

THE RELEASE OF ALUMINUM FROM ALUMINOSILICATE MINERALS. I. KINETICS

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Abstract—The rates of release of Al by $M NH_4NO_3$ (pH 3) from minerals saturated with Al ions at pH 3 suggest that Al ions migrated from the surface layers and the matrix cores of kaolinite, montmorillonite, illite, and biotite, but only from the matrix core of muscovite mica. From the 0.25–0.5 μm kaolinite and montmorillonite, part of the 'surface' Al is released 'instantaneously' and the rest by first order kinetics, but the coarse 1.5–2.5 μm kaolinite has only the former component. From illite and biotite, 'surface' Al is released by 'bulk diffusion' kinetics suggesting the existence of disturbed peripheral layers of finite thickness. The diffusion coefficients, D_m , for the matrix core follow the trend: mica = biotite > illite > montmorillonite > kaolinite.

Based on models proposed in previous work, the ionic composition of the 'surface' Al is calculated. This shows that (1) this composition varies according to the mineral from 3 to 100% Al^{3+} , the remainder being in the hydrolyzed form, and (2) the apparent hydrolysis constants are different for each mineral and significantly different from those of Al ions in solution.

Key Words—Aluminum, Biotite, Illite, Kaolinite, Montmorillonite.

INTRODUCTION

The determination of exchangeable Al in acid soils and its differentiation from slowly released nonexchangeable Al has occupied the attention of many research workers. A method commonly used is successive extraction with an unbuffered salt solution (e.g., KCl, NH_4Cl , NH_4NO_3) adjusted to the soil pH (Skeen and Sumner, 1967; Sivasubramaniam and Talibudeen, 1972; Prakash and Bhasker, 1974; Cabrera and Talibudeen, 1977). Bache and Sharp (1976a) attributed this slowly released Al to disordered aluminosilicates, Al interlayers in vermiculite clays and organic Al complexes in soils. Not much attention has been paid however to similar measurements of the kinetics of Al extraction from pure minerals such that rate parameters can be evaluated, especially for the 'slow release' reaction, and related to such measurements with acid soils.

The total exchangeable cations, including Al, displaced by unbuffered salt solutions from acid soils has been shown to be larger than the CEC measured by one of the standard methods (Lin and Coleman, 1960; Bache, 1970; Lim and Talibudeen, 1975). This suggests that displaced Al ions have a charge <3+ per Al atom, i.e., they are adsorbed as partially hydrolyzed Al ions on mineral surfaces. From studies on the composition of the solution of Al extracted from acid soils and clays, the existence of polymeric Al species on mineral surfaces has been suggested (Chakravarti and Talibudeen, 1961; Bache, 1974; Dalal, 1975; Smith and Emerson,

1976). Also Brown and Newman (1973) demonstrated the adsorption by bentonite of a basic cation with OH/Al ratio of 2.5. (For a comprehensive review see Coulter, 1969). More recently Bache and Sharp (1976b) were able to distinguish analytically between mononuclear and polynuclear Al ions in soil solutions.

The work described hitherto (except Lin and Coleman, 1960; Smith and Emerson, 1976) has been on natural materials whose surface properties concerning adsorbed Al are affected by their history. In our measurements we pretreated the various minerals so that they had a common background before kinetic extractions of Al commenced.

MATERIALS AND METHODS

Minerals

Some properties of the minerals used in this work are given in Table 1. Specific surface areas (SA) were determined by the adsorption of ethylene glycol vapor (Rawson, 1969). Cation exchange capacities (CEC) were determined by NH_4^+ adsorption as described below.

Al-saturation of the minerals

Ten milliliters of 0.1 N $Al(NO_3)_3$ solution adjusted to pH 3, were added to 0.5 g of the air-dry mineral with 0.2 g of glass beads (<100 mesh) in weighed 15 ml polypropylene centrifuge tubes. After shaking overnight, the tubes were centrifuged at 20,000 g for 30 to 90 min at $20 \pm 1^\circ C$, and the supernatant solution rejected. This treatment was repeated 3 times to ensure that the concentration and pH of the final supernatant were those of the added Al solution. The tubes were then reweighed to determine the amount of entrained solution. All experiments were done in triplicate at $20 \pm 2^\circ C$.

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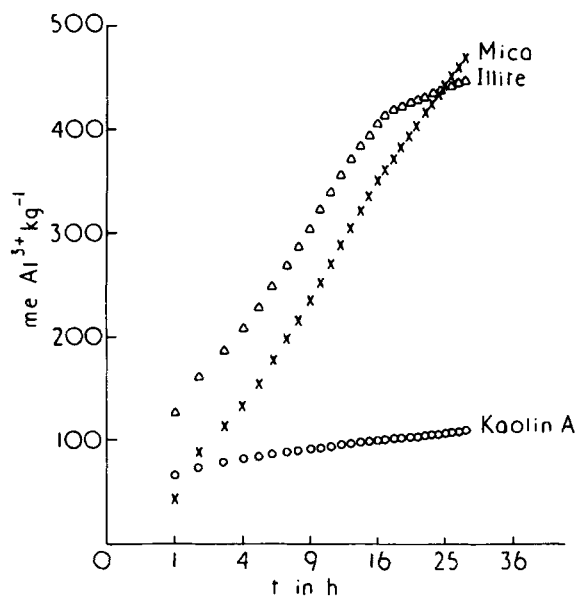


Fig. 1. Cumulative amounts of Al extracted (in meq $\text{Al}^{3+} \text{ kg}^{-1}$) with time by $\text{M NH}_4\text{NO}_3$ (pH 3.0) from kaolinite A, muscovite mica, and Fithian illite saturated with Al^{3+} ions at pH 3.0.

Rates of Al extraction

The Al-saturated minerals were successively extracted with 10 ml aliquots of 1.0 M NH_4NO_3 at pH 3 by shaking for 1 hr on a Rolamix shaker, centrifuging at 17,000 rpm and decanting the supernatant solution for Al analysis and pH measurement. The tubes were then reweighed to determine the Al solution entrained in the solid. The Al extracted at each sampling time was obtained by correcting the total Al found in solution for this entrained Al. The whole process was repeated up to 28 hr. The NH_4 -saturated minerals were then washed several times with 10 ml aliquots of 95% ethanol to remove the entrained NH_4NO_3 solution. The total N in the solids was determined after Kjeldahl digestion to give the CEC. Aluminum in the supernatant solutions was analyzed for by the method of Jayman and Sivasubramaniam (1974).

RESULTS AND DISCUSSION

Rate of Al extraction

For all the minerals except mica, the curvilinear plot 'cumulative Al extracted, Al_t vs. $(\text{time})^{1/2}$ ' became linear after some time depending on the nature of the mineral. Kaolin A illustrates the behavior of kaolin B and montmorillonite, and illite that of biotite (Figure 1). These curves represent rate processes governing the extraction of at least two categories of Al in the solid (i.e., Al on the mineral surfaces and Al in the octahedral layers; Figure 2a). The linear part of the plot at $t > 4$ hr for kaolin A and $t > 16$ hr for illite (Figure 1) suggests that the slower process (Table 2) results from the exchange diffusion of protons inwards and Al to the surface through the octahedral layer. The Al exchanging from the surface layers at time t , $\text{Al}_t^{(s)}$, is obtained by subtracting from Al_t , that associated with the slower process, $\text{Al}_t^{(m)}$. The total Al released thus, $\text{Al}_\infty^{(s)}$, is the intercept of the linear part of ' $\text{Al}_t:t^{1/2}$ ' plot.

The release of Al from surface sites (velocity constant k_s) by cation exchange with a large excess of NH_4^+ can be expressed by the first order equation

$$d[(\text{Al}_\infty^{(s)} - \text{Al}_t^{(s)})/\text{Al}_\infty^{(s)}]/dt = -k_s(\text{Al}_\infty^{(s)} - \text{Al}_t^{(s)}) \quad (1)$$

The integrated form (boundary conditions $t = 0, \infty$; $(\text{Al}_\infty^{(s)} - \text{Al}_t^{(s)})/\text{Al}_\infty^{(s)} = 1, 0$) gives a linear plot of ' $\ln(\text{Al}_\infty^{(s)} - \text{Al}_t^{(s)})/\text{Al}_\infty^{(s)}:t$ ' with zero intercept. Such a straight line plot is obtained for kaolin A and montmorillonite, but with a finite intercept indicating a very rapid exchange reaction before 1 hr, which accounts for 79% and 85% of the 'surface' Al in kaolinite A and montmorillonite respectively. The first order rate constants are therefore calculated after correcting $\text{Al}_\infty^{(s)}$ and $\text{Al}_t^{(s)}$ for this Al released 'instantaneously' by our method of measurement (Table 2). For the coarse kaolin B, nearly all (ca. 98%) of this 'surface' Al exchanges out 'instantaneously'.

The release of such rapidly exchanging 'surface' Al from illite and biotite does not follow equation (1). However, the ' $\text{Al}_t^{(s)}:t^{1/2}$ ' plot is linear up to 17 and 10

Table 1. Description of minerals.

Mineral	Particle size μm	% H_2O in air-dry mineral (a)	SA m^2/g (b)	CEC meq kg^{-1} (a)	Surface charge density	
					meq $\text{m}^{-2} \times 10^4$	nm^2 per unit charge
Kaolinite A (St. Austell)	0.25-0.5	1.0	87	76	9	1.9
Kaolinite B (St. Austell)	1.5-2.5	0.6	67	32	5	3.5
Montmorillonite (Upton)	0.2-1	8.9	804	733	9	1.8
Mica (muscovite)	>1	0.5	19	124	65	0.25
Illite (Fithian No. 35)	<1	3.5	251	237	9	1.8
Biotite (Ontario)	<50	0.8	12	47	39	0.42

(a) On dry weight at 110°C over SiO_2 gel.

(b) On dry weight at 60°C over SiO_2 gel.

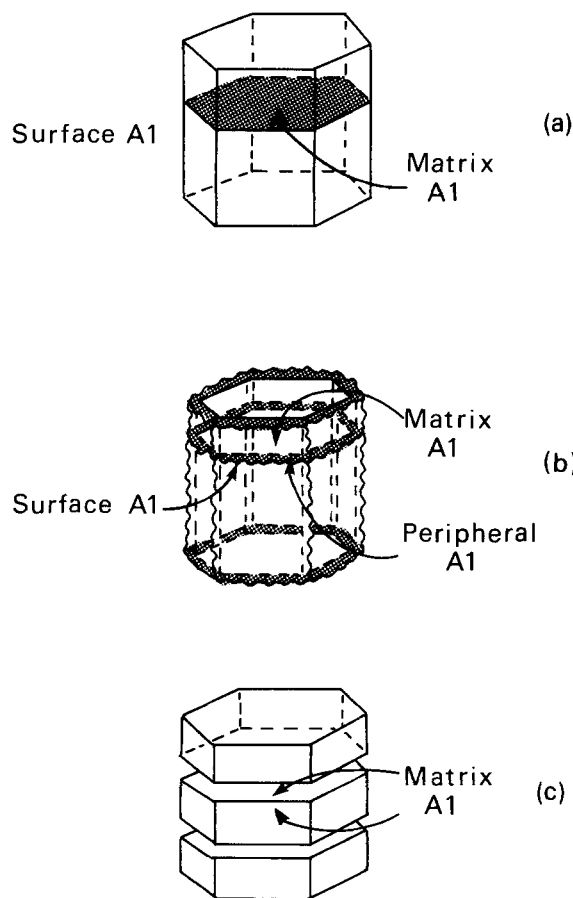


Fig. 2. Idealized diagrammatic representations of (a) 'surface' and 'matrix' regions in kaolinites A and B and montmorillonite; (b) surface, peripheral, and matrix regions in illite and biotite; (c) comminution of mica during extraction.

hr of extraction, respectively, suggesting that 'surface' Al is released from peripheral region of finite thickness by a 'bulk diffusion' process (Table 2 and Figure 2b). The intercept of the ' $Al_t^{(s)}:t^{1/2}$ ' plot is practically zero for biotite and 21 meq $Al^{3+}kg^{-1}$ for illite, indicating

that in illite, about 7% of the 'surface' Al is released 'instantaneously.' Therefore, little or no 'surface' Al exchanges for NH_4^+ ions in these minerals. The possible nature of Al ions released from these minerals in the initial faster reaction is discussed in the next section.

Diffusion in the peripheral region of illite and biotite and in the mineral matrix of all the minerals can be represented by the diffusion equation (2), adapted from Crank (1956). For cylindrically shaped mineral particles, the 'non-steady state' diffusion of Al ions radially outwards, where a vanishingly small concentration of Al is maintained at the surface, is given by

$$(b) \quad \frac{M_t}{t} = \frac{4M_\infty}{\pi^{1/2}} \left(\frac{D}{a^2}\right)^{1/2} \frac{1}{t^{1/2}} - \frac{DM_\infty}{a^2} \quad (2)$$

for small values of t , where M_t and M_∞ are the amounts of Al at time t and on completion of the process, a is the radius of the cylinder and D the diffusion coefficient. The ' $M_t/t:1/t^{1/2}$ ' plot enables D to be calculated from the slope $(4M_\infty/\pi^{1/2})(D/a^2)^{1/2}$ if a and M_∞ are known. The cylinder radius a (Table 3) was calculated from the specific surface area (SA, Table 1), the density of the minerals (taken as 2.65 g cm^{-3}) and assuming diameter: thickness ratios of 4 for kaolinite and 10 for smectite and micas (Talibudeen and Weir, 1972). Values of M_∞ for the diffusion of Al from the surface layers of illite and biotite, $Al_\infty^{(s)}$, were determined from the intercept of the ' $Al_t:t^{1/2}$ ' plot as described earlier. (For illite it was corrected for the 21 meq $Al^{3+} kg^{-1}$ of 'surface' Al 'instantaneously' released.) For the Al diffusing from the mineral matrix, M_∞ was taken as the total Al content of each mineral, Al_T (Table 3).

Diffusion coefficients of Al in the surface layers of illite and biotite, D_s , are, respectively, about 10^4 and 10^2 times larger than their corresponding values for the mineral matrix, D_m (Table 2). The D_s value for illite is larger than for biotite suggesting that the Al in the peripheral layer is more easily dissolved from illite than

Table 2. Kinetics of Al extraction (in meq kg^{-1}) by $M NH_4NO_3$ at pH 3 by batch 'leaching.'

Mineral	'Fast' process		'Slow' process	
	Regression	Intercept	Regression	Intercept
	Equation (1)	$\ln (Al_t/Al_\infty):t$	Equation (2)	$Al_t:t^{1/2}$
Kaolin A	-0.31	-0.18	7.6	68.4
Kaolin B	insignificant		5.9	24.1
Montmorillonite	-0.26	-0.01	11.5	805.0
	Equation (2)	$Al_t:t^{1/2}$	Equation (2)	$Al_t:t^{1/2}$
Illite	69.5	21.0	29.7	290.8
Biotite	65.4	-5.7	14.1	231.7
Mica	<5 hr	—	84.6	-34.2
	5-16 hr	—	113.0	-102.9
	>16 hr	—	90.8	-12.8

Note: For all correlations, $r^2 > 0.980^{***}$.

Table 3. Calculated Al content, 'equivalent cylinder' radius, and characteristic constants of the kinetics of Al extraction with M NH₄NO₃ (pH 3).

	"a" cylindrical radius × 10 ⁹	Al _T mol eq kg ⁻¹ (b)	Al ₀ ^(c) mol eq kg ⁻¹ (c)	k _s s ⁻¹ × 10 ⁸	D _m cm ² s ⁻¹ × 10 ²⁰
Kaolin A	2.6	23,200	70	8.6	3.6
Kaolin B	3.4	23,200	25	—	3.8
Montmorillonite	4.5(a)	11,900	888	7.2	84
				D _s cm ² s ⁻¹ × 10 ¹⁷	D _m cm ² s ⁻¹ × 10 ²⁰
Mica	24	22,700	—	—	49
Illite	11(a)	15,200	319	34	2.1
Biotite	37	6700	230	6.7	38

(a) Radius considering the external surface area.

(b) Approximate values calculated from theoretical composition taken from various sources.

(c) On dry weight at 110°C over SiO₂ gel.

from biotite. For the slow process, D_m values (Table 3) follow the trend: biotite > illite > montmorillonite > kaolin B = kaolin A, indicating that the dissolution of the matrix Al in M NH₄NO₃ of pH 3 decreases in this order. The D_m value for biotite is 10⁴ times greater than for kaolinite. This sequence coincides with the weathering sequence given by Jackson et al. (1948). One of the factors enumerated by Jackson et al. (1952), responsible for this weathering sequence, is the "de-alumination" of the aluminosilicates.

Mica behaves differently from the other minerals. The initially constant slope at $t < 5$ hr of the 'Al_t:t^{1/2}' plot increases up to 16 hr of extraction and then becomes constant (Table 2). We suggest that this initial increase is caused by the creation of new edge surfaces during the treatment with M NH₄NO₃ at pH 3 by the exfoliation and splitting of mica sheets (Figure 2). So the diffusion coefficient, D_m , calculated (Table 3) is for Al released at times >16 hr with M_∞ equal to the total Al in the mica, and is the same as that for biotite.

Ionic composition of Al sorbed in 'surface' layers

The pH of the extracts were initially higher than that of the extractant, decreasing gradually to a value approximately constant and slightly different for each mineral (Table 4 and Figure 3). We attribute this initial increase of pH to more basic forms of Al ions in the surface regions of the minerals than expected at pH 3 in solution (see also Chakravarti and Talibudeen, 1961, in clay minerals; Lim and Talibudeen, 1975, and Cabrera and Talibudeen, 1977, in acid soils). The values of surface-held Al expressed as meq Al³⁺ are higher than the corresponding CEC, except with both kaolins for which they are equal within experimental error (Table 1 and 3).

To calculate the proportions of various ionic Al species that could explain these observations, we have tested three models.

(i) Model A: Using the simplest, unpolymerized, forms of Al³⁺ and Al(OH)²⁺ as the two more important species at pH 3–4, together with CEC and surface-held Al values, two simultaneous equations were formulated. By solving these, positive values of Al³⁺ and AlOH²⁺ were obtained (Table 4) with montmorillonite and illite. With biotite an indeterminate negative value for Al³⁺ was obtained; indeterminate amounts of Al(OH)²⁺ and Al(OH)₂⁺ forms were also obtained if a corresponding model was fitted to the data.

(ii) Model B and C: The existence of monomeric species in acid Al solutions has been questioned by many authors (Brosset, 1952; Brosset, Biedermann and Sil-lén, 1954; Aveston, 1965; Stol, van Helden and de Bruyn, 1976). Brosset et al. (1954) proposed that the main product of hydrolysis is [Al₆(OH)₁₅]³⁺ (Model B), whilst Aveston (1965) suggested [Al₁₃(OH)₃₂]⁷⁺ (Model C), together with traces of [Al₂(OH)₂]⁴⁺.

Our results were also analyzed on the basis of these species as unique hydrolysis products (Table 5), showing that the discrepancies between CEC and Al values are more realistically explained by these models than by assuming the existence of unpolymerized species in Model A. Although precise values cannot be ascribed on the basis of these experiments, apparent 'surface'

Table 4. Supernatant pH during Al extraction and the composition of surface-held Al as unpolymerized ionic species (see text: Model A).

	pH _i (a)	pH _f (b)	Model A		
			% Al ³⁺	% Al(OH) ²⁺	% Al(OH) ₂ ⁺
Kaolin A	3.3	3.0	100	0	0
Kaolin B	3.2	3.0	100	0	0
Montmorillonite	4.2	3.0	48	52	0
Mica	4.2	3.3	—	—	—
Illite	4.3	3.1	23	77	0
Biotite	3.6	3.0	—	—	—

(a) Mean pH up to 2 hr of extraction.

(b) Constant pH reached during the final extractions.

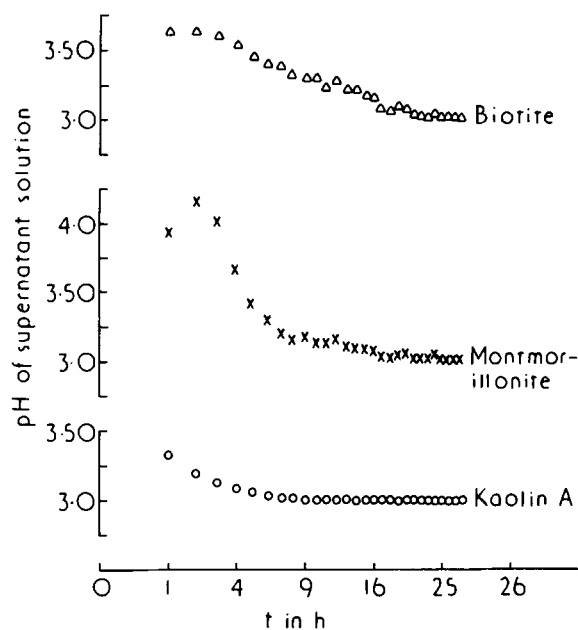


Fig. 3. Progressive change in pH of the $M \text{NH}_4\text{NO}_3$ extract for kaolinite A, montmorillonite, and biotite. (The curve for kaolinite B is similar to that for kaolinite A, and for mica and illite to that for montmorillonite.)

hydrolysis constants for montmorillonite, illite, and biotite were obtained for solid:solution ratios of 1:20 (Table 5) assuming that the adsorbed ions were distributed in the supernatant solution. To calculate this, we also assumed that the pH of the mineral:M NH_4NO_3 suspension in the reaction period up to 2 hr approximated closely to that resulting from the buffering action of hydrolyzed Al ions on the mineral surface. The values for the expressions $\log[\text{Al}_6(\text{OH})_{15}^{3+}] - 6 \log[\text{Al}^{3+}]$ and $\log[\text{Al}_{13}(\text{OH})_{32}^{7+}] - 13 \log[\text{Al}^{3+}]$ were smaller, except for biotite (Figure 4), than those calculated from the hydrolysis constants, $\beta_{15,6} = 10^{-47}$ in 2 M NaClO_4 at 20°C (Brosset et al., 1954) and $\beta_{32,13} = 10^{-104.5}$ in M NaClO_4 at 25°C (Aveston, 1965). (For the thermodynamic constant $\beta_{15,6}^{(0)}$, Richburg and Adams, 1972, gave a value of 10^{-36} at 25–40°C.) This leads to *apparent* hydrolysis constants of Al ions adsorbed at the surfaces of montmorillonite and illite that are smaller than those

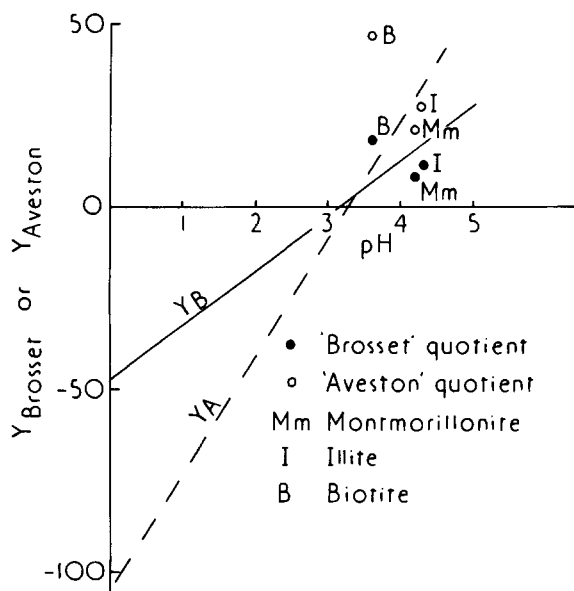


Fig. 4. Relationships between the 'Brosset' (Y_B) and 'Aveston' (Y_A) quotients and pH (see Table 4). *Full line and full circles*: Brosset et al. (1954) theory and results, where $Y_B = \log[\text{Al}_6(\text{OH})_{15}^{3+}] - 6 \log[\text{Al}^{3+}]$ and $\beta_{15,6} = 10^{-47}$ in 2 M NaClO_4 at 20°C. *Broken line and open circles*: Aveston (1965) theory and results, where $Y_A = \log[\text{Al}_{13}(\text{OH})_{32}^{7+}] - 13 \log[\text{Al}^{3+}]$ and $\beta_{32,13} = 10^{-104.5}$ in M NaClO_4 at 25°C. (Mm = montmorillonite; I = illite; B = biotite.)

of Al ions in solution (cf. Low, 1955, for H-Al bentonite, Lim and Talibudeen, 1975, for acid soils, and Pyman et al., 1975, for Al bentonite). For biotite, however, the larger values of $\beta_{15,6} = 10^{-36}$ and $\beta_{32,13} = 10^{-68}$ result from abnormally large values of Al determined in the equilibrium solution compared with those predicted by the 'Brosset et al.' and 'Aveston' β constants quoted above, suggesting that the correction for Al in the solution entrained during sample preparation was underestimated in the experiment.

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Table 5. Composition and apparent hydrolysis constants of surface-held Al calculated from Models B (Brosset et al., 1954) and C (Aveston, 1965).

	Model B			Model C		
	Al^{3+}	$\text{Al}_6(\text{OH})_{15}^{3+}$	$\beta_{15,6}$ (a)	Al^{3+}	$\text{Al}_{13}(\text{OH})_{32}^{7+}$	$\beta_{32,13}$ (b)
	millimole kg^{-1}			millimole kg^{-1}		
Montmorillonite	234.0	10.3	$10^{-54.7}$	233.0	4.9	$10^{-112.9}$
Illite	73.5	5.5	$10^{-53.5}$	73.0	2.6	$10^{-109.8}$
Biotite	5.5	12.2	$10^{-35.8}$	2.3	5.7	$10^{-87.6}$

(a) $\beta_{15,6} = 10^{-47}$ in 2 M NaClO_4 at 20–40°C (Brosset et al., 1954).

(b) $\beta_{32,13} = 10^{-104.5}$ in M NaClO_4 at 25°C (Aveston, 1965).

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Резюме- Скорости высвобождения Al с помощью $M NH_4NO_3$ (pH 3) из минералов, насыщенных ионами Al при pH=3 позволяет предположить, что ионы Al мигрировали из поверхностных слоев и изнутри образцов каолинита, монтмориллонита, иллита и биотита, но только изнутри образцов слюды мусковита. Из 0.25-0.5 μm каолинита и монтмориллонита, часть "поверхностного" Al высвобождается "ментально" и остальной-согласно кинетике первого порядка, но грубозернистый 1,5-2,5 μm каолинит имеет только первый компонент. Из иллита и биотита, "поверхностный" Al высвобождается согласно "объемной диффузионной" кинетике, предполагающей существование наружных периферийных слоев ограниченной мощности. Диффузионные коэффициенты, D_{in} , для внутренних частей образцов следуют тенденции: слюда > биотит > иллит > монтмориллонит > каолинит.

На основе моделей, предложенных в предыдущей работе, был вычислен ионный состав "поверхностного" Al . Эти вычисления показывают, что 1/ этот состав изменяется в соответствии с минералом от 3 до 100% Al^{3+} , остальная часть находится в гидролизной форме и 2/ удельные гидролизные постоянные различны для каждого минерала и значительно отличаются от этих же параметров для ионов Al в растворе.

Kurzreferat- Die Geschwindigkeiten, mit denen Al durch 1 molare Ammonium-nitratlösung, bei pH 3 aus mit Al gesättigten Mineralien gelöst wird, deutet darauf hin, daß Al Ionen von den Oberflächen und den Gesteinsinnern von Kaolinit, Montmorillonit, Illit und Biotit, aber nur vom Innern des Muskowit-Glimmer, freigesetzt werden. Von den 0,25-0,5 μm Kaoliniten und Montmorilloniten wird ein Teil des Oberflächen-Al unverzüglich herausgelöst und der Rest folgt Kinetik erster Ordnung; grobes, 1,5-2,5 μm Kaolinit jedoch besitzt nur die erstere Komponente. Von Illit und Biotit wird Oberflächen-Al via Massendiffusionskinetik freigesetzt, was auf die Existenz einer veränderten peripheren Schicht mit begrenzter Dicke hindeutet. Die Diffusionskoeffizienten, D_m , für das Gesteinsinnere haben die folgende Tendenz: Glimmer \approx Biotit > Illit > Montmorillonit > Kaolinit. Auf Basis von vorgeschlagenen Modellen von früherer Arbeit, wird die ionische Zusammenstellung des Oberflächen-Al berechnet. Damit wird gezeigt, (1) die Zusammensetzung variiert mit dem Mineral von 3 bis 100 % Al(III), mit dem Rest in hydrolysiertes Form; und (2) die scheinbaren Hydrolysenkonstanten sind unterschiedlich für jedes Mineral und sehr anders als die Konstanten für Al-Ionen in Lösung.

Résumé- Les vitesses de libération de l'Al par $M \text{NH}_4\text{NO}_3$ (pH 3) d'ions saturés d'Al à un pH de 3 suggère que les ions d'Al ont émigré des couches de surface et du noyau de la matrice de kaolinite, d'illite et de biotite, mais seulement du noyau de la matrice de mica muscovite. De 0.25-0.5 μm de kaolinite et de montmorillonite, une partie de l'Al "de surface" est libérée "instantanément" et le reste par cinétique de premier ordre; mais la kaolinite grossière de 1.5-2.5 μm est entièrement libérée "instantanément". L'Al de surface est libérée par "diffusion en masse" cinétique de l'illite et de la biotite, suggérant l'existence de couches déformées d'épaisseur finie. Les coefficients de diffusion, D_m , suivent la tendance suivante pour le noyau de la matrice: mica \approx biotite > illite > montmorillonite > kaolinite.

En se basant sur des modèles proposés dans une étude précédente, la composition ionique de l'Al de "surface" est calculée. Ceci montre que (1) cette composition varie d'après le minéral de 3 à 100% d'Al, le restant étant dans une forme hydrolysée et (2) les constantes d'hydrolyse sont différentes pour chaque minéral et diffèrent d'une manière significative de celles d'ions d'Al en solution.