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ADSORPTION OF HYDROXY-Al BY CERTAIN PHYLLOSILICATES AND ITS RELATION TO K/Ca CATION EXCHANGE SELECTIVITY*

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Abstract—The adsorption of hydroxy-Al by the 2–0·2 μ size fractions of muscovite, biotite, K-depleted micas, vermiculite and montmorillonite was studied. The differences in the amounts of hydroxy-Al adsorbed were apparently related to the expansibility and layer charge of minerals, the ionic saturation and degree of K-depletion, the basicity (OH/Al ratio) of the equilibrating hydroxy-Al solution, and the solution–clay ratio. The CEC reduction was not necessarily proportional to the amount of Al adsorbed because CEC reduction may occur through occupation of cation exchange sites by hydroxy-Al, or through hindrance to the entry of the replacing cation to these sites. Aluminum interlayering generally increases the K/Ca cation exchange selectivity (CES) of Na-vermiculite and K-depleted biotite, whereas the K/Ca CES of Na-montmorillonite was little affected. The basicity of the initial hydroxy-Al solution appeared to affect the K/Ca CES of Na-vermiculite and K-depleted biotite by controlling the amount of hydroxyl–Al adsorbed. The data indicate that in addition to the "propping effect", hydroxy-Al interlayers may affect the K/Ca CES through the following mechanisms; (1) the "preferential occupation" of Ca adsorbing sites, and/or (2) the "retarding effect" on the entry of the more hydrated Ca ions.

INTRODUCTION

PARTIALLY interlayered expansible phyllosilicates have been found in many soils and sediments (Jackson, 1963; Rich, 1968). Hydroxy-Al appears to be the most common component of the non-exchangeable interlayer materials of soils. Because of the significant effects of hydroxy-Al interlayers on many physico-chemical properties of soils, considerable efforts have been devoted to investigate the nature of hydroxy-Al interlayers and the process of their formation.

It has been reported that aluminium interlayering of vermiculite, by preventing K-fixation and collapse at the edges of the mineral, may affect cation selectivity by permitting the entry of K-size ions into partially opened mica (Rich and Black, 1964). K-size ions are thus selected at wedge sites, whereas large hydrated ions such as Ca and Mg are excluded. In view of the importance of aluminum interlayering in pedogenesis, it is considered that in addition to the structural and charge properties of minerals (Schachtschabel, 1940; Schwertmann, 1962; Wiklander, 1964; Dolcater *et al.*, 1968), the effect of hydroxy-Al interlayers on cation exchange selectivity deserves increasing attention.

The objectives of this study are; (1) to compare the adsorption of hydroxy-Al by micas, K-depleted micas, vermiculite and montmorillonite, and (2) to examine the effect of aluminum interlayering on the K/Ca exchange selectivity of certain phyllosilicates and to interpret some of the mechanisms involved in the effect.

MATERIALS AND METHODS

The phyllosilicate minerals used were obtained from Ward's Natural Science Establishment, New York. The geographic origins of the minerals were: montmorillonite from Upton, Wyoming, U.S.A.; vermiculite‡ from Transvaal, South Africa; biotite from Bancroft, Ontario, Canada; muscovite from Effingham township, Ontario, Canada.

The montmorillonite sample was lightly crushed to pass a 60-mesh sieve and then suspended in distilled water. The vermiculite sample was purified by the H_2O_2 flotation method of Jackson (1956) and then wet ground in a Waring blendor. The biotite and muscovite samples were broken into

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‡This vermiculite sample is an interstratified mica–vermiculite, but a simple term "vermiculite" will be used when referring to this sample thereafter in this manuscript.

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thin flakes and wet ground. The mineral samples were then fractionated to the 2–0·2 μ size range using the procedures described by Jackson (1956).

The montmorillonite and a portion of the vermiculite were Na-saturated by 5 washings with 1N NaCl. The remaining portion of vermiculite was K-saturated in a similar manner using 1N KCl. The excess chloride was removed by washing first with water and then by 100% methanol.

Sodium tetraphenylboron (NaTPB) was used to remove K from biotite and muscovite. The extracting solutions used were: 1N NaCl-0·2N NaTPB-0·01M EDTA for biotite and 1·7N NaCl–0·3N NaTPB-0·01M EDTA for muscovite (Scott and Smith, 1966). 2-g portions of each of the mineral sample were treated with 40 ml of the appropriate extracting solution. Each mineral was aged in the extracting solution at room temperature for various time intervals to obtain a wide range of K-depletion levels. After aging, the samples were centrifuged and the precipitated potassium tetraphenylboron was removed from the mineral cake by washing five times with 0·5N NaCl in 60% acetone–water solution (Reed and Scott, 1966). The excess chloride was then removed by washing with 100% methanol.

The hydroxy-Al solutions of the basicity (OH/Al ratio) of 2·0 and 2·5 were prepared by the method described by Hsu and Bates (1964a); the final Al concentration was 0·02M. The hydroxy-Al solutions were added to the minerals at a rate of 5 ml/min with continuous stirring. The majority of the samples were treated with 50 ml of hydroxy-Al solution per g of mineral. Certain samples (Table 2) were each divided into two portions; one portion was equilibrated with 50 ml per g and the other portion was equilibrated with 250 ml per g. The freshly prepared suspensions, stored in flasks, were shaken in an end-over-end shaker for 30 min and then aged for 6 weeks at room temperature. After aging, the suspensions were centrifuged and the supernatant solution saved for Al determination. The clay cake was washed once with water and then with 100% methanol till chloride free.

The amount of Al in the supernatant solution after aging was determined by the aluminon method (Hsu, 1963). The amount of Al adsorbed was calculated by the difference between the initial Al concentration and the Al concentration of the solution after aging. The non-extractable Al was determined by the difference between the Al adsorbed and that extracted from the aluminated minerals* by five extractions with 1N NaCl solution.

*Minerals aged in hydroxy-Al solution.

Cation exchange capacity values of the minerals before and after adsorption of hydroxy-Al were determined by the centrifuge washing method, employing Ca as the saturating cation and Mg to replace the Ca. The exchangeable Ca was determined by atomic absorption spectrophotometry.

The method used for the determination of the K/Ca exchange selectivity of the minerals is essentially that of Dolcater *et al.* (1968). Samples of 100 mg were treated once with 20 ml of 0·5N NaCl, and then treated seven times with 20 ml of a mixed solution which was 0·005N with respect to each of the two cations K and Ca. The adsorbed K and Ca and the entrained solution were displaced by neutral 0·5N $Mg(OAc)_2$. The displaced K and Ca were determined by flame emission and atomic absorption, respectively. The amounts of exchangeable K and Ca were calculated by subtracting the amounts of displaced K and Ca from those of K and Ca in the entrained solution. The K/Ca cation exchange selectivity (CES) of the exchange materials was expressed as the equivalent ratio of exchangeable K and Ca. The K/Ca CES so determined is different from the sorption selectivity computed from the difference between the composition of the solution added and that of the supernatant solution after the exchange reaction.

Total K values of the minerals studied were analyzed by digestion of samples with HF and $HClO_4$ (Pratt, 1965) and then determined by flame emission. The Na–montmorillonite sample was found to be void of K (Table 1). The vermiculite sample on the other hand contained 87 m-equiv. K/100g clay. The K contents of biotite and muscovite are similar to those reported in the literature (Scott and Reed, 1962; Reed and Scott, 1966).

RESULTS AND DISCUSSION

Adsorption of hydroxy-Al

Na-montmorillonite adsorbed the maximum or very nearly the maximum amount of Al available,

Table 1. K content of the minerals studied

Mineral	K content (m-equiv./100 g)
Na-montmorillonite	0
Na-vermiculite	87*
Biotite	191
Muscovite	215

*Equivalent to 46 per cent mica, estimated on the basis of trioctahedral mica containing 9 per cent K_2O (Alexiades and Jackson, 1965).

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where 1g of mineral sample was aged in 50 ml of hydroxy-Al solution (Table 2). The mineral, due to its expansibility, did not restrict the adsorption of Al polymers at either basicity. Na-vermiculite adsorbed a smaller amount of polymer than did Na-montmorillonite. This is in line with the observation of Carstea (1968). The Al polymers in solution, with an initial basicity of 2·1 and below, are believed to be in the form of single ring units of composition $[Al_6(OH)_{12}]^{6+}$ or double ring units, $[Al_{10}(OH)_{22}]^{8+}$ (Hsu and Bates, 1964a). These units are relatively small, approximately 10 Å and 14 Å respectively in diameter and 5 Å in thickness, and just fit the interlayer space of vermiculite (Hsu and Bates, 1964b). Montmorillonite would, therefore, offer less resistance to the entry of these polymers. Hsu and Bates (1964b) further stated that at the basicity of 2·5 and above, the polymers gradually increase in size and develop in the *c* direction as well as in *a* and *b*. These polymers would have to be sheared into single layer units before they could enter the interlayer space of vermiculitic minerals. Moreover, the vermiculite sample used in the present study contains 46% mica (Table 1) and is thus more limited in its capacity to adsorb Al polymers.

In comparison to Al adsorption at the basicity of 2·0, more hindrance to the entry of Al polymers would be expected for Na-vermiculite at the basicity of 2·5. However, the amount of Al adsorbed by this mineral at the lower solution–clay ratio did not appear to be significantly affected by the initial basicity of the hydroxy-Al solution (Table 2). The vermiculite sample studied may contain a certain amount of montmorillonite (Alexiades and Jackson, 1965) which would adsorb large polymers.

Biotite and muscovite possessing predominantly external planar and edge sites were found to adsorb about 5 mg Al/g clay (Table 2). This is comparable to the amount of hydroxy-Al adsorbed by micas of the same size after repeated K saturation (Huang and Kozak, 1970). Consequently, interlayer adsorption would be essentially non-existent. The K-saturated vermiculite adsorbed about 9 mg Al/g clay. Some adsorption other than that due to external planar and edge sites may occur. The additional adsorption may be attributed to interlayer sites. In the first place, collapse of the mineral upon K-saturation may have been incomplete. Secondly, the K is not native K, thus the layers will not be held together as tightly as would otherwise be expected. Thirdly, the possible presence of montmorillonite (Alexiades and Jackson, 1965) which does not collapse upon K-saturation provides a probable source for interlayer adsorption.

The 48 per cent K-depleted biotite adsorbed a similar amount of Al polymers from the solution of the lower basicity as compared to Na-vermiculite (Table 2). Both contain quite comparable amounts of mica. The polymers at this basicity would enter quite readily into the interlayer spaces of the K-depleted biotite. The amount of Al adsorbed

Table 2. Adsorption of hydroxy-Al by various minerals after aging in hydroxy-Al polymer solutions

Mineral*	mg Al adsorbed/g clay OH/Al = 2·0	OH/Al = 2·5
Na-montmorillonite	25·8	27·0
	58·7†	57·8†
Na-vermiculite	21·6	21·0
	27·6†	24·6†
K-vermiculite	8·6	9·9
Biotite	5·0	5·5
48% K-depleted biotite	23·2	14·9
63% K-depleted biotite	27·0	17·5
	30·6†	22·5†
70% K-depleted biotite	26·9	14·8
82% K-depleted biotite	27·0	15·1
Muscovite	4·5	4·4
44% K-depleted muscovite	4·8	4·3
49% K-depleted muscovite	6·0	4·6
57% K-depleted muscovite	7·0	6·6

*All samples aged in 50 ml of polymer solution per g of clay unless otherwise stated.

†250 ml of polymer solution per g of clay.

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by the 48% K-depleted biotite from the solution of higher basicity is considerably less than that from the solution of lower basicity, and also less than that of Na-vermiculite at a comparable basicity. The predominant cause is probably steric hindrance to the entry of the larger Al polymers. Montmorillonite is likely not present in the K-depleted biotite as in the case of the South African vermiculite.

At the basicity of 2·0 and the lower solution-clay ratio, the maximum amount of Al available in the systems was adsorbed by K-depleted biotite in each case, except for the 48 per cent K-depleted biotite (Table 2). The more highly K-depleted samples have more interlayer sites available for adsorption. However, at the basicity of 2·5 and the lower solution–clay ratio, the amount of Al adsorbed by the more highly K-depleted biotite is quite similar to that by 48 per cent K-depleted biotite.

The K-depleted muscovite samples adsorbed very little hydroxy-Al above that attributable to external planar and edge sites (Table 2). This appears to be due to charge effect and steric hindrance to the entry of the Al polymers and/or blocking of the openings to the interlayer spaces as reflected in the CEC reduction (Table 3). This interpretation is substantiated by the observation of Scott and Smith (1966) that muscovite treated with NaTPB has higher layer charge and lower expansibility than Na-degraded biotite.

The ratio of hydroxy-Al solution to clay affects the total amount of Al adsorbed (Table 2). If more polymer solution per g of clay were made available, the mineral's adsorption capacity would be more completely satisfied. The work of Hsu and Rich (1960) also shows that solution volume is significant in retention of Al by Dowex 50 cation exchange resin. In the present study, Na-montmorillonite was found to adsorb more than twice as much Al at the higher solution–clay ratio (Table 2). Na-vermiculite and 63 per cent K-depleted biotite adsorbed more Al at the higher solution–clay ratio also, but the increase was not as large; the additional adsorption is probably due to the presence of a larger number of smaller polymers available for adsorption.

A significant reduction in CEC occurred in the majority of minerals upon adsorption of hydroxy-Al (Table 3). The CEC reduction for Na-vermiculite was found to be much more drastic in comparison to Na-montmorillonite. At the lower solution–clay ratio, almost the same amount of Al was adsorbed by Na-vermiculite at the basicities of 2·0 and 2·5 (Table 2), but the CEC reduction was significantly less at the higher basicity. The data indicate that the smaller polymers were more effective in reducing the CEC of Na-vermiculite. At the higher solution–clay ratio, the CEC reduction of the Na-vermiculite is also greater at the lower basicity. The higher charge per Al atom as well as the greater amount of Al adsorbed at this basicity may account for the differences in the CEC reduction. The CEC reduction of K-vermiculite after adsorption of hydroxy-Al was small in comparison to Na-vermiculite (Table 3). K-vermiculite, however, adsorbed much less Al polymer (Table 2). Therefore, a high CEC reduction would not be expected.

It is interesting to note that the trends with the 63% K-depleted biotite are quite similar to Na-vermiculite in many aspects (Table 3). Greater CEC reduction occurred at the lower basicity where the amounts of Al adsorbed were higher (Table 2). At the higher basicity there was a drastic CEC reduction ranging from 33 to 70 per cent (Table 3) due to the increase in the ratio of hydroxy-Al solution to clay.

Table 3. Effect of hydroxy-Al adsorption on the CEC of minerals

		CEC (Ca/Mg), m-equiv./100g							
		OH/Al = 2·0				OH/Al = 2·5			
		Ratio of aging solution to mineral				Ratio of aging solution to mineral			
		50 ml/g		250 ml/g		50 ml/g		250 ml/g	
Mineral	Check	CEC	% CEC reduction	CEC	% CEC reduction	CEC	% CEC reduction	CEC	% CEC reduction
Na-montmorillonite	92·2	74·6	19·1	57·6	37·5	67·8	26·5	61·0	33·8
Na-vermiculite	130·9	46·1	64·8	20·1	84·7	57·3	56·2	32·3	75·3
K-vermiculite	111·4	93·6	16·0			92·6	16·9		
63% K-depleted biotite	96·2	17·1	82·2	13·2	86·3	64·1	33·4	28·7	70·2
49% K-depleted muscovite	48·1	19·1	60·3			45·3	5·8		

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With the 49 per cent K-depleted muscovite there was a reduction of CEC by 60 per cent at the basicity of 2·0 (Table 3). In view of the level of the adsorption of hydroxy-Al (Table 2), some of the smaller polymers appeared to be sterically pinched at the openings to interlayer spaces thus hindering the entry of Ca ions. At the higher basicity slightly less Al was adsorbed (Table 2); the polymers were larger and apparently not fixed at the openings to interlayer positions. Therefore, the CEC reduction was very small.

The CEC reduction does not appear to be proportional to the amount of non-extractable Al adsorbed by the various minerals studied (Fig. 1).

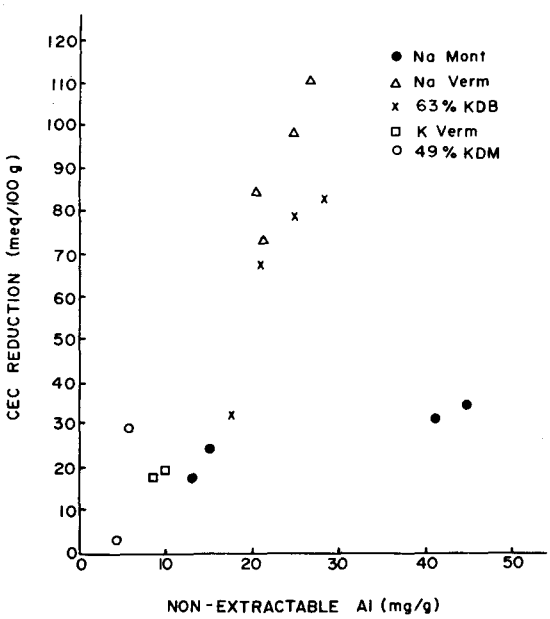


Fig. 1. Relationship of the non-extractable Al adsorbed by various minerals and their CEC reduction (Mont = montmorillonite, Verm = vermiculite, KDB = K-depleted biotite, and KDM = K-depleted muscovite).

One mineral may adsorb only small polymers whereas another can adsorb both small and large ones. CEC reduction may occur due to occupation of sites or to the blocking of the exchange reaction. The latter mechanism is apparently quite important to the minerals with wedge zones, higher layer charge and more limited expansibility. The ratio of mg of Al retained/m-equiv. of CEC reduction is estimated to be 246, 100, 24, 21 and 4 for Na-montmorillonite, K-vermiculite, K-depleted biotite, Na-vermiculite, and K-depleted muscovite, respectively. The present observation substantiates the proposal that steric blocking of exchange by hydroxy groups may occur in hydroxy precipitate–clay systems (Rich, 1968).

*Effect of hydroxy-*Al *adsorption on* K/Ca *exchange selectivity*

The adsorption of Al polymers by Na-montmorillonite had little effect on the K/Ca CES of this mineral (Table 4). The absence of wedge zones (Table 1) and large interlayer expansibility of the mineral must be the dominant explanations for this result.

The results for Na-vermiculite and 63 per cent K-depleted biotite aged at the higher solution–clay ratio (Table 4) indicate a significant increase in K/Ca CES. It has been proposed that K ions can move more easily in the "propped open" interlayer space than in interlayer space where the silicate layers tend to collapse about the K ions (Rich and Black, 1964). Therefore, the K can reach the wedge zones and can be selected preferentially. In addition to this mechanism, other factors may be important in determining the K/Ca selectivity. A very significant factor may be the "preferential occupation" by the Al polymers on exchange sites that normally would adsorb Ca. The polymers due to their size normally would not be adsorbed at wedge zones, but rather in the more expanded interlayer positions. Therefore, the sites that normally would adsorb Ca ions would be occupied

Table 4. Effect of hydroxy-Al adsorption on K/Ca CES of selected minerals

		K/Ca CES			
		OH/Al = 2·0		OH/Al = 2·5	
		Ratio of aging solution to mineral		Ratio of aging solution to mineral	
Mineral	H_2O*	50 ml/g	250 ml/g	50 ml/g	250 ml/g
Na-montmorillonite	0·05	0·06	0·04	0·06	0·04
Na-vermiculite	0·34	0·61	1·73	0·52	1·66
63% K-depleted biotite	1·08	1·92	2·81	0·91	2·51

*The K/Ca CES values of each mineral aged at the two H_2O/clay ratios were averaged.

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by the Al polymers whereas wedge sites would be relatively unaffected upon adsorption of hydroxy-Al. This would result in the concentration of K retaining sites on interlayers. The hydroxy-Al interlayers may also create a "retarding effect" on the entry of the more hydrated Ca ions, thereby effectively increasing the selectivity towards the less hydrated K ions. It has been proposed that hydroxy-Al polymers tend to populate near the edges of particles (Dixon and Jackson, 1962; Frink, 1965). If this accumulation of Al polymers is sufficient, the "retarding effect" on the entry of Ca would result. With respect to hydrated size, the K, being smaller than Ca, may still quite easily pass between the hydroxy-Al islands and move further to the interior part of the interlayer spaces.

The initial basicity of the Al polymers also appears to have some effect on the K/Ca CES of Na-vermiculite and K-depleted biotite (Table 4). The less adsorption of Al polymer at the higher basicity (Table 2) results in the reduction of the CES to below the value found for the lower basicity study. With fewer polymers in the interplayer spaces, both the "propping effect" favoring the entry of K ions and the "retarding effect" hindering the entry of Ca ions will be reduced. Also, the number of Ca adsorbing sites occupied by the polymers will be less. Therefore, the adsorption of Ca over K is favored by this decrease in Al polymer adsorption.

A model showing the presence of hydroxy-Al islands in a weathered mica has been proposed by Rich and Black (1964). Although the "propping effect" may increase the K selectivity, it is possible that the continuance of the wedge zone due to mineral collapse may be limited by the "propping effect" of hydroxy-Al islands under certain circumstances. In such a case, the preferential selectivity of the mineral towards K relative to Ca will be decreased and thus the CES should decrease. This may explain why the CES of 63 per cent K-depleted biotite at the lower solution–clay ratio and the initial basicity of 2·5 is even lower than that of the non-aluminated samples (Table 4). In this case, 17·5 mg of Al/g of clay has been adsorbed (Table 2). This may not create a sufficiently large "retarding effect" and/or "preferential occupation" to overcome the discontinuity of the wedge zone upon adsorption of hydroxy-Al polymers. At the higher solution–clay ratio and the initial basicity of 2·5, 22·5 mg of Al/g of clay was adsorbed (Table 2). The increase of 5 mg of Al/g of clay appears to be sufficient to create a more pronounced "retarding effect" and/or "preferential occupation" and, therefore, increases the K/Ca CES.

The data presented in Table 5 further reveal the significance of the two mechanisms proposed in this study. With the K-depleted and non-aluminated biotite, the amounts of K and Ca exchangeable in 0·5N $Mg(OAc)_2$ after treating with the equilibrating solution were 30·3 and 28·0 m-equiv./100 g, respectively. With those aged at the basicity of 2·0 and the lower solution–clay ratio, the amounts of K and Ca exchanged decreased to 12·1 and 6·3 m-equiv./100 g, respectively. At the same basicity, but higher solution–clay ratio, the amount of Ca exchanged was reduced still more. At the basicity of 2·5 and the lower solution–clay ratio, the amounts of K and Ca exchanged were 24·6 and 26·9 m-equiv./100 g, respectively. At the same basicity and the higher solution–clay ratio, the reduction in Ca exchanged was much greater than in K.

Table 5. The effect of hydroxy-Al adsorption of Na-vermiculite and K-depleted biotite on the amount of K and Ca exchangeable in 0·5N $Mg(OAc)_2$ after equilibrating with a mixed solution which was 0·005N with respect to K and Ca

		Cation exchanged (m-equiv./100g)			
		K		Ca	
		Ratio of aging solution to mineral		Ratio of aging solution to mineral	
Mineral	Aging solution	50 ml/g	250 ml/g	50 ml/g	250 ml/g
63% K-depleted biotite	H_2O*	30·3	30·3	28·0	28·0
	OH/Al = 2·0	12·1	13·8	6·3	4·9
	OH/Al = 2·5	24·6	20·6	26·9	8·2
Na-vermiculite	H_2O*	32·4	32·4	95·1	95·1
	OH/Al = 2·0	15·3	11·4	25·3	6·6
	OH/Al = 2·5	18·2	17·1	34·7	10·3

*The values obtained at the two H_2O/clay ratios were averaged.

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A similar type of relationship exists for Na-vermiculite (Table 5). In comparison with the non-aluminated sample, at the higher solution–clay ratio, the reduction in K exchanged was from 32·4 to 11·4 m-equiv./100 g at the lower basicity and 32·4 to 17·1 m-equiv./100 g at the higher basicity. The reduction in Ca exchanged, however, was from 95·1 to 6·6 m-equiv./100 g and 95·1 to 10·3 m-equiv./100 g, respectively.

It is thus evident that the "preferential occupation" of Al polymers on exchange sites which normally would be occupied by Ca ions, and/or the "retarding effect" exerted by Al polymers on the entry of the more hydrated Ca ions are important factors in influencing the K/Ca CES of 2:1 phyllosilicates which have wedge zones and rather limited interlayer expansibility.

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Résumé—On a étudié l'adsorption d'hydroxy-Al par les fractions comprises entre 0,2 et 2 μ des minéraux suivants: muscovite, biotite, micas appauvris en K, vermiculite et montmorillonite. Les différences trouvées dans les quantités d'hydroxy-Al adsorbé sont apparemment reliées à l'aptitude au gonflement et à la charge du minéral, à la saturation ionique et au degré de remplacement du potassium, à la basicité (rapport OH/Al) de la solution d'hydroxy-Al en équilibre, et au rapport solution-argile. La réduction de CEC n'est pas néessairement proportionnelle à la quantité d'aluminium adsorbé du fait que cette réduction de CEC peut provenir soit de l'occupation des sites d'échange cationique par l'hydroxy-Al, soit de l'obstacle créé à l'accès des cations échangeurs à ces sites. L'aluminium placé dans l'espace interfeuillet augmente en général la sélectivité d'échange cationique (CES) K/Ca pour la vermiculite-Na et la biotite appauvrie en K, tandis que la CES K/Ca pour la montmorillonite Na est peu affectée. La basicité de la solution initiale d'hydroxy-Al semble affecter la CES K/Ca de la vermiculite-Na et de la biotite appauvrie en K, en contrôlant la quantité d'hydroxy-Al adsorbé. Les données indiquent qu'en plus d'un "effet de cale", l'hydroxy-Al interfeuillet peut affecter la CES K/Ca par les mécanismes suivants; (1) occupation préférentielle des sites d'adsorption du calcium, et/ou (2) effet retardateur sur l'entrée des ions Ca plus hydratés.

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Kurzreferat – Die Adsorption von Hydroxy–Al durch 2–0·2 μ Grösse Fraktionen von Muskowit, Biotit, K-armem Glimmer, Vermiculit und Montmorillonit wurde untersucht, Die Unterschiede in den Mengen von adsorbiertem Hydroxy–Al standen offenbar in einer Beziehung zu der Expandibilität und Schichtladung der Minerale, der ionischen Sättigung und dem Mass an K-Verarmung, der Basizität (OH/Al Verhältnis) der abgleichenden Hydroxy–Al Lösung und dem Verhältnis Lösung/Ton. Die Verminderung der CEC war nicht unbedingt proportional der Menge von absorbiertem Al weil ja eine Verminderung der CEC durch Besetzung von Kationenaustauschstellen durch Hydroxy–Al, oder durch Verhinderung des Zutrittes der Ersatzkationen an diese Stellen erfolgen kann. Zwischenlagerung von Aluminium erhöhte im allgemeinen die K/Ca Kationenaustauschselektivität (CES) von Na–Vermiculit and K-armen Biotit, während die K/Ca CES von Na–Montmorillonit wenig berührt war. Die Basizität der ursprünglichen Hydroxy–Al Lösung schien einen Einfluss auf die K/Ca CES von Na–Vermiculit und K-armem Biotit auszuüben durch Steuerung der Menge von adsorbiertem Hydroxy–Al. Die Messwerte deuten darauf hin, dass die Hydroxy–Al Zwischenschichten neben ihrer "Stützwirkung" die K/Ca CES durch die folgenden Mechanismen beeinflussen können: (1) die "Vorzugsbesetzung" von Ca–adsorbierenden Stellen, bzw. (2) die "verzögernde Wirkung" auf den Zutritt der stärker hydratisierten Ca–Ionen.

Резюме — Изучен характер поглощения гидрокси –Al фракциями 2–0,2 мк мусковита, биотита, слюды с пониженным содержанием K, вермикулита и монтмориллонита. Различия в количестве поглощенного гидрокси –Al оказались связанными со способностью к разбуханию и зарядом слоев минералов, ионным насыщением и степенью дефицита K, основностью (отношение OH/Al) равновесного раствора гидрокси –Al и отношением раствор — глина. Уменьшение катионно-обменной емкости (КОЕ) не было обязательно пропорционально количеству поглощенного Al, поскольку уменьшение КОЕ может происходить вследствие заселения положений обменных катионов гидрокси –Al или является результатом затрудненного вхождения обменных катионов. Внедрение алюминия между слоями обычно увеличивает избирательность катионного обмена K/Ca в Na–вермикулите и биотите с дефицитом K, в то время как избирательность катионного обмена K/Ca в Na–монтмориллоните изменяется очень незначительно. Основность исходного раствора гидрокси –Al, как оказалось, влияет на избирательность катионного обмена K/Ca в Na–вермикулите и биотите с дефицитом K, контролируя количество поглощенного гидрокси –Al. Полученные данные свидетельствуют о том, что помимо «эффекта закрепления» межслоевой гидрокси –Al может воздействовать на избирательность катионного обмена K/Ca по следующим механизмам: 1) посредством «предпочтительного заселения» положений адсорбированного Ca, и/или 2) вследствие «эффекта замедления» вхождения более гидратированных ионов Ca.

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