APPARENT CHARGE HETEROGENEITY IN KAOLINS IN RELATION TO THEIR 2:1 PHYLLOSILICATE CONTENT

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Abstract—Measurements of the differential heats of K-Ca exchange are used to show that 6 groups of sites (ranging from −13.8 to −5.1 kJ/eq and with as many as 4 in any one sample) exist in kaolins that range from 0 to 15% in their 2:1 phyllosilicate content. These heat values, coupled with entropies of exchange, suggest that 0.1–10% vermiculitic, micaceous, and smectitic layers are present, presumably interstratified with kaolinitic layers which are assumed to have no permanent charge. Changes in the activity coefficients of adsorbed K with K saturation confirm these conclusions qualitatively. Thus, f_K values at $x \to 0$ correlate inversely ($r^2 = 0.655$) with the content of vermiculite + partially expanding micas, and x values at maximum f_K indicate the content of vermiculite + nonexpanding mica + partially expanding micas ($r^2 = 0.732$).

Key Words—Cation exchange, Enthalpy, Heat, Kaolin, Smectite, Surface charge.

INTRODUCTION

From measurements of the pH dependence of positive and negative charges in eight kaolin species, Schofield and Samson (1953, 1954) deduced that in suspensions, these minerals can be deflocculated by adding stoichiometric amounts of NaOH, deflocculating anions, Na-montmorillonite, or Na-illite. More importantly, they suggested a method for determining the point of net zero charge and for detecting the presence of very small amounts of 2:1 phyllosilicates that contribute to the permanent negative charge (i.e., pH-independent charge) in these kaolins. Subsequently, Bolland *et al.* (1976) and Mashali and Greenland (1976) used similar methods to determine the charge characteristics of hydrous oxides and kaolinite. These workers, Jepson *et al.* (1976), and Jepson and Rowse (1975), using adsorption isotherms and electron microscopy, concluded that many kaolins have a small permanent charge, independent of pH. Schofield and Samson's measurements showed that a kaolin of unknown origin supplied by Merck did not have a permanent charge.

In view of the importance of the presence of 2:1 phyllosilicates in kaolins for certain ceramic applications and as fillers for natural rubbers (Yvon *et al.*, 1980), attempts have been made to identify such contamination by other physical means, but quantitative estimation has proved difficult. Schofield and Samson (1953, 1954) suggested that an ionic substitution of Al for Si of ~0.25% in the ideal structural formula, $Al_4Si_4O_{10}(OH)_8$, would account for the pH-dependent charge in some kaolinites. To investigate this possibility, Jepson and Rowse (1975) used microprobe analysis to measure Al/Si ratios in individual clay crystals. Georgia kaolinite, with an Al/Si ratio of 0.997 ± 0.018 was shown to be free of Al-for-Si substitution, unlike Blackpool kaolinite from St. Austell which had an Al/Si ratio of 0.967 ± 0.018 (sample A, Table 1). These authors suggested that

kaolinites with Al/Si ratios <0.967 contain separate mineral phases. High-resolution electron microscopy (Lee *et al.*, 1975) showed the random occurrence of "10-Å layer" (mica) ellipsoids in a Georgia kaolinite and "10-Å" and "14-Å layer" (vermiculite) ellipsoids in Frantex B kaolinite, a 'fireclay' type from France.

In the present study, heat measurements of K-Ca exchange, as described by Goulding and Talibudeen (1980) have been performed on six kaolins for the quantitative determination of such impurities.

MATERIALS AND METHODS

The 6 kaolins were selected and supplied, at the request of the authors, by Dr. W. B. Jepson, English Clays Lovering Pochin & Co. Ltd., Cornwall, England, to give a range of 2:1 phyllosilicate impurities determined by X-ray powder diffraction (XRD). The kaolins have been arranged in Tables 1 to 4 in order of increasing impurity content. As reported by W. B. Jepson and P. D. Salt (private communication) the samples were pretreated and their mineral composition determined by XRD as follows:

Separation and pretreatment

Three thousand kilograms of clay from a well-kaolinized stope in a pit was slurried with water and then agitated with an air stream. Unwanted coarse material was separated from finer particles by passing the slurry through a 200 mesh British Standard Sieve screen and then a multistage hydrocyclone to yield clay of <5-μm particles. After filtration, the clay was dried at 50°C to 0.1% weight of water.

X-ray powder diffraction analysis

Powder analysis. A sample holder was filled with dry powder, tapped 30 times, and loaded into a goniometer. Scans were made with divergence and scatter slits set

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to cover the 2θ ranges for (1) kaolinite, mica, and tourmaline, (2) quartz, feldspar, and quartz, and (3) quartz. The tourmaline, quartz, and feldspar concentrations were calculated from peak heights, and the kaolinite and mica concentrations from peak areas.

Smear analysis. Kaolinite, mica, and montmorillonite concentrations were determined from peak heights in an XRD trace of a flat smear which was prepared from a smooth paste of the dry powder with a 20% aqueous solution of glycerol. (XRD powder analysis data were used to calculate the concentrations of tourmaline, quartz, and feldspar.) Mica and kaolinite concentrations agreed well with those determined by XRD powder analysis.

Experimental procedure

The clays were calcium saturated before the heats of the K-Ca exchange reaction and the exchange isotherms were determined (Goulding and Talibudeen, 1980). The methods for determining changes in the differential heat of exchange, $-d(\Delta H_x)/dx$, with fractional K saturation, x, and for relating sites with constant differential heats to specific 2:1 phyllosilicates were described by Goulding and Talibudeen (1980) and Talibudeen and Goulding (1983).

Briefly, the calcium-saturated solid was reacted with increasing amounts of KCl solution in the calorimeter and the heat output after each KCl increment was recorded. The plot of the successive summation, ΔH_x, of these differential heats against x was extrapolated to $x = 1$ to give $\Delta H_{x=1}$, the integral heat of the reaction. This was shown to be the same as ΔH_0, the standard enthalpy of the reaction. An analysis of the ΔH_x:x relationship by a Maximum Likelihood Computer Program (Ross, 1978) confirmed the visual prognosis that, for samples in which more than one different groups of sites occurred, the relationship did not change continuously but consisted of up to 4 linear parts in any one sample. The slopes of these parts denoted groups of sites with constant differential heats of K-Ca exchange which were identified with specific 2:1 phyllosilicates. 'Pure' mica and montmorillonite layers were considered as end members of these phyllosilicates on a scale which was proposed to be related to interlayer expansion by ethylene glycol or glycerol. 'Pure' vermiculite and hydrous mica layers were suggested to be intermediate members. The weight percentage of each 'pure' phyllosilicate in a sample was obtained by relating the x value for that component to its total layer charge per unit weight.

RESULTS AND DISCUSSION

Composition

The data in Table 1 show that the mineralogical composition and the other characteristics of the kaolins differ to various extents. The <2-μm fraction is the main component of these samples, especially samples A and B which, by XRD analysis, are apparently free of 2:1 phyllosilicates, a conclusion not confirmed by the measurements described in this paper. Sample F contains more than twice the amount of the <0.2-μm fraction than the other samples and its cation-exchange capacity (CEC) and surface area are much greater. When heated to 110°C, the residual weights of samples A to E were the same, 0.9953 ± 0.0027 g/g (referred to the original sample at ambient temperature and humidity), but that of sample F was appreciably less. These differences are attributed to the montmorillonite impurity in sample F. Ignition to constant weight at 900°C gave residues of very similar weight for *all* samples, 0.8601 ± 0.0054 g/g. Surface charge densities increase with the concentration of the 2:1 phyllosilicates; however, none of these properties indicate precisely the exact nature and amounts of the '2:1 layer' mineral impurities in these samples.

Integral thermodynamic functions

With the exception of sample E, the ΔG_0 values increase (i.e., become more positive) with increasing 2:1 phyllosilicate content (Table 2). The ΔS_0 values show that replacing Ca by K on exchange sites introduces the highest degree of order in samples D and F which have appreciable amounts of hydrous micas, with vermiculite and with montmorillonite, respectively. Sample B has smaller amounts of these minerals, hence a less negative ΔS_0 value, than samples D and F. Notably, sample E exhibits a positive entropy change of 3.3 J/K/eq, a property observed for pure muscovite mica (Goulding and Talibudeen, 1980). Samples A, B, and C, of low 2:1 layer mineral content, give similar values for these standard functions.

The ΔG_0 and ΔH_0 values observed for these kaolins are more negative than those for the smectites reported earlier (Talibudeen and Goulding, 1983), especially the ΔG_0 values. Also, the ΔS_0 values are more positive for the kaolins than for the smectites, which may signify that the entropic contribution of the mica component of the kaolins (reported for muscovite mica by Goulding and Talibudeen in 1980) is dominant. The random and uncommon interstratification of single 2:1 layers between kaolinite layers could also contribute to this difference.

Differential heats of Ca → K exchange

Six main groups of sites, as defined by exothermic differential heats $[-d(\Delta H_x/dx)]$ were noted, ranging from 13.6 to 5.1 kJ/eq (Table 3). As in previous work (Goulding and Talibudeen, 1980; Talibudeen and Goulding, 1983), these groups can be assigned to vermiculite (13.6 kJ/eq), true mica (10.9 kJ/eq), hydrous micas (9.4 and 8.2 kJ/eq), and montmorillonite (7.2 and 5.1 kJ/eq) on the assumption that kaolinite layers have no permanent negative charge. The amounts of these 2:1 phyllosili-

Table 1. Physical and mineralogical composition of six kaolins.

Sample	Source[1]	2:1 phyllosilicate content by XRD[2] (%)	Particle size fraction in μm			Dry weight at		Cation exchange capacity		Surface area of Ca-clay by EG vapor sorption (m²/g)	Surface charge density of Ca-clay ($\mu eq/m^2$)
			<0.2	0.2–2.0 (%)	>10	100°C	900°C (g/g of Ca-clay)	K-clay	Ca-clay ($\mu eq/g$)		
A	'Blackpool' St. Austell Batch 2	0	2	80	0	0.9968	0.8578	17	17	42	0.405
B	'Jordan' Georgia, USA Batch 2	m = trace	5	75	1	0.9901	0.8530	25	25	48	0.521
C	'Blackpool' St. Austell Batch 3	m = 3	<10 μm = 99%		1	0.9957	0.8611	15	30	50	0.600
D	'Lee Moor' Devon Batch 1	m = 5	4	66	1	0.9975	0.8673	25	30	46	0.552
E	'Blackpool' St. Austell Batch 4	m = 11	3	70	1	0.9963	0.8664	15	30	48	0.625
F	'Cholwich town' Devon Batch 1	m = 10 mm = 5	10	60	1	0.9385	0.8540	60	145	150	0.967

[1] Courtesy of W. B. Jepson, English Clays Lovering Pochin and Co. Ltd. Batch numbers in Column 2 indicate different sampling times. In Column 3, m = mica; mm = montmorillonite; v = vermiculite.

[2] See text for description of technique.

cates, calculated on this basis (Table 4), suggest that, despite the XRD evidence (Table 1), all the kaolins contain small amounts of phyllosilicates. If an ideal kaolinite has no ionic substitution of Al for Si in the tetrahedral layer, or of Mg for Al in the octahedral layer (and hence no permanent negative charge), none of the kaolins described in this paper can be classed as ideal kaolinites.

The predicted expansion by ethylene glycol treatment from 'none' to 'full,' given in the headings to columns 2 to 7 (Table 4), relate to the $-d(\Delta H_x)/dx$ values ascribed to six groups of sites in smectites by Talibudeen and Goulding (1983) when the differential heats of K-Ca exchange sites are related to the expandability of interlayer space by adsorption of water and ethylene glycol. The '10.9 kJ/eq' sites were assigned to non-expanding, 'true' mica layers, the '9.4 kJ/eq' and '8.7 kJ/eq' sites to partially expanding, hydrous mica layers, and the '7.5,' '6.6,' and '5.7 kJ/eq' sites to fully expanding, 'true' montmorillonite layers.

These results generally agree with the approximate 2:1 phyllosilicate composition given in column 3 of Table 1, but they quantify the compositions in a manner that has not been possible hitherto by other methods at such low levels. Thus, sample A is the purest in kaolinite content, although it contains vermiculite, mica, and hydrous mica layers totalling 0.9% (w/w). Sample D also contains 0.4% vermiculite layers, but the mica contents of samples C to F are much smaller than those given by XRD suggesting that the XRD results are un-

reliable. On the other hand, sample F appears to be the most impure sample by both XRD and differential enthalpy measurements, although its mica content seems to be overestimated by XRD also. It is pertinent to point out that samples A and B are considered not to contain any 2:1 layer minerals, based on viscosity measurements of aqueous suspensions to which small amounts of 2:1 layer minerals had been added (private communication: W. B. Jepson).

Activity coefficient of adsorbed potassium

Changes in the activity coefficient, f_K, of adsorbed K with K saturation of the negative charge, x_K, are reliable though qualitative indicators of mineralogical composition (Talibudeen, 1971; Goulding and Talibu-

Table 2. Standard free energy, enthalpy and entropy of the reaction: $Ca-(clay)_2 + 2K^+ \rightarrow 2K-clay + Ca^{2+}$.

Sample	$-\Delta G_0$ (kJ/eq)	$-\Delta H_0$[1] (kJ/eq)	$-\Delta S_0$ (J/K/eq)
A	8.0	10.1	6.9
B	6.7	8.0	4.3
C	7.4	9.3	6.3
D	5.3	10.0	15.5
E	9.0	8.0	−3.3
F	3.9	7.0	10.2
St. Austell	4.4	9.1	14.2

[1] $\Delta H_0 = \Delta H_{x=1}$, extrapolated value by calorimetry.

Table 3. Groups of sites with constant differential heats of Ca → K exchange and the amount of CEC apportioned to each group.

Sample	CEC of Ca-form (μeq/g)	$-d(\Delta H_x)/dx$ (kJ/eq) (K exchange in CEC (μeq/g))					Residual mean squares (kJ/eq)$^2 \times 10^3$ (degrees of freedom)	
							Line	Curve
A	17	13.7 (3.3)	10.8 (3.9)	—	8.7 (9.8)	—	—	0.669 (11)	8.635 (14)
B	25	—	—	9.4 (9.0)	—	7.2 (16.0)	—	0.538 (12)	1.290 (13)
C	30	—	11.0 (12.3)	—	8.2 (17.7)	—	—	0.319 (13)	3.854 (14)
D	30	13.4 (9.7)	—	9.4 (6.0)	8.0 (14.3)	—	—	0.539 (12)	4.096 (15)
E	30	—	—	9.1 (7.1)	8.0 (13.0)	7.2 (9.9)	—	0.167 (10)	0.654 (13)
F	145	—	—	9.6 (14.9)	8.2 (20.2)	7.1 (66.0)	5.1 (43.9)	0.278 (13)	2.377 (18)
Mean		13.6	10.9	9.4	8.2	7.2	5.1		
Standard error of mean		±0.2	±0.2	±0.2	±0.2	±0.2	—		

deen, 1980). Thus, in the f_K:x relationships (Figure 1), the x value when f_K is at a maximum corresponds with sites having the highest $-d(\Delta H_x)/dx$ values. These comprise non-expanding mica, and partially expanding vermiculite + hydrous mica. The x_K value for the maximum f_K correlates significantly with the total content of the mica, vermiculite, and '¼ expansion' hydrous mica ($r^2 = 0.732$; DF = 5).

Likewise, f_K values at $x_K \to 0$ indicate crystal lattice stability of the K 'fixing' minerals (Talibudeen, 1971), high f_K values denoting low stability, and low ability to 'fix' K and *vice versa*. It is proposed here that *expanding* 2:1 phyllosilicates with the highest '$-d(\Delta H_x)/dx$' values, i.e., vermiculite and the '¼' and '½' expansion hydrous micas, are responsible for K fixation. Thus, a significant inverse correlation was seen between f_K (when $x_K \to 0$) and the summed contents of these minerals in Table 4 ($r^2 = 0.655$; DF = 5).

CONCLUSIONS

It is not possible from these measurements of changes in the differential heats of K-Ca exchange with K saturation to distinguish between the random occurrence of such small amounts of 2:1 phyllosilicates in kaolinite as microscopic volumes of separate phases or as 2:1 layers interstratified with the 1:1 kaolinite layers. The high resolution electron microscopy evidence of Lee *et al.* (1975) and the electron microscopy microprobe analysis work of Jepson and Rowse (1975) suggest that both possibilities exist. The predominance of one over the other must result from the specific conditions during the genesis of each kaolinite, i.e., by the weathering of mica or by formation in mixtures poor in silica. However, these differential enthalpy measurements are unique in the precision with which they can assay such small amounts of 2:1 layer minerals in kaolinite, as also

Table 4. Kaolinite and 2:1 phyllosilicate content (%) of kaolin samples.[1]

Sample no.	Mineral (predicted expansion by EG treatment)					
	Kaolinite (None)	Mica (None)	Vermiculite (Quarter)	Hydrous mica		Montmorillonite (Full)
				(Quarter)	(Half)	
A	99.14	0.16	0.13	—	0.58	—
B	98.32	—	—	0.45	—	1.23
C	98.47	0.49	—	—	1.04	—
D	97.78	—	0.39	0.30	0.84	—
E	98.12	—	0	0.36	0.77	0.76
F	89.62	—	0	0.75	1.19	8.45
Theoretical layer charge (μeq/g)	—	2511	2460	(2000)[2]	(1700)[2]	1300

[1] Calculated on the basis of the theoretical layer charge by ionic substitution of Al for Si and Mg for Al in 2:1 phyllosilicates.
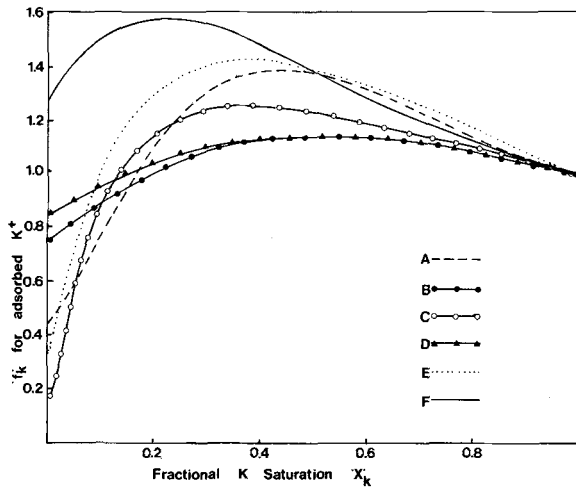[2] Interpolated values.

Figure 1.   Change in the activity coefficient of adsorbed K, f_K, with K saturation of the exchangeable layer charge, x_K. A–F = different kaolins as listed in Table 1.

those of micaceous minerals in the smectites (Talibudeen and Goulding, 1983).

ACKNOWLEDGMENTS

The kaolinite samples and their descriptive analyses (asterisked in Table 1) were supplied by Dr. W. B. Jepson of English Clays Lovering Pochin & Co. Ltd., to whom grateful acknowledgment is made for helpful discussion as well.

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Резюме—Использовались измерения величин дифференциальной теплоты обмена К-Са для показания, что в каолинах, содержащих от 0 до 15% 2:1 филлосиликатов, находится 6 различных групп мест (от −13,8 до −5,1 кдж/экв и в количестве до 4 в одном образце). Эти величины, связанные с энтропией обмена, указывают на присутствие 0,1 до 10% вермикулитовых, слюдовых и смектитовых слоев переслаивающихся, вероятно, с каолинитовыми слоями, которые не имеют постоянного заряда. Изменения коэффициентов активности адсорбированного К в зависимости от насыщения К подтверждают кочественно эти выводы. В таком случае, величины f_K при x → 0 обратно пропорциональны (r² = 0,655) содержанию вермикулита + частично-расширяемых слюд. Величины x при максимальном f_K указывают на содержание вермикулита + нерасширяемые слюды + частично-расширяемые слюды (r² = 0,732). [Е.С.]

Resümee—Messungen der differentiellen Wärme des K-Ca-Austausches zeigten gewöhnlich, daß 6 Arten von Plätzen (von −13,8 bis −5,1 kJ/Äqu und mit bis zu 4 Arten in einer Probe) in Kaolinen vorkommen, die von 0–15% ihres 2:1 Phyllosilikatgehaltes ausmachen. Diese Wärmewerte zusammen mit den Austauschentropien deuten darauf hin, daß 0,1–10% vermiculitische, glimmerartige und smektitische Lagen vorhanden sind, wahrscheinlich in Wechsellagerung mit kaolinitischen Lagen, von denen man annimmt, daß sie keine permanente Ladung haben. Veränderungen in den Aktivitätskoeffizienten f_K von adsorbiertem Kalium bei K-Sättigung bestätigen qualitativ diese Schlußfolgerungen. Daher sind die f_K-Grenzwerte für Molenbruch x → 0 umgekehrt proportional (r² = 0,655) dem Gehalt an Vermiculit + teilweise expandierbaren Glimmer, und die x-Werte bei maximalem f_K zeigen den Gehalt an Vermiculit + nicht expandierbarem Glimmer + teilweise expandierbarem Glimmer (r² = 0,732) an. [U.W.]

Résumé—Des mesures des chaleurs différentielles de l'échange K-Ca sont employées pour montrer que 6 groupes de sites (s'étageant de $-13,8$ à $-5,1$ kJ/eq et avec jusqu'à 4 dans un échantillon donné) existent dans des kaolins qui s'étagent de 0 à 15% quant à leur contenu 2:1 en phyllosilicate. Ces valeurs de chaleur, accouplées avec des entropies d'échange, suggèrent que $0,1$–10% de couches vermiculitiques, micacées et smectitiques sont présentes, que l'on présume être interstratifiées avec des couches kaolinitiques suposées être sans charge permanente. Des changements dans les coéfficients d'activité de K adsorbé avec saturation de K confirment qualitivement ces conclusions. Ainsi, les valeurs f_K à $x \rightarrow 0$ sont inversément apparentées ($r^2 = 0,655$) au contenu en vermiculite + micas à expansion partielle, et les valeurs x à f_K maximum indiquent le contenu en vermiculite + mica non-expansible + micas à expansion partielle ($r^2 = 0,732$). [D.J.]