KAOLINS: SOURCES OF DIFFERENCES IN CATION-EXCHANGE CAPACITIES AND CESIUM RETENTION

C. H. Lim, M. L. Jackson, R. D. Koons, and P. A. Helmke

Department of Soil Science, University of Wisconsin Madison, Wisconsin 53706

Abstract—Seven kaolins from Georgia (southeastern U.S.A.), ranging from high to low commercial grade, were characterized by X-ray powder diffraction and chemical techniques to establish that the variation in quality was caused by impurities. The Ca and Cs cation-exchange capacities (CEC) varied from 2.67 to 8.17 and from 3.29 to 8.77 meq/100 g, respectively. Selective dissolution and correlation analyses strongly indicated that expandable 2:1 minerals, particularly smectite $(1.2-5.9%)$, were responsible for most of the observed variations in Ca CEC ($r = 0.85^*$). The external surface CEC of kaolinite ranged from 0 to 1 meq/ 100 g. The positive significant correlation ($r = 0.90**$) between the Ca CEC and the K-mica content (0– 3.9%) suggested that Ca CEC may be related to the degree of mica weathering through an expandable mineral stage.

The Cs-retention capacity $(0.19-1.14 \text{~meq}/100 \text{~g})$ was closely related to Cs-measured vermiculite content $(r = 0.80^*)$, and this content plus specific surface $(R = 0.93^{**})$ or mica content $(R = 0.86^*)$. The Cs retention appeared to be primarily related to the presence of interlayer wedges at micalvermiculite XY interfaces.

Key Words—Cation-exchange capacity, Cs retention, Interlayer wedges, Kaolinite, Vermiculite.

INTRODUCTION

The low cation-exchange capacity (CEC) of kaolinite, compared to that of expandable phyllosilicates, is thought by some to result from ionic substitution (Bolland *et al.,* 1976) and to be pH-independent. However, it is thought by others to arise from exposed -SiOH and -AIOH sites (Ferris and Jepson, 1975) and to be pHdependent. Differences in the CEC of various kaolins have been attributed to differences in the degree of crystallinity (Murray and Lyons, 1960), surface area (Ormsby *et al.,* 1962), and the presence of impurities, particularly montmorillonite (Hinckley and Bates, 1960; Bundy *et al., 1966).*

Small amounts of montmorillonite impurity in kaolin clays have an adverse effect on rheology of kaolinite suspensions (Lyons, 1958). The fixation of Cs^{137} is minimal or negligible for monomineralic kaolinite or expanded montmorillonite (Schulz *et al.,* 1960). Interleaved micaceous components (Lee *et al.*, 1975), occurring as impurities in kaolinite, may be responsible for the strong fixation of radionuclides such as Cs^{137} (Francis and Brinkley, 1976; Komarneni, 1978).

The objectives of this paper are to characterize a series of field-grade kaolins with different CEC and rheological properties by mineralogical, chemical, and X-ray powder diffraction techniques, and to correlate and identify the sources of the differences in the CEC and Cs-retention capacity of the kaolins.

MATERIALS AND METHODS

Six commercial kaolins from Twiggs County and one (sampie 3) from Wrens, Georgia (courtesy of A. C.

Kunkle of the J. M. Huber Corporation), were examined. Random powder specimens were prepared for X-ray diffraction (XRD) analysis with Ni-filtered *CuKa* radiation and a scanning speed of 2°20/min. An empirical crystallinity index (Johns and Murray, 1959) was determined by comparing the intensity ratio of the $(02\bar{1})$ and (060) reflections obtained with a scanning speed of $0.5^{\circ}2\theta$ /min. XRD analyses were also made of Li-DMSO- (Abdel-Kader *et al.,* 1978) and Cs-Hz-DMSO- (Jackson and Abdel-Kader, 1978) intercalated kaolins. An intercalation index was computed as a ratio of the intensity of the 11.2- \AA peak to the sum of the intensities of the 7.1- and 11.2- \AA peaks.

Total K_2O and MgO contents were determined by HF digestion in sealed polypropylene bottles, saturated H_3BO_3 treatment (Jackson, 1975), and atomic absorption spectrophotometry (AA). The elemental analyses were performed in duplicate. Specific surface data were obtained by the glyceröl mono-interlayer sorption method of Milford and Jackson (1962).

CEC determinations

For determinations of exchange capacities for Ca and K, 0.20-g samples were saturated with Ca^{2+} by three washings with 0.5 N CaCl₂ followed by five more with 0.01 N solution. Excess salt in the day paste was determined by the weighing method of Jackson (1975). The exchangeable Ca plus that in the excess salt was replaced by washing the paste five times with 0.5 N $MgCl₂$. Calcium was determined by atomic absorption spectrophotometry. The amount of exchangeable Ca, designated as CaEC (meq/100 g), was obtained by sub-

Copyright © 1980, The Clay Minerals Society 223

tracting the amount of excess salt Ca, as calculated from the concentration and the weight of excess solution, from the total Ca.

The amount of exchange capacity with K was determined on the same sampie after the CaEC determination. Potassium saturation was achieved by washing the sampie three times with 0.5 N KCI, once with 0.02 N KCI in water, and four times with 0.02 N KCI in 80% methanol (Jackson, 1975). After the last washing, the tube was weighed, dried overnight at 110°C, and again weighed to obtain the weight of the sampie plus excess KCI solution. The exchangeable K plus excess salt K was extracted by five washings of 0.5 N NH₄OAc, and the total K was determined by flame emission spectrophotometry. The amount of exchangeable K, designated as *K/EC (meq/100* g), was obtained by subtraction of the amount of excess salt K from the total K.

CsEC determinations were carried out essentially the same as the CaEC determinations. However, each CsCl solution used was tagged with Cs^{137} . The exchangeable plus excess Cs was extracted with 0.5 N $NH₄OAC$ or 0.5 N CaCl, solutions in two separate sets of samples. The extracted Cs^{137} was radio-assayed by high resolution gamma-ray spectroscopy with an NaI detector. The amount of exchangeable Cs, designated as CsEC, was calculated as the difference between total Cs and excess salt Cs and expressed as CsEC by $NH₄$ ⁺ or Ca2+ replacement. A measure of the Cs-retention capacity was afforded by the difference in CsEC obtained by the replacement of Cs^+ with NH_4^+ vs. that with Ca²⁺. All reported CEC values represent the average of duplicate determinations.

Quantitative mineralogical analysis

A quantitative estimate of the mineralogical composition ofkaolins was made by the chemical allocation procedure (Jackson, 1975). The mica content was calculated based on an allocation of 10% K₂O to mica. The vermiculite content was derived from the equation (Alexiades and Jackson, 1966):

$$
\% \text{ Verm} = [(\text{CaEC} - \text{K/EC})/(154)](100) \tag{1}
$$

A second vermiculite content ("Verrn") was calculated by substitution of the CsEC (replacement by $NH₄$ ⁺) for CaEC (replacement by Mg²⁺). The montmorillonite content was calculated from the simplified equation (Jackson, 1975):

% Mont =
$$
[(K/EC - y)/(110 - y)](100)
$$
 (2)

in which $y =$ the CEC (meg/100 g) attributable to the external surfaces of various minerals present in the bulk sample.

Selective dissolution of kaolinite (Jackson, 1975) was carried out to concentrate the impurities. The sample was first preheated in a muffle furnace to 550°C for 4 hr. A O.I-g subsampie was dispersed and boiled in 100 ml

Figure 1. X-ray diffractograms of Mg^{2+} -saturated, glycerolsolvated kaolin samples 2 and 6 before and after selective dissolution of kaolinite (NaOH-SDA after 550°C), illustrating the impurities.

of 0.5 N NaOH for 2.5 min in a stainless steel beaker. After boiling, the sample in the beaker was immediately cooled in a basin of cold water. The cool suspension was centrifuged, and the residue was saved for subsequent analysis. This procedure was repeated with a succession of sampies until a sufficient amount of residue was collected for the XRD, CaEC, and K/EC determinations described above.

RESULTS AND DISCUSSION

Nature of the kaolins

Only trace to negligible amounts of impurities, except for mica and expandable 2: 1 layers in sampIes 5, 6, and 7, could be detected in XRD patterns of the original kaolins (Figure 1; Table 1). A small amount of expandable 2:1 layers $\left\langle \frac{-5}{\%} \right\rangle$ may escape detection by XRD analysis if they are interstratified with kaolinite as the principal mineral. Their presence is revealed by chemical properties (Tables 2 and 3). The identification and quantification of montmorillonite and other impurities in kaolins is important because the impurities contribute to excess viscosity of kaolin suspensions, and decreased brightness of paper coatings may preclude commercial use.

The high intercalation index of many of the kaolins

Sample RO.	Impurities detectable with XRD	Inter- calation index ¹	Specific surface (m^2/g)	Empirical crystal- linity index ²
1		0.94	77.6	0.36
2		0.97	75.8	0.34
3		0.72	94.8	$\overline{}^3$
4		0.94	104.3	0.25
5	Mica	0.94	102.5	0.23
6	Mica; expandable $2:1$ phases	0.96	105.8	0.21
7	Mica; expandable $2:1$ phases	0.92	113.7	0.12

Table 1. Some properties indicative of impurities in the kaolins.

¹ The 11.2 Å/(7.2 Å + 11.2 Å) XRD peak-height ratios of DMSO-intercalated kaolinites (Jackson and Abdel-Kader, 1978).

² The $(02\overline{1})/(060)$ peak-height ratios on the diffractograms of random powder sampies (Johns and Murray, 1959).

³ Kaolin sample with ill-defined (021) peak (Wrens, Georgia, sampie 3).

studied (>0.90, Table 1) indicates that kaolinite with intercalation disorder or kaolinite type IV ("fireclay"; Range *et al.,* 1969) is a minor constituent except in sample 3 which has an intercalation index of 0.72 . A similar sampie of disordered kaolin has been shown to consist of interleaved 10-Ä mica components between 7-Ä kaolinite layers (Lee *et al.,* 1975). The absence of chlorite was confirmed by the Cs-Hz-DMSO intercalation index of unity. The crystallinity indices of the sampies (Table 1) are low and decrease with the kaolin commercial quality indexes assigned beforehand from 1 to 7. The changes in indices may be the result of inherently poor layer stacking order of kaolins or the accentuation of the (060) peak by the presence of dioctahedral expandable 2:1 layers. The amounts of the latter increased (Table 3) directly with the degree of disorder. The $(02\bar{1})$ peak of sample 3 was not discernable because of disorder in 3 dimensions.

The presence of impurities in the kaolin sampies was particularly indicated by their high specific surfaces of

Table 2. Cation-exchange capacity and elemental analyses of the kaolins.

Sample	CaEC	K/EC ¹	MgO	$K_{2}O$
no.	(meq/100 g)		(%)	(%)
	2.67	2.29		
2	3.22	2.57	0.02	0.01
3	3.84	3.19	0.01	0.07
4	4.15	3.56	0.03	0.02
5	4.76	4.20	0.03	0.04
6	6.98	6.01	0.04	0.14
	8.17	7.04	0.11	0.39

¹ Slash denotes oven-drying before $NH₁$ ⁺ replacement of K+.

Table 3. Mineralogy of the kaolins.

Sample no.	Kaolinite ¹ $(\%)$	Mont- morillonite (%)	Vermiculite (%)	Mica (%)
	98.5	$1.2\,$	0.3	
2	96.9	2.6	0.4	0.1
3	96.4	2.5	0.4	0.7
4	95.6	3.8	0.4	0.2
5	95.9	3.3	0.4	0.4
6	94.6	3.4	0.6	1.4
	89.5	5.9	0.7	3.9

¹ Kaolinite (%) = 100 – (% Mont. + % Verm. + % Mica).

77 to 113 m^2/g (Table 1). The surface area of pure kaolinite determined by the BET method ranges from 10 to 15 m²/g (Ormsby *et al.*, 1962). Expandable 2:1 layers have a high specific surface of about 800 m²/g (Jackson, 1975), hence small amounts of such materials in kaolins can significantly increase the net surface area. The trend of the MgO content (Table 2) relates to the content of montmorillonite (Table 3).

The presence of mica and expandable 2: 1 layers in the residue is clearly illustrated by kaolins 2 and 6 (Figure 1) after kaolinite removal. The presence of these minerals was also noted in residues of sampies 1-4 which did not contain amounts of impurities sufficient to show by XRD of the whole sampie. The qualitative evidence for the presence of trace amounts of mica and expandable 2: 1 minerals occurring as impurities in kaolins, as indicated by SDA and XRD, is supported by the chemical methods for quantitative mineralogical composition (Table 3).

CEC differences

The CaEC of the kaolins ranged from 2.67 to 8.17 meq/100 g (Table 2). Correlation analysis of CaEC with montmorillonite content ($r = 0.85^*$), specific surface $(r = 0.84^*)$, crystallinity index $(r = -0.95^{**})$, and MgO content ($r = 0.89$ **) indicated that the CEC of the kaolins is significantly related to montmorillonite impurities (Table 4). Montmorillonite impurity is responsible for most of the observed differences in CaEC of these kaolin clays as it is inherently defined by the specific surface, crystallinity index, and MgO content (1 to 1.3 meq/100 g for each 1% present).

The vermiculite content is nearly constant and makes up 0.3 to 0.7% of the kaolins (Table 3). It cannot fully account for the observed CEC differences; however, it may contribute partially to the CEC. Mica(expressed as K_2O , Table 4) is not a strong contributor to CEC because of its inherently low CEC $(6-10 \text{ meq}/100 \text{ g})$, but co-varies with the CaEC ($r = 0.90^{**}$, Table 4) of its expandable-mineral weathering products ($r = 0.84^*$, Table 4), as discussed by Jackson (1963). The CEC differences, therefore, may be related to the degree of mica weathering to expandable minerals.

Table 4. Correlation coefficients (r) of CaEC and of montmorillonite content with various properties of the kaolins.

	Montmorillonite content	Specific surface	Crystallinity index ¹	Intercalation index	K_2O (%)	${MgO} (%)$
CaEC	$0.85*$	$0.84*$	$-0.95**$	0.14	$0.90**$	$0.89**$
Montmorillonite content	$-$	$0.84*$	$-0.93**$	0.12	$0.84*$	$0.95**$

¹ $I_{(021)}/I_{(060)}$ of kaolinite.

* Significant at 95% confidence interval.

** Significant at 99% confidence interval.

Cs *retention*

The CsEC obtained by extraction with $NH₄$ ⁺ ions was higher than the CaEC by 0.1 to 1.6 meq/ 100 g (Table 5). Cations with low hydration energy, such as K^+ , $NH₄⁺$, Rb⁺, and Cs⁺, can seek out interlayer wedge sites at the phase boundary between K-depleted zones and remnant mica cores (Jackson, 1963; Dolcater *et al.,* 1968). Conversely, cations with high hydration energy, such as Mg^{2+} , Ca^{2+} , and Sr^{2+} , encounter steric hindrance at these sites and are not selectively adsorbed. The selective adsorption of Cs^+ over Ca^{2+} in vermiculites has been demonstrated (Sawhney, 1964). The CsEC obtained by Ca^{2+} as the displacing cation was greater than the CaEC in sampies 1-4. The lower CsEC in samples 5, 6, and 7 can be attributed to more $Cs⁺$ being retained against Ca^{2+} replacement. The higher mica and vermiculite contents (Table 3) in the latter three samples (higher wedge-like interfaces) could account for this observation.

CsEC determined by displacement with $NH₄$ ⁺ ions was consistently greater than with Ca^{2+} (Table 5). This is contrary to an ion-exchange process whereby interlayer alkali ions are displaced more effectively by divalent alkaline earths than by other large monovalent ions (Barshad, 1954). $Cs⁺$ ions with a small hydration

Table 5. Some properties related to Cs retention of the kaolins.

Sample по.		C _{sEC}		Cs ¹³⁷		
	by $NH4$ ⁺ (meg/ (100 g)	bу $Ca2+$ (meq/ (100 g)	CaEC by Mg^{2+} (meq) (100 g)	retention capacity ¹ (meq) (100 g)	Verm ² (%)	"Verm" ³ (%)
1	3.29	3.10	2.67	0.19	0.25	0.65
2	4.05	3.64	3.22	0.41	0.42	0.96
3	5.39	4.25	3.84	1.14	0.42	1.43
4	5.33	4.64	4.15	0.69	0.38	1.15
5	5.50	4.69	4.76	0.81	0.36	0.84
6	7.01	6.50	6.98	0.51	0.63	0.65
7	8.77	7.82	8.17	0.95	0.73	1.12

¹ Difference between CsEC, replacing cation, NH_4 ⁺ vs. Ca^{2+} .

² Verm (%) = $[(CaEC - K/EC)/(154)](100)$ (Alexiades and Jackson, 1966).

3 CsEC used instead of CaEC in the above.

energy and high polar bonding apparently tend to fix tightly in the ditrigonal cavities within interlayer wedges where the more hydrated Ca^{2+} ions are not effective in displacing them. That $NH₄$ ⁺ and K⁺ ions replaced Cs+ ions fixed at wedge sites and interlayer positions more readily and completely than Ca^{2+} and Mg^{2+} ions has been reported (Schulz *et al.,* 1960; Coleman *et al.,* 1963; Sawhney, 1964). Thus, in the selective adsorption of $Cs⁺$ by micaceous minerals, similarity of size, charge, and hydration of the displacing cation evidently determines displacement effectiveness. The difference in CsEC, determined by Cs displacement with $NH₄$ ⁺ instead of Ca²⁺, can be regarded as a measure of the Cs-retention capacity (Table 5 and Figure 2).

Simple correlation analysis of Cs-retention capacity against other variables (Table 6) indicated that Cs retention was significantly correlated with "Verm" $(r =$ 0.80*). The normal vermiculite content (Verm), cal-

Figure 2. Cs retention of the kaolins $(Cs_{NH_4} - Cs_{Ca})$ as a function of their cation-exchange capacities.

Cs retention, $CsNH4 - Csca$	Simple correlation (r)	Multiple correlations ¹ (R)	
"Verm"	$0.80*$		
Specific surface	0.63	$0.93**$	
Mont.	0.55	$0.86*$	
Mica	0.45	$0.86*$	
Verm.	0.38	$0.86*$	
Intercalation index	-0.70	$0.82*$	

Table 6. Correlation coefficients of Cs retention vs. other properties of the kaolins.

¹ Multiple correlation coefficients of Cs-retention capacity vs. "Verm" and one other property.

* Significant at 95% confidence interval.

** Significant at 99% confidence interval.

culated from CaEC, showed a much lower coefficient $(r = 0.38)$. The relatively high negative correlation $(r = 1.38)$ -0.70) with intercalation index illustrates that ordered kaolinites retain less $Cs⁺$ against replacement by either $NH₄$ ⁺ or Ca²⁺ than do disordered kaolinites.

Multiple correlation analysis of Cs-retention capacity with "Verm" and specific surface was more highly correlated $(R = 0.93^{**})$ than with the other double sets (Table 6). Cs retention showed a high multiple correlation ($R = 0.86$ ^{*}) with mica content and "Verm" (Table 6), although it was poorly correlated with mica by itself. Interestingly, the mica content was highly correlated with CEC and montmorillonite content (Table 4). The foregoing multiple correlations were similar to those with montmorillonite or with intercalation index, indicating that mica and its expanding mineral weathering products (wedges at mica-vermiculite-montmorillonite XY plane interfaces; Jackson, 1963, Figure I) are closely related to Cs retention. The high multiple correlation of Cs retention with "Verm" and specific surface thus appears to be accounted for by the close association of mica weathering products with the kaolins, including the disordered kaolin (sample 3) from Wrens, Georgia.

Estimate of CEC of kaolinite

The montmorillonite content determined (by *K/EC*) after selective dissolution (NaOH-SDA after 550°C heating) of kaolinite ranged from 1.2 to 5.9% (right hand column, Table 7). The possible CECs of the kaolinites are arrayed as 0 to 5 meq/lOO g to allow the caJculation of the montmorillonite content determined for sampIes 1-7. As can be seen, the best fitting series of calculated montmorillonite contents of the seven clays is obtained under the assumed kaolinite CEC of 0.5 meq/IOO g. Since the correlation coefficients are approximately equal ($r = 0.90$ to $0.91**$) for the assumed CEC values of 0 to 1 meq/ 100 g, the CEC value of the principal mineral, kaolinite (Table 3), is indicated to fall in that range. It is likely that the high CEC values for kaolinite (2 to 15 meq/lOO g) reported in the literature overestimate the CEC attributable to pure kaolinite.

CONCLUSIONS

Selective dissolution and elemental techniques amplify and reinforce XRD in identifying mica and expandable layer silicate impurities present in varying, often small, amounts in kaolins (Table 3). Nearly pure kaolinites occur in intimate association with mica, vermiculite, and montmorillonite, even in high-kaolinite deposits, in agreement with Keller and Haenni (1978) that monomineralic kaolinite is rare.

Highly significant correlation coefficients (Tables 4 and 6) between CaEC, specific surface, montmorillon-

	Montmorillonite content ¹ $(\%)$ Assuming CEC at pH 7 of the external surface of the minerals, mostly kaolinite (meq/100 g): 0 0.5 5.03 3.6 ² 1.0					
Sample no.						
	2.08	1.63	1.18			1.17
	2.34	1.89	1.44			2.55
	2.90	2.46	2.01			2.50
	3.24	2.79	2.35			3.83
	3.82	3.38	2.94	0.56		3.31
	5.46	5.03	4.60	2.27	0.96	3.36
	6.40	5.97	5.54	3.23	1.94	5.86
Correlations (r)	$0.91**$	$0.91**$	$0.90**$	0.72	0.71	

Table 7. Estimate of CEC of the kaolins.

¹ Calculated using the formula (Jackson, 1975): Mont $(\%) = [K/EC - y)/(110 - y)](100)$, $y = \text{meq}/100 \text{ g}$ of CEC attributable to the external surface of the minerals, instead of assuming 5.

 2 van Olphen (1966).

³ Alexiades and Jackson (1966).

• Determined on residue after selective dissolution (NaOH-SDA after 550°C) of kaolinite; calculated in footnote 1, assuming $y = 0$.

** Correlation coefficients, significant at 99% confidence interval; r relates montmorillonite percentage before and after SDA.

ite, MgO, vermiculite, mica, and Cs-retention properties of aseries of kaolins suggest the formation of mica at one stage of the genetic history of the c1ay.

Cs is exchanged by crude kaolins in greater amounts than are K or Ca (Table 5). The Cs retention vs. replacement by $NH₄$ ⁺ as compared with that by Ca indicates that Cs can penetrate further into the XY plane wedges of the mica/vermiculite than can $NH₄^+$, K⁺, or $Ca²⁺$. Kaolins with a low intercalation index (high intercalation disorder, e.g., fireclay) fix much $Cs⁺$ against replacement by $NH₄⁺$ or Ca²⁺.

The CEC at pH 7 of pure kaolinite ranges from 0 to 1 meq/lOO g of kaolinite, after the CEC of expandable mineral impurities in the kaolins has been accounted for (Table 7).

ACKNOWLEDGMENTS

This research was supported in part under College of Agricultural and Life Sciences projects 1123 and 1336; in part by the National Science Foundation grant EAR-76-19783; and in part by the Ecological Sciences Branch, Division of Biomedical and Environmental Research, U.S. Department of Energy, Contract E4-76-S-02-1S15; through an International Consortium for Interinstitutional Cooperation in the Advancement of Learning (ICICAL). Appreciation is expressed to the several readers and the editor for many helpful suggestions. Appreciation also is extended to Ms. C. M. Jackson for her care in typing the manuscript.

REFERENCES

- Abdel-Kader, F. H., Jackson, M. L., and Lee, G. B. (1978) Soil kaolinite, vermiculite, and chlorite identification by an improved lithium DMSO X-ray diffraction test: *Soil Sei. Soc. Amer. J.* 42, 163-167.
- Alexiades, C. A. and Jackson, M. L. (1966) Quantitative clay mineralogical analysis of soils and sediments: *Clays* & *C[ay Minerals* **14,** 35-52.
- Barshad, 1. (1954) Cation exchange in micaceous minerals: I. Replaceability of ammonium and potassium from vermiculite, biotite, and montmorillonite: *SoU Sei.* 78, 57-76.
- Bolland, M. D. A., Posner, A. M. , and Quirk, J. P. (1976) Surface change on kaolinites in aqueous suspension: *Aust. J. Soil Res.* 14, 197-216.
- Bundy, W. M., Johns, W. D., and Murray, H. H. (1966) Interrelationships of physical and chemical properties of kaolinites: *Clays* & *Clay Minerals* 14,331-345.
- Coleman, N. T., Lewis, R. J., and Craig, D. (1963) Sorption of cesium by soils and its dis placement by salt solutions: *Soil Sei. Soc. Amer. Proc.* 27,290-294.
- Dolcater, D. L., Lotse, E. G., Syers, J. K., and Jackson, M. L. (1968) Cation exchange selectivity of some clay-sized

minerals and soil materials: Soil Sci. Soc. Amer. Proc. 32, 795-798.

- Ferris, A. P. and Jepson, W. B. (1975) The exchange capacities of kaolinite and the preparation of homoionic clays: *J*. *Colloid Interface Sei.* 51, 245-259.
- Francis, C. W. and Brinkley, F. S. (1976) Preferential adsorption of Cs¹³⁷ to micaceous minerals in contaminated fresh water sediment: *Nature* 260, 511-513.
- Hinckley, D. N. and Bates, T. F. (1960) Evaluation of the amount and distribution of montmorillonite in some Georgia and South Carolina kaolins: *Clays & Clay Minerals* 8, 18-21.
- Jackson, M. L. (1963) Interlayering of expansible layer silicates in soils by chemical weathering: *Clays* & *Clay Minerals* 11, 29-46.
- Jackson, M. L. (1975) Soil Chemical Analysis-Advanced *Course:* 2nd ed., 10th printing, published by the author, Madison, Wisconsin, 895 pp.
- Jackson, M. L. and Abdel-Kader, F. H. (1978) Kaolinite intercalation procedure for all sizes and types with X-ray diffraction spacing distinctive from other phyllosilicates: *Clays & C[ay Millerals* 26, 81-87.
- Johns, W. D. and Murray, H. H. (1959) Empirical crystallinity index for kaolinite: *Prag . Abstr. Geol. Soc. Amer. 70,* 1624.
- Keller, W. D. and Haenni, R. P. (1978) Effects of micro-sized mixtures of kaolin minerals on properties of kaolinites: *Clays* & *Clay Minera[s* 26, 384-396.
- Komameni, S. (1978) Cesium sorption and desorption behavior of kaolinites: *Soil Sci. Soc. Amer. J.* 42, 531-532.
- Lee, S. *Y .,* Jackson, M. L., and Brown, J. L. (1975) Micaceous occlusions in kaolinite observed by ultramicrotomy and high resolution electron microscopy: *Clays* & *Clay Minerals* 23, 125-129.
- Lyons, S. C. (1958) Clays: *Tappi Monograph* 20, 57-115.
- Milford, M. H. and Jackson, M. L. (1962) Specific surface determination of expansible layer silicates: Science 135, 929-930.
- Murray, H. H. and Lyons, S. C. (1960) Further correlation of kaolinite crystallinity with chemical and physical properties: *Clays* & *Clay Minerals* 8, 11-17.
- Ormsby, W. C., Shartsis, J. M., and Woodside, K. H. (1962) Exchange behavior of kaolins of varying degrees of crystallinity: *J. Amer. Ceram. Soc.* 45, 361-366.
- Range, K. J., Range, A., and Weiss, A. (1969) Fire-clay type kaolinite or fire-clay mineral? Experimental classification of kaolinite-halloysite minerals: *Proc. 3rd Int. Clay Conf.*, Tokyo, **1,** 3-13.
- Sawhney, B. L. (1964) Sorption and fixation of microquantities of Cs by clay minerals: effect of saturating cations: *Soil Sci. Soc. Amer. Proc.* 28, 183-186.
- Schulz, R. K. , Overstreet, R., and Barshad, I. (1960) On the soil chemistry of cesium-137: *Soil Sei.* 89, 16-27.
- Van Olphen, H. (1966) Collapse of potassium montmorillonite clays upon heating--" potassium fixation": *C[ays* & *Clay Minera[s* 14, 117-132.

(Received 29 *April 1979; accepted* 26 *December 1979)*

Резюме-Семь каолинов из Джорджии (юго-восток США), представленные в диапазоне от высокодо низкокачественных коммерческих марок, были охарактеризованы порошковым методом рентгеноструктурного анализа и химическими анализами, чтобы доказать что изменения качества вызываются примесями. Катионно-обменные способности (KOC) Са и Cs изменялись от 2,67 до 8,17 и от 3,29 до 8,77 М.ЭК./100 г соответственно. Селективные анализы растворения и корреляции убедительно доказали, что расширяющиеся минералы 2:1, особенно смектит (1,2-5,9%), обусловили большинство замеченных изменений КОС Са (г = 0,85*). Наружная поверхностная КОС каолинита колеблется от 0 до 1 М.ЭК./100 г. Существенная положительная корреляция (г = 0,90**) между КОС Са и содержанием К-слюды (0-3,9%) указывает на то, что КОС Са может быть связана со степенью выветривания слюды в течение фазы расширения минерала.

Способность удержания Cs $(0,19-1,14 \text{ M.} \text{JK.}/100 \text{ r})$ тесно связана с измеренным по Cs содержанием вермикулита ($r = 0.80^*$) и этим содержанием плюс удельной поверхностью ($R = 0.93^{**}$) или содержанием слюды ($R = 0.86*$). Удержание Cs, по-видимому, связано в основном с присутствием межслойных клиньев в промежутках XY слюда/вермикулит. [N.R.]

Resümee-Sieben Kaoline aus Georgia (südöstliche USA), die von hoch- bis niedrig-qualitativ reichen, wurden mittels Röntgenpulverdiffraktometrie und chemischen Methoden charakterisiert, um festzustellen, daß die Qualitätsunterschiede durch Verunreinigungen hervorgerufen werden. Die Ca- und Cs-Kationenaustauschkapazitäten, (CEC), variierten von 2,67 bis 8,17 bzw. von 3,29 bis 8,77 mÄq/100 g. Selektive Auflösungs- und Korrelationsanalysen zeigen sehr stark an, daß quellfähige 2: 1 Minerale, vor allem Smektit (1,2-5,9%), für die meisten der beobachteten Variationen in der Ca CEC (r = 0,85*) verantwortlich sind. Die CEC der äußeren Oberfläche von Kaolinit reicht von 0-1 mÄq/100 g. Die positive beachtliche Korrelation (r = 0,90**) zwischen der Ca CEC und dem Gehalt an K-Glimmer (0-3,9%) deutet darauf hin, daß die Ca CEC im Zusammenhang stehen könnte mit dem Ausmaß, in dem die Glimmerverwitterung durch ein Stadium eines quellfähigen Minerales geht.

Die Cs-Retentionskapazität (0,19-0,14 mÄq/100 g) stand in engem Zusammenhang mit dem Cs-gemessenen Vermiculitgehalt ($r = 0.80^*$) und mit diesem Gehalt plus spezifischer Oberfläche ($R = 0.93^{**}$) bzw. Glimmergehalt ($\overline{R} = 0.86^*$). Die Cs-Retention scheint vor allem mit der Anwesenheit von Zwischenschichtkeilen an den Glimmer/Vermikulit XY Grenzflächen im Zusammenhang zu stehen. [U.W.]

Résumé—Sept kaolins de Géorgie (Sud Est des E.U.) s'étageant de grade commercial haut à bas ont été caractérisés par diffraction poudrée aux rayons-X et par des techniques chimiques pour établir que la variation en quantité était causée par des impuretés. Les capacités d'échange de cations Ca et Cs (CEC) ont varié de 2,67 à 8,17 et de 3,29 à 8,77 meq/100 g, respectivement. Les analyses de dissolution sélective et de corrélation ont intensément indiqué que les mineraux expansibles 2:1, la smectite en particulier, (1,2-5,9%), étaient responsables pour la plupart des variations observées dans Ca CEC ($r = 0.85$ *). La surface externe CEC de la kaolinite s'étageait de 0 à 1 meq/100 g. La corrélation positive significative (r = 0,90**) entre Ca CEC et le contenu en mica-K (0–3,9%) suggère que Ca CEC peut être apparenté au degré d'altération du mica à travers un stage minéral expansible. La capacité de retention-Cs $(0, 19-1, 14 \text{~meq}/100$ g) était apparentée de près au contenu en vermiculite mesuré Cs ($r = 0.80$ *), et ce contenu plus la surface spécifique $(R = 0.93**)$ ou le contenu en mica $(R = 0.86*)$. La rétention de Cs semblait être principalement apparentée à la présence de parties interfeuillets aux interfaces mica/vermiculite XY. [D.J.]