodzolization (2–5 cm) exist. The major part of the watershed is made of well-drained acid brown soils on the top, quickly giving way downslope to hydromorphic "sols dégradés" near shallower springs. Deeper springs originate directly from the granitic saprolite in situations showing a marked change of slope. Six elementary watersheds have been monitored since 1978, of which two will be presented here: site F11 (38 samples) representative of deeper springs originating from the granitic arena or saprolite, whereas site F14 (48 samples) is representative of the shallower situations originating from lower soil horizons. X-ray diffractometry (XRD) analysis of the clay fraction of soil horizons and of the granitic sap-

rolite shows the general occurrence of quartz, kaolinite, illites and of aluminous hydroxy-vermiculites. These latter minerals are non-swelling vermiculites that only partly collapse by heating. Chemical extractions by citrate and oxalate show that Al-hydroxide is the dominant constituent of their interlayers (Aurousseau et al., 1987) and is responsible for this behaviour. Those interlayers could be considered as an alternate form of gibbsite from a geochemical point of view.

Spring waters were collected in Margeride (14 samples, July 1984), in situations previously studied (Bourrié, 1978), and in Mont Lozère (5 samples, July 1984) in the south of the Central Massif on a granitic massif, at elevations ranging from 1200 to 1500 m above sea level, with higher annual rainfall (1000–1200 and 1500–2500 mm in Margeride and Mont Lozère, respectively; Dupraz, 1984) and lower average temperature (~6°C).

Spring waters and soil waters were collected in Paimpont (center of Brittany) on sandstones ("grès armoricain") (6 samples, April 1983). Those waters originate from the lower horizons of podzols and "sols dégradés" which afford data from more acidic environments than in Fougères (Aurousseau et al., 1987).

##### 4.2. Tropical climate

Two watersheds (B and F) were chosen among the ten watersheds of the experimental station Écerex near Sinnamary (French Guyana), on Precambrian mica schists (Bonidoro formation). Temperature is quite constant around 25°C and annual rainfall exceeds 3000 mm, mainly during the rainy season that lasts 6 months. The two watersheds are covered by primary rainforest on ferrallitic soils several metres thick, where the only minerals present are kaolinite, quartz, gibbsite and Fe-oxides and -oxyhydroxides. In these watersheds flood waters (peak flow waters) were collected during the rains, and recession waters when the flow decreased. Whereas the former are mainly

surface waters, the latter originate from sub-surface circulation. In addition, catchment *F* allowed to collect groundwaters between storm events. 34 samples have been collected in watershed *B* and 29 in watershed *F* since 1984.

#### 4.3. Lysimeter experiments

Leaching experiments were performed on soil columns consisting of undisturbed cores from the different horizons of acid brown soils in Fougères, in order to separate the role of these horizons in the acquisition of solutes. The columns were leached with distilled water, in the laboratory ( $T \approx 20^\circ\text{C}$ ). The data (Grimaldi, 1981) will be re-interpreted here as they widen the range of pH data at medium temperature.

#### 4.4. Analytical methods

Temperature and pH were measured in the field; the pH measurement cell was checked in the laboratory against N.B.S. standards ( $\pm 0.001$  unit of pH), corrected for use with a saturated calomel electrode (Covington et al., 1983) using a  $0.1\text{-}\mu\text{V}$  resolution voltmeter (Solartron® 7066) and thermostated cell. This cell was then used with a portable pH meter and classical pH buffers ( $\pm 0.02$  units of pH) used to calibrate the meter. The sample was maintained thermostated in the flow of the water at the same temperature during the measurement. An aliquot was filtered in the field using Millipore® filters, 25-nm pore diameter, under  $\text{N}_2$  pressure and immediately acidified with Merck® Suprapur  $\text{H}_2\text{SO}_4$ . No other manipulation or dilution was necessary prior to total dissolved Al analysis by graphite furnace atomic absorption for waters from Fougères. Waters from Guyana were filtered at 10-nm pore diameter. Na, K, Mg and Ca were analyzed by flame emission or atomic absorption spectrophotometry. Alkalinity was analyzed by acidimetric titration using Gran's method (Bourrié, 1976). Sulphate, chloride, nitrate and silica were analyzed by standard colorimetric procedures.

All major elements were analyzed after filtration at  $0.45\text{-}\mu\text{m}$  pore diameter.

### 5. Results

The samples can be divided into two groups: the first at medium and quasi-constant temperature, close to  $25^\circ\text{C}$ , from Guyana waters and soils leachates, the second at lower and variable temperatures, from  $4^\circ$  to  $14^\circ\text{C}$ , consists of waters of temperate climate. Ionic strength is very low, ranging from  $2 \cdot 10^{-4}$  to  $2 \cdot 10^{-3}$  M. Sulphate is also very low, ranging from 0.4 to  $10\text{ mg l}^{-1}$ . Major anions are  $\text{Cl}^-$  and  $\text{HCO}_3^-$ .  $\text{NO}_3^-$  is always negligible except in some soil leachates where nitrification occurred, resulting in the release of Al (see p. 411 and Fig. 2). These general features allow us to use the Debye-Hückel extended law for the computation of activity coefficients. Total organic carbon was

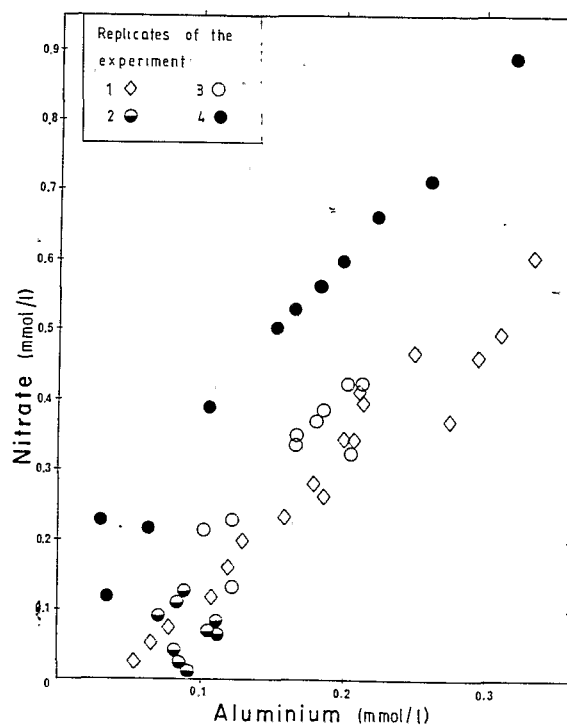


Fig. 2. Plot of  $[\text{Al}]_{\text{total}}$  vs.  $[\text{NO}_3^-]$  in soil leachates (from Grimaldi, 1981). Concentrations in  $\text{mmol l}^{-1}$ . Different symbols correspond to replicates of leaching of the A horizon.



analyzed in some spring waters from Fougères and ranges from 3 to 6 mg l<sup>-1</sup> C, close to the limit of detection of the method (2–3 mg l<sup>-1</sup> C), and waters are not colored. It seems thus unlikely that an appreciable amount of Al is complexed with organic matter, as it would necessitate a very high proportion of active sites in the organic soluble fraction. Hydroxycomplexes are thus likely to be the dominant forms of Al in our solutions. The results can thus be first discussed by plotting directly the analytical data (log [Al]<sub>total</sub> vs. pH, Fig. 3) for the two groups of samples, that may be compared with the solubility curve for gibbsite. The curve at 25°C was computed directly from the polynomial fitted by May et al. (1979), with consideration of Al(OH)<sub>3</sub>:

$$\begin{aligned}
 [\text{Al}]_{\text{total}} = & 2.95 \cdot 10^8 [\text{H}^+] + 2.23 \cdot 10^3 [\text{H}^+]^2 \\
 & + 8.77 \cdot 10^{-3} [\text{H}^+] + 2.23 \cdot 10^{-9} \\
 & + 9.93 \cdot 10^{-15} / [\text{H}^+] \quad (2)
 \end{aligned}$$

The curve at 10°C was computed from the data from Fritz (1981), which leads to:

$$\begin{aligned}
 [\text{Al}]_{\text{total}} = & 8.85 \cdot 10^8 [\text{H}^+]^3 + 3.507 \cdot 10^3 [\text{H}^+]^2 \\
 & + 1.26 \cdot 10^{-2} [\text{H}^+] + 1.782 \cdot 10^{-9} \\
 & + 1.021 \cdot 10^{-16} / [\text{H}^+] \quad (3)
 \end{aligned}$$

These curves are thus the expression of the *single monomeric model*. Our samples are not alkaline (pH < 7.4) so that the present debate about which allotropic form of gibbsite controls Al at high pH (May et al., 1979; Couturier et al., 1984) has no bearing here.

Waters under temperate climate appear largely supersaturated with respect to gibbsite. With one exception, this is even the case of waters issued from podzols and "sols dégradés", where gibbsite is absent and known to be unstable. At 25°C, waters from Guyana are largely supersaturated with respect to gibbsite, whereas soil leachates are undersaturated or close to saturation. In this latter case, in fact nitrification occurred in soil columns from upper horizons – where organic matter provides a source

of nitrogen – due to more favourable temperature conditions in the laboratory. This results in the correlation observed (Fig. 2) between Al and NO<sub>3</sub><sup>-</sup>. As a consequence, pH decreases and the path of evolution tends to an increasing undersaturation, i.e. all protons supplied by nitrification are not instantaneously used in hydrolytic reactions. It appears then that for spring waters and Guyana waters, as pH increases to > 5, paths of evolution cross the saturation curve, leading to an increasing oversaturation (Fig. 3). However, the shallower spring in Fougères (open circles) follows a path different from the deeper one (closed circles), the latter showing lower supersaturation and even no supersaturation at all. The same pattern is observed in Guyana where the recession waters (Fig. 3, open circles) are closer to the saturation curve than storm-flow (flood) waters (× symbols). This suggests that, after an initial stage of supersaturation, as residence time increases waters tend to equilibrate with gibbsite.

Activity diagrams (Figs. 4 and 5) clearly illustrate that the monomeric model is inadequate, as it leads to large supersaturation of waters with respect to gibbsite, kaolinite (up to 4 logarithmic units), and even at low temperatures aluminosilicate gel and amorphous Al(OH)<sub>3</sub>. Gibbsite would even be stable in waters from lower horizons of podzols and from "sols dégradés". When activities are computed after the monomeric-polymeric model (Figs. 6 and 7), scattering of data is greatly reduced. Al appears to be controlled by some form of Al(OH)<sub>3</sub> as no decrease of log a<sub>Al<sup>3+</sup></sub> + 3pH is observed when silica increases.

Spring waters from different granitic massifs, Mont Lozère, Margeride and Fougères (Fig. 6) give values of IAP for Al(OH)<sub>3</sub> very close to 9, i.e. the value of gibbsite at the average temperature (10°C) in a wide range of varying dissolved silica concentrations, and largely over the gibbsite-kaolinite equilibrium and the quartz solubility values. At medium temperature (Fig. 7), values obtained in Guyana waters are

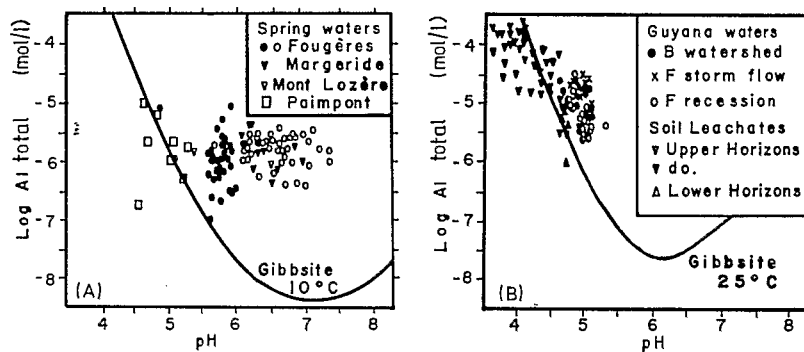


Fig. 3. Plot of  $\log [Al]_{total}$  vs. pH (A) waters from temperate climate, average temperature 10°C; and (B) waters from Guyana and soil leachates, temperature quasi-constant (25°C). Al concentration in  $\text{mol l}^{-1}$ .

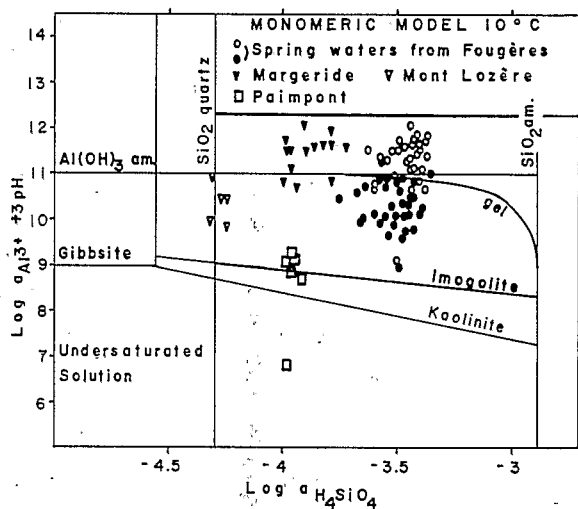


Fig. 4. Activity diagram: activities computed after the monomeric model. Stability fields for minerals are computed at 10°C, but activities used to plot the data are computed at the very temperature of the sample.

slightly lower than 9, but higher than gibbsite solubility at 25°C. It must be noted that there is no appreciable change of slope as gibbsite-kaolinite equilibrium is crossed, and waters are not controlled by kaolinite. With only one exception in Guyana, silica does not exceed the quartz solubility, and a great number of samples – that could not be separately plotted – stay near the point ( $\log a_{Al^{3+}} + 3pH = 8.8$ ;  $\log a_{H_4SiO_4} = -4$ ). This can be explained according to our model: as soon as the kaolinite solubility is exceeded, kaolinite stops dissolving, but does

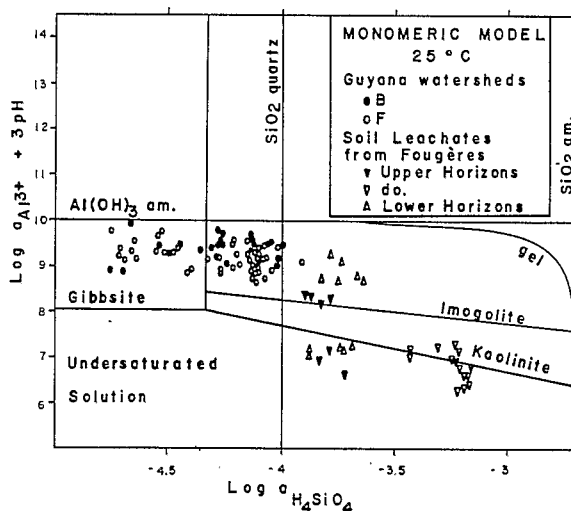


Fig. 5. Activity diagram: activities computed after the monomeric model, 25°C.

not form readily enough to prevent Al remaining at a high level, controlled by gibbsite. Quartz is then in those ancient ferrallitic soils the only source of silica. An end-point for the path of evolution of water is reached when quartz stops dissolving. This confirms the validity of the solubility of quartz from undersaturation. But the end-point is not the kaolinite-quartz equilibrium value as was predicted by Fritz and Tardy (1973), which would maintain Al at a lower level ( $\log a_{Al^{3+}} + 3pH = 7.7$ , with our values). The end-point observed in Guyana waters is the following:  $pH = 5.1$ ,  $\log a_{H_4SiO_4} = -4.1$  to  $-4.0$ ,  $\log$

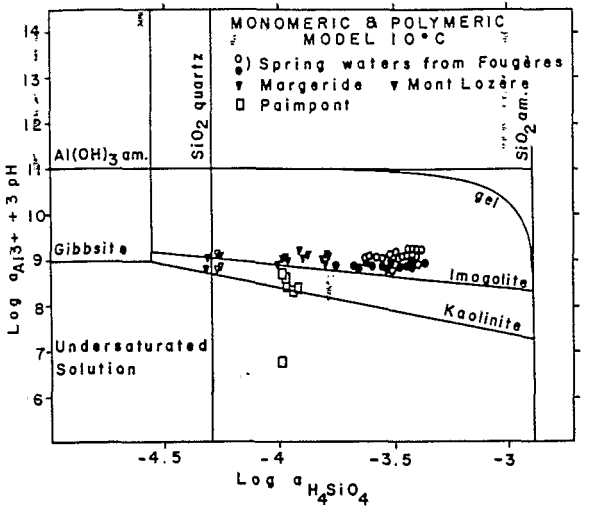


Fig. 6. Activity diagram: activities computed after the monomeric-polymeric model. The same number of samples was used as in Fig. 4, but the points are too close to be separately plotted with the same scale.

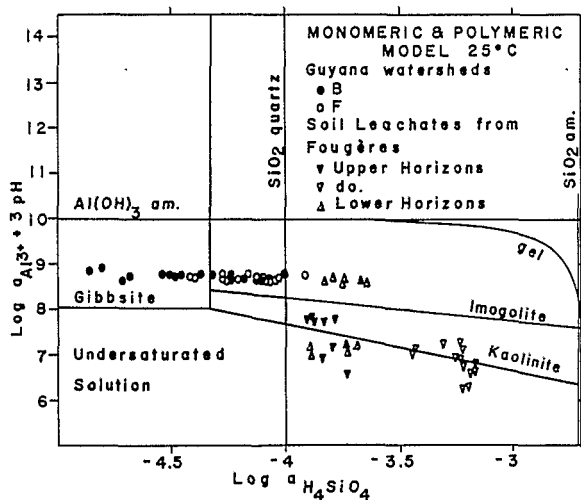


Fig. 7. Activity diagram: activities computed after the monomeric-polymeric model, 25°C. Same remark as in caption to Fig. 6.

$[Al]_{total} = -5.6$  to  $-5.2$ . This composition is frequently observed at the end of recession and during dry periods, whereas lower values of silica are observed during rains, when flow rate is higher.

Soil leachates show higher values of dissolved silica as feldspars and micas are present in the profile, and quartz solubility is exceeded, as is well known at temperatures of  $<60^\circ\text{C}$  (Fritz and Tardy, 1973). Soil leachates from lower horizons, where acidification did not occur by nitrification, show about the same values of  $\log a_{Al^{3+}} + 3pH$  as in Guyana, whereas lower values are observed in upper horizons where nitrification occurred, due to pH decrease more than compensating Al release.

IAP for gibbsite, written as  $\log a_{Al^{3+}} + 3 \log a_{OH^-}$ , can be plotted vs. temperature (Fig. 8), and compared with the solubility curve for gibbsite, as computed previously (Bourrié, 1981), using the polynomial fitted to  $C_p^0(T)$  data by Hemingway et al. (1977). Samples from the different granitic massifs under temperate climate show a continuous variation from  $4^\circ$  to  $13^\circ\text{C}$ , which is reversibly followed when temperature changes. At the same temperature, IAP is lower in the deeper spring in Fougères than in the shallower one. The difference between the samples and the theoretical solubility reaches 0.8 logarithmic unit at  $25^\circ\text{C}$  in the tropical samples. This is not much as compared to the uncertainty on the solubility product of gibbsite. However, the use of this relation as a predictive tool for total Al or as a low-temperature geothermometer is not straightforward as the computation of IAP implies the use of the measured temperature. Moreover, for given values of  $T$  and IAP, the prediction of total Al implies that IAP - or the solubility product of gibbsite - is multiplied by the stoichiometric coefficient of Al in the polymer. With an uncertainty of 0.1–0.2 units for the  $\log K$  of gibbsite, this leads to 1.3–2.6 logarithmic units for the uncertainty of total Al. The physical meaning of this is that total Al may vary widely with low variations of IAP of gibbsite, i.e. the polymer form acts as a buffer between the monomeric compartment and gibbsite, at short residence times. The limitations for the use at low temperatures of equilibrium relationships as geothermometers or as predictive tools for total

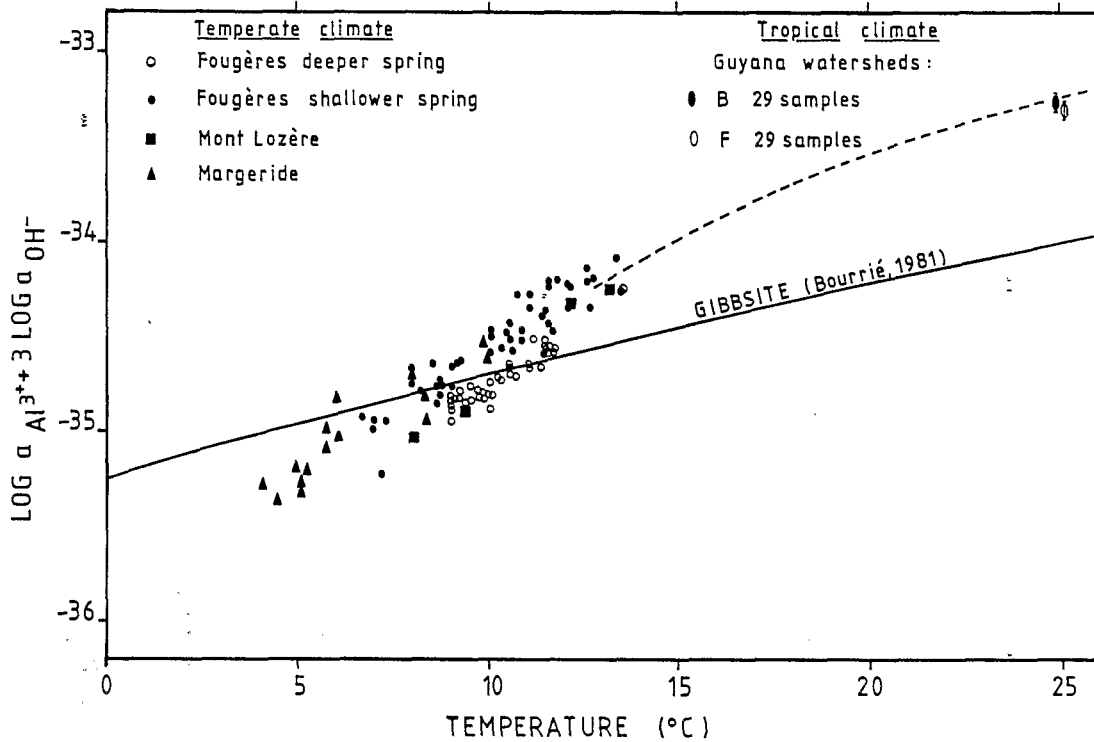


Fig. 8. Plot of  $IAP_{\text{gibbsite}}$  vs. temperature. Data from Fougères (deeper spring and shallower spring), Margeride and Mont Lozère under temperate climate, and from Guyana under tropical climate. Solubility curve for gibbsite is from Bourrié (1981), after Hemingway et al. (1977).

Al, knowing pH and  $T$ , are clearly the following:

- (1) polymeric species are not well characterized at  $25^{\circ}\text{C}$  and not at all at lower temperatures, nor in a wide range of ionic strengths; and
- (2) monomeric-polymeric reactions are not truly at equilibrium.

## 6. Discussion – A new reaction scheme for Al precipitation

The reduction of the scattering of data when the polymeric form is considered is due to the fact that the higher total Al is at a given pH, the higher the proportion of Al as a polymer. Of course, Fig. 3 clearly implies that there is not a single value of total Al at given pH and temperature, but that total Al ranges between a higher limit with monomeric and polymeric forms at equilibrium with each other and a lower limit with only monomeric forms. In this respect, it

would be of no use to consider gibbsites of different solubilities, unless one type of gibbsite is fitted to each sample. The observation of the distinct behaviour of shallower and deeper springs in Fougères and of storm flow and recession flow in Guyana indicates that residence time of water is the major parameter.

The following reaction scheme can thus be proposed (Fig. 9): when pH is  $< 5$ , monomeric species, specifically  $\text{Al}^{3+}$  and  $\text{Al}(\text{OH})^{2+}$ , dominate. Computation shows that the activity of polymeric species is very low. As pH increases to  $> 5$ ,  $\text{Al}(\text{OH})^{2+}$  polymerizes, and gibbsite saturation is reached and slightly exceeded. However, gibbsite precipitation is slow as supersaturation is low, so that a pool of polymer forms is built up that prevents amorphous aluminosilicate gel and amorphous  $\text{Al}(\text{OH})_3$  saturations to be reached. In some cases, waters leave the soil and the weathering zone at that

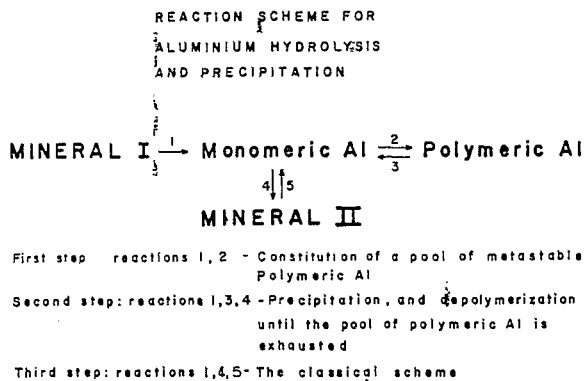


Fig. 9. Reaction scheme for Al precipitation.

stage. When residence time increases, gibbsite precipitation proceeds and monomeric species are used, which in turn results in the depolymerization of the polymer, until the previously built-up pool is exhausted. Ultimately, the composition of the solution reaches the classical gibbsite-monomeric species equilibrium curve.

This scheme is different from the one proposed by Smith and Hem (1972) in that the polymer forms they considered were a continuous series leading from monomeric species to the hexagon, the double hexagon and to gibbsite nuclei by progressive edge-to-edge coalescence. However, an edge-to-edge coalescence is unlikely in homogeneous solution, as it gives high areas of contact between the polymer and the solution. On the contrary, a face-to-face coalescence between two hexagons of octahedrally coordinated Al leads to our polymer, by creating a tetrahedral cavity for the 13th Al ion, with a lower area of contact between the polymer and the solution. Moreover, the polymer obtained by Smith and Hem (1972) during ageing of solutions was such that the ratio  $R$  defined as the number of protons consumed by the hydrolysis of the polymer divided by the number of Al atoms in the polymer ranged from 2.73 to 2.87. For our polymer, this ratio is  $R=36/13=2.77$ , so that our polymer is compatible with their results. The major difference is that our polymer cannot structurally be a

precursor of a nucleus of gibbsite, so that it leads to a branched kinetics instead of a linear kinetics: polymer formation is a "cul-de-sac".

## 7. Conclusions

The monomeric model for aqueous species of Al in waters is inadequate at pH's of  $> 5$ , when residence times are short. In this case most Al is present as a polymer. The consideration of this polymer allows us to compute more accurate IAP's for aluminosilicate minerals. However, this polymer is not truly in equilibrium with monomeric species. As precipitation proceeds, monomeric species are depleted and depolymerization occurs, coupled with precipitation. The application of this model to the interpretation of the chemistry of natural waters under temperate and tropical climate shows that Al is effectively controlled by gibbsite and that the polymer compartment contributes to buffering of the variations of Al. Most waters are supersaturated with respect to kaolinite, i.e. it remains intact in most environments and may form, but does not control Al concentration. More detailed structural and kinetic data are necessary regarding heretofore neglected Al polymers in aqueous solutions.

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