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CHARGE HETEROGENEITY IN SMECTITES

OSCAR TALIBUDEEN AND KEITH W. T. GOULDING

Rothamsted Experimental Station, Harpenden
Hertfordshire AL5 2JQ, United Kingdom

Abstract—The heterogeneity of sites for Ca→K exchange was examined by microcalorimetry in the <0.2-μm fractions of some selected smectites. Six groups of sites, ranging in exothermic exchange enthalpy ($-d(\Delta H_x)/dx$) from 5.7 to 10.9 kJ/eq were identified. In Wyoming bentonites, only three groups with enthalpies of 5.7 to 7.5 kJ/eq were distinguished, although in the 0.2–1.0-μm fraction, a 10.7-kJ/eq group was also observed. Redhill and Camp Berteau smectites contained, in addition, groups with enthalpies of 8.7–10.9 kJ/eq, but a New Mexico sample only had groups with the higher values. Thus, the exchange enthalpies of four main groups of sites (reclassified from those observed) appear to be inversely related to the extents of interlayer expansion in the samples by the adsorption of polar molecules. Consequently, a 'true montmorillonite,' such as a <0.2-μm Wyoming bentonite, contains only fully expanding layers with $-d(\Delta H_x)/dx$ values between 5.7 and 7.5 kJ/eq. As such, it is less heterogeneous and should have a much greater swelling capability than Camp Berteau montmorillonite which has, in addition, groups with exchange enthalpies of 8.7 and 10.3 kJ/eq.

Key Words—Cation exchange, Enthalpy, Smectite, Surface charge, Swelling.

INTRODUCTION

Goulding and Talibudeen (1980) reported recently that six groups of homoenergetic sites can be distinguished in aluminosilicates and soils when changes in the differential enthalpy of exchange, $-d(\Delta H_x)/dx$, are measured calorimetrically. The analysis of the changes in $-d(\Delta H_x)/dx$ with increasing K saturation, x, suggested a stepwise Ca→K exchange in which groups with the more negative enthalpies were saturated with K at the lower K concentration. Where expanding layer minerals were encountered, the differential entropy, $-d(\Delta S)/dx$:x, relationship predicted that in each group of sites, Ca→K exchange increased the structural order *in that group* to a maximum until the group was fully saturated with K. The $-d(\Delta S)/dx$ value then immediately changed to a minimum corresponding with maximum structural disorder in the next group. This process repeated itself until all groups of sites were saturated with K.

Lee *et al.* (1975) examined two kaolinites by high resolution electron microscopy and demonstrated the presence of occluded islands of micaceous layers interleaved with kaolinite layers, such islands accounting for the K content of the samples. This observation suggests that impurities that bind K strongly in a more inert layer-silicate matrix occur in discontinuous random interstratification with the parent body. Such impurities have therefore been difficult to separate and identify. For the montmorillonites, no such visual evidence is available at present, but differences in size distribution, morphology and orientation of particles, charge density of the layers, interparticle swelling in water, intraparticle expansion on adsorbing polar molecules, organic cations, and water, and the distribution of Na, Mg, and Ca in fine and coarse clay fractions have all been used to characterize smectites from various sources (e.g., Byrne, 1954; Roberson *et al.*, 1968; Lagaly and Weiss, 1976).

Using the microcalorimetric method described previously (Talibudeen *et al.*, 1977), the present study characterizes the surface charge distribution of six 'standard' montmorillonites with greater precision than has been achieved hitherto by other techniques, and thus defines experimentally a fundamental property of a 'true' montmorillonite. The initial comparison is between different samples of Wyoming bentonite and then between single samples of montmorillonites from different locations. Finally, the results are related to those obtained by other workers using different techniques.

MATERIALS AND METHODS

The six smectites examined are three samples of Wyoming bentonite A, B, and C, from two consignments obtained from F. W. Berk & Co. over a gap of ca. 25 years (presumably from different pits), samples from Redhill, Surrey, England, and Camp Berteau, Morocco, obtained from A. H. Weir (Weir, 1965), and 'Montmorillonite No. 11' from Santa Rita, New Mexico, supplied by Ward's Natural Science Establishment. For all samples except the New Mexico smectite, chemical analyses and layer charge distribution were given by Weir (1965). Properties of all samples relevant to this study are given in Table 1.

Preparation of clay fractions. The <0.2-μm fractions of all samples and the 0.2–1.0-μm fraction of the Wyoming bentonites were separated as follows: the crushed clay was saturated with Na by washing with 1 M NaCl. The >0.2-μm fraction was sedimented from a 1% salt-

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free suspension by centrifuging. The <0.2-μm fraction was flocculated from the supernatant suspension by making it one molar in NaCl. The flocculate was washed with water and absolute alcohol until free of chloride, then with petroleum ether, and air dried. The amounts of the <0.2-μm fraction in the untreated samples were: Wyoming bentonite (mean of A, B, and C) 49%, Redhill 65%, Camp Berteau 24%, and New Mexico 19%. The 0.2–1.0-μm fraction of the Wyoming bentonites was similarly washed and dried.

Ca-saturation. The Na-clay was saturated with Ca by washing with 0.5 M $CaCl_2$ until free of Na and processed as described above to an air-dry powder.

Surface area. Surface areas of the Ca-saturated clays were determined by the vapor phase adsorption of ethylene glycol.

Thermodynamic parameters. For Ca→K exchange, differential and integral enthalpies, $-d(\Delta H_x)/dx$ and ΔH_x, respectively, were determined at 30°C using a modified LKB microcalorimeter (Talibudeen *et al.*, 1977; Goulding and Talibudeen, 1980). Standard free energies, ΔG_0, were determined by the 'Gaines and Thomas' analysis of the exchange isotherms (Goulding and Talibudeen, 1980). These values were determined from measurements with Ca-saturated smectites which were pre-equilibrated with water in a paste to ensure that their negatively charged sites were accessible to K ions for the exchange reaction.

RESULTS AND DISCUSSION

Gross properties

Large differences in the gross properties of the Ca-saturated smectites can be seen from the data listed in Table 1. Similar differences were observed in the amounts of <0.2-μm clay in the untreated samples, except for the unusually small quantity in the Wyoming bentonites, i.e., Redhill > Wyoming bentonite > Camp Berteau > New Mexico. The dehydration weights, cation-exchange capacities (CEC), and surface areas of the <0.2-μm fraction of the three Wyoming bentonites were similar. The coarse fraction had a larger dehydration weight and a similar surface area, but a much smaller CEC, resulting in its much smaller surface charge density (SCD).

The dehydration weights of the <0.2-μm fractions of the Redhill, Camp Berteau, and New Mexico smectites were greater than those of the Wyoming bentonites. The CEC of the seven materials were in the order New Mexico > Camp Berteau = Redhill > 'fine' Wyoming bentonites ≫ 'coarse' Wyoming bentonite. The surface area of the Camp Berteau smectite (764 m^2/g) was larger than those of the other materials (674–698 m^2/g). Thus, the trend of the derived SCD is New Mexico > Camp Berteau = Redhill = 'fine' Wyoming bentonites ≫ 'coarse' Wyoming bentonite.

The standard thermodynamic functions (Table 2) for the four Wyoming bentonite samples were generally similar except that the ΔH_0 and ΔS_0 values for the coarse Wyoming bentonite A were more positive than those for the fine fractions of bentonites A, B, and C. This is in keeping with the smaller SCD of the coarse fraction and suggests that Ca→K exchange had less effect on the re-ordering of the silicate layers of the coarser material than of the finer material.

The ΔG_0 values for the Redhill, Camp Berteau, and New Mexico materials were more negative than those for the Wyoming bentonite, the order of K preference being New Mexico > Camp Berteau > Redhill. However, the ΔH_0 values for the Redhill and Camp Berteau samples were similar to those for the three 'fine' Wyoming bentonites so that their calculated ΔS_0 values were more positive (mean −14.37 and −17.84 J/K/eq, respectively). This difference in entropy change indicates that with K-saturation, the rearrangement of silicate sheets, adsorbed cations, and interlayer water was less regular in the Redhill and Camp Berteau samples than in the 'fine' Wyoming bentonites. The ΔS_0 value for 'coarse' Wyoming bentonite was essentially the same as those for the Redhill and Camp Berteau materials, suggesting that the forces binding adjacent silicate sheets

Table 1. Description of Ca-saturated montmorillonites.[1]

Sample	Particle size (μm)	Weight (g) on dehydration at 105°–110°C	Weight (g) on dehydration at 900°C	Surface area by EG vapor sorption (m^2/g)	CEC (μeq/g)	Surface charge density (μeq/m^2)
Wyoming bentonite A	0.2–1.0	0.922	0.874	698	700	1.00
Wyoming bentonite A	<0.2	0.833	0.766	689	1050	1.52
Wyoming bentonite B	<0.2	0.834	0.771	678	1050	1.55
Wyoming bentonite C	<0.2	0.834	0.766	689	1000	1.52
Redhill smectite	<0.2	0.899	0.827	698	1120	1.60
Camp Berteau smectite	<0.2	0.894	0.819	764	1150	1.50
New Mexico smectite	<0.2	0.903	0.822	674	1350	2.00
Mean standard error	—	—	—	13	29	0.15

[1] Analyses are given per gram of clay dried at 40°C.

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Table 2. Standard thermodynamic parameters for Ca→K exchange.

Clay	$-\Delta G_0$ (kJ/eq)	$-\Delta H_0$ (kJ/eq)	$-\Delta S_0$ (J/K/eq)
Wyoming bentonite A (0.2–1.0 μm)	1.32	6.07	15.66
Wyoming bentonite A	1.71	6.59	16.10
Wyoming bentonite B	1.46	6.95	18.11
Wyoming bentonite C	1.14	6.99	19.30
Mean	1.41	6.65	17.29
Redhill smectite	1.88	6.41	14.94
Camp Berteau smectite	2.71	6.89	13.79
New Mexico smectite	3.88	9.28	17.81
Mean standard error	±0.29	±0.22	±1.62

The standard enthalpy $-\Delta H_0$ is taken to be equal to $\Delta H_{x=1}$, measured by microcalorimetry.

together (and also their associated cations and water molecules) in the clay crystallites were similar. By contrast, the ΔG_0 and ΔH_0 values for the New Mexico sample were much more negative than for the 'fine' Wyoming bentonites so that their calculated ΔS_0 values were similar. Thus, the enthalpic factor was the driving force for Ca→K exchange in the New Mexico sample, possibly because of its higher SCD.

Diffuse double layer theory, which considers only coulombic nonspecific interactions between cations and the charged surface, predicts that K selectivity in Ca→K exchange should decrease with increasing SCD. This type of K selectivity has been observed experimentally in work with soil series selected for contrasting texture and mineralogical composition of their clay fractions. However, Weir (1965) found that the K retained by six montmorillonites, against exchange by 1 M ammonium acetate, increased with the charge on their silicate sheets. Such retention of K may be related to K selectivity so that Weir's evidence probably highlights the importance of specific interactions between cations and the surface, which is supported in the present work by the comparative series for

$-\Delta G_0$: New Mexico > Camp Berteau > Redhill = Wyoming bentonites;
$-\Delta H_0$: New Mexico ⩾ Camp Berteau = Redhill = Wyoming bentonites;
SCD: New Mexico > Camp Berteau = Redhill = 'fine' Wyoming bentonites > 'coarse' Wyoming bentonite A.

However, as stated above, the structural order of the layers (which affects entropies of exchange) is equally important, cf. the 'coarse' Wyoming bentonite and Camp Berteau materials. Thus, a complex relationship between coulombic, specific, and entropic forces determines overall K selectivity, rather than any single factor.

Differential heats of Ca→K exchange

An analysis of the $-d(\Delta H_x)/dx$:x relationship by an iterative method (Goulding and Talibudeen, 1980) identified regions of constant $-d(\Delta H_x)/dx$. (Statistical residual-mean squares for 'straight lines' and 'single curve'

Table 3. Groups of sites with constant differential enthalpies of Ca→K exchange and the amount of cation-exchange capacity apportioned to each group.

Clay	CEC of Ca form (μeq/g)	$-d(\Delta H_x)/dx$ (kJ/eq) (amount in μeq/g of CEC)						Residual mean square (degrees of freedom) $(kJ/eq)^2 \times 10^3$	
								Lines	Curve
Wyoming bentonite A (0.2–1.0 μm)	700	10.70 (40)	—	—	—	6.50 (164)	5.20 (496)	0.239 (20)	1.848 (23)
Wyoming bentonite A	1050	—	—	—	7.31 (155)	6.43 (895)	—	0.166 (11)	0.578 (11)
Wyoming bentonite B	1050	—	—	—	7.80 (279)	6.80 (771)	—	0.246 (13)	0.401 (13)
Wyoming bentonite C	1000	—	—	—	7.62 (179)	6.85 (821)	—	0.542 (16)	1.024 (16)
Redhill smectite	1120	—	9.44 (93)	—	7.49 (309)	—	5.77 (718)	0.073 (10)	0.087 (12)
Camp Berteau smectite	1150	10.26 (53)	—	8.65 (207)	7.43 (447)	—	6.06 (443)	0.139 (8)	0.230 (12)
New Mexico smectite	1350	11.73 (246)	–	8.74 (1104)	—	—	—	0.243 (12)	0.850 (12)
Mean $-d(\Delta H_x)/dx$		10.9	9.4	8.7	7.5	6.6	5.7		
Standard error of mean	—	0.75	—	0.06	0.19	0.21	0.44		

Unless specified otherwise, all samples are <0.2 μm particle size.

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Table 4. Percentage of layer charge for various extents of interlayer expansion by water or ethylene glycol predicted by enthalpy measurements.

	Predicted expansion (by molecular adsorption)					
				Full (bimolecular)		
				High	Medium	Low
Clay	None	Quarter (semimolecular)	Half (unimolecular)	K-selectivity		
Wyoming bentonite A 0.2–1.0 μm	5.7 (1.59)	—	—	—	23.4	70.9
Wyoming bentonite A	—	—	—	14.8	85.2	—
Wyoming bentonite B	—	—	—	26.6	73.4	—
Wyoming bentonite C	—	—	—	17.9	82.1	—
Redhill smectite	—	8.3 (3.70)	—	27.6	—	64.1
Camp Berteau smectite	4.6 (2.11)	—	18.0 (8.24)	38.9	—	38.6
New Mexico smectite	18.2 (9.79)	—	81.8 (44.0)	—	—	—

The percentages (w/w) of true and hydrous mica layers are based on the theoretical K content of 'true mica' layers of 2511 μeq/g. Unless otherwise specified, all samples are <0.2 μm particle size.

fits are given in Table 3.) Such a separation is a much more precise guide to the similarities and differences between these so-called 'standard' montmorillonites than their gross physicochemical properties. Six such groups were identified with significantly different mean $-d(\Delta H_x)/dx$ values of 10.9, 9.4, 8.7, 7.5, 6.6, and 5.7 kJ/eq. The 10.9-kJ/eq group is tentatively assigned to nonexpanding 'true mica' layers, the 9.4-kJ/eq and 8.7-kJ/eq groups to partially expanding 'hydrous mica' layers, and the 7.5-kJ/eq, 6.6-kJ/eq, and 5.7-kJ/eq groups to fully expanding 'true montmorillonite' layers (Table 4).

Odom and Low (1978) used a similar classification when relating the b dimensions of the <0.2-μm fractions of six Na-saturated montmorillonites to their specific surface areas and to the mass ratio (water adsorbed at 42.6 cm water tension)/(montmorillonite). They concluded that for these materials with a CEC range of 660–1150 μeq/g, the fraction of unexpanded layers at a water tension of 42.6 cm was constant at a value of 0.18, and the fraction of partially expanded layers was not significantly different from 0. Although these results cannot be compared precisely with the present results, they provide some support for the mechanisms described in our hypothesis, which was evolved to relate the present results to the differences in the expandibility of various montmorillonites on adsorption of water and ethylene glycol. Odom and Low (1978) found that the distribution of unexpanded, partially and fully expanded layers in the Otay and Cameron montmorillonites (SCD > 2.0 μeq/m^2) was similar to that for Belle Fourche and Upton montmorillonites (SCD ~ 1.0 μeq/m^2). A similar comparison by our differential enthalpy measurements between, for example, the New Mexico smectite (SCD = 2.0 μeq/m^2) and the Upton montmorillonite (SCD = 1.50 μeq/m^2), suggests that Odom and Low's conclusion is most unlikely.

Tables 3 and 4 show that the 'fine' fraction of the Wyoming bentonites are similar in that they contain similar amounts of fully expanding layers having high and medium K-binding strength, a conclusion based on the groups with constant $-d(\Delta H_x)/dx$ identified in them. We propose that smectites composed only of such a distribution of K-adsorbing groups should be classified as 'true' montmorillonites, and suggest that this is the most precise definition of a 'true montmorillonite.' The 'coarse' Wyoming bentonite A is clearly differentiated from the fine materials in having 1.59% (w/w) of true mica layers (=5.7% of its CEC) and a different distribution of 'true' montmorillonite layers. The mica layers increase progressively from 3.7% in the Redhill, 10.4% in the Camp Berteau, to 53.8% in the New Mexico samples when comparing the fine fractions. Thus, the <0.2-μm fraction of Wyoming bentonite may be regarded as a 'true' montmorillonite and taken as a reference standard. We suggest that the group with the smallest K-binding strength, i.e., a $-d(\Delta H_x)/dx$ value of 5.20 kJ/eq found in the 'coarse' Wyoming bentonite, occurs on very thin sheets of the 'true' montmorillonite that are so firmly wrapped round the large particles that they cannot be separated into the <0.2-μm fraction by our fractionation procedure. The gradation of binding strength into these three cateogries of fully expanding layers is likely to be the result of 'edge' and 'planar' effects of three degrees of specificity for K, incorporating, amongst other properties, different extents of layer curvature.

The New Mexico sample is exceptional in many ways,

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in CEC, SCD (Table 1), ΔG_0 and ΔH_0 values (Table 2), in the absolute and relative distributions of $-d(\Delta H_x)/dx$ values (Table 3), and hence in the distribution of expandible and nonexpandible layers (Table 4). In particular, the $-d(\Delta H_x)/dx$ value of 11.73 kJ/eq for true mica layers is about 11% more than we have found for such layers in this work and previously (Goulding and Talibudeen, 1980, Table 3). This difference may be caused by a micaceous component with an abnormal SCD (cf. Table 1). If so, Tables 3 and 4 suggest that *all* of the CEC, but only 54% of the weight, is accounted for by nonexpanding and partially expanding charged layers and that 46% of the silicate sheets are uncharged.

Classification of the heterogeneity of charge

Irregular periodicity along the c axis in piperidine and dodecylamine complexes of montmorillonite suggest that montmorillonites are made up of different mixed-layer sequences of sheets of various chemical compositions, or, that they incorporate minor structural irregularities (Byrne, 1954). Using alkyl ammonium ions of increasing chain length, Lagaly and Weiss (1976) characterized about 200 montmorillonites into six groups based on layer charge distribution. Using a similar technique, Stul and Mortier (1974) found that Wyoming bentonite had 9 and Camp Berteau montmorillonite 6 interlayer-cation density classes, the former being the most heterogeneous of the six montmorillonites examined. They found that no layer-charge density class dominated the physicochemical properties of these materials and that ionic substitution was discontinuous, its contribution to the gross SCD being different for each sample.

Čičel and Machajdik (1981) examined 12 montmorillonites by X-ray powder diffraction (XRD) after NH_4- and K-saturation and subsequent adsorption of water and ethylene glycol (EG). Three types of "montmorillonite layers" were observed: nonexpanding, expanding to one layer, and expanding to two layers of adsorbed molecules (cf. Table 4). We suggest that the groups of constant $-d(\Delta H_x)/dx$ evaluated in the present study are related to the zonal expansion of interlayer space and that only fully expanding layers, relating to the three smallest values of $-d(\Delta H_x)/dx$ in Table 3, can be attributed to 'true' montmorillonite layers. Čičel and Machajdik (1981) also observed a 'one EG-layer' complex in all of their samples, similar to our observations with montmorillonites, other than Wyoming bentonite, where the $-d(\Delta H_x)/dx$ predicted substantial proportions of partially expanding layers. These authors also demonstrated this heterogeneity of charge by the expansion of some unexpanded 10-Å layers by EG but not by water. Their XRD results led them to conclude that "there appears to be a prevailing random distribution of layers in the structure" and that "it is sometimes difficult to decide whether a sample formed by (the) three kinds of layers represents a zonal or (an) ordered mixed layering."

Thus, although the surface charge of smectites can be split into about 10 different classes by other techniques, none of which are said to dominate their physicochemical properties, our work demonstrates that three *major* groups of homoenergetic sites exist which affect these properties, especially Ca→K exchange behavior and inter- and intraparticle swelling.

Tributh (1975) suggested, from XRD work, that the charge heterogeneity in montmorillonites from bentonite deposits does not change appreciably with particle size. Our results (Table 4) contradict this for Wyoming bentonite demonstrating yet again that current XRD techniques are not sensitive enough to pick up such differences (see also Goulding and Talibudeen, 1980). However, Tributh also asserted that in soil clays, charge heterogeneity does change considerably with particle size, as we found previously (Goulding and Talibudeen, 1979). We are investigating this further with several contrasting soils by microcalorimetry.

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Резюме—Исследовалась гетерогенность мест обмена Ca→K путем микрокалориметрии во фракциях размером <0,2 μм некоторых отобранных смектитов. Определено шесть групп мест в диапазоне экзотермической обменной энтальпии ($-d(\Delta H_x)/dx$) от 5,7 до 10,9 кДж/экв. В бентонитах из Лаеминга наблюдались только три группы с энтальпиями от 5,7 до 7,5 кДж/экв, хотя во фракции размером 0,2–1,0 μм была найдена также группа с энтальпией 10,7 кДж/экв. Смектиты Редгилл и Камп Берто дополнительно содержали группы с энтальпиями от 8,7 до 10,9 кДж/экв, но образец из Нового Мексика содержал только группы с высшими значениями. Поэтому, кажется, что обменные энтальпии четырех главных групп мест (переклассифицированных из наблюдаемых) являются обратносвязанными со степенью межслойной экспансии, возникающей из адсорбции полярных молекул. Следовательно, "настоящий монтмориллонит," такой как <2 μм бентонит из Лаеминга содержит только полностью набухаемые слои со значенями $-d(\Delta H_x)/dx$ между 5,7 и 7,5 кДж/экв. Как таковой этот бентонит является менее гетерогенным и должен иметь намного большую набухающую способность, чем монтмореллонит из Камп Берто, который кроме того имеет группы с обменными энтальпиями от 8,7 до 10,3 кДж/экв. [E.C.]

Resümee—Es wurde die Heterogenität der Ca→K-Austauschplätze in der Fraktion <0,2 μm einiger ausgewählter Smektite mittels Mikrokalorimetrie untersucht. Dabei wurden sechs Arten von Plätzen identifiziert, deren exotherme Austauschenthalpie ($-d(\Delta H_x)/dx$) von 5,7 bis 10,9 kJ/äquivalent reicht. In den Bentoniten von Wyoming wurden nur drei Arten unterschieden mit Enthalpien von 5,7–7,5 kJ/äquivalent. In der Fraktion 0,2–1,0 μm wurde zusätzlich eine Art mit 10,7 kJ/äquivalent beobachtet. Smektite von Redhill und Camp Berteau enthielten zusätzlich Arten mit Enthalpien von 8,7–10,9 kJ/äquivalent. Eine Probe aus New Mexico enthielt nur Arten mit höheren Werten. Es scheinen sich daher die Austauschenthalpien der vier Hauptarten von Plätzen (die aus den beobachteten Arten neu klassifiziert wurden) umgekehrt proportional zum Quellvermögen der Proben bei der Adsorption polarer Moleküle zu verhalten. Infolgedessen enthält ein "echter" Montmorillonit, wie z.B. die Fraktion <0,2 μm des Bentonites von Wyoming, nur vollständig expandierte Lagen mit $-d(\Delta H_x)/dx$-Werten zwischen 5,7 und 7,5 kJ/äquivalent. Als solcher ist er weniger heterogen und sollte eine viel größere Quellfähigkeit haben als der Camp Berteau Montmorillonit, der zusätzlich Arten mit Austauschenthalpien von 8,7 und 10,3 kJ/äquivalent hat. [U.W.]

Résumé—L'hétérogénéité des sites pour l'échange Ca→K a été examinée par microcalorimetrie dans les fractions <0,2 μm de quelques smectites choisies. On a identifié six groupes de sites dont l'enthalpie d'échange exothermique ($-d(\Delta H_x)/dx$) s'étageait de 5,7 à 10,9 kJ/eq. Dans des bentonites du Wyoming, on n'a distingué que trois groupes avec des enthalpies de 5,7 à 7,5 kJ/eq, quoique dans la fraction, 0,2–1,0 μm, un groupe 10,7 kJ/eq a aussi été observé. Des smectites de Redhill et de Camp Berteau contenaient en plus des groupes avec des enthalpies de 8,7–10,9 kJ/eq, mais un échantillon de New Mexico n'avait que des groupes avec des valeurs plus hautes. Ainsi, les enthalpies d'échange de quatre groupes principaux de sites (reclassifiés à partir de ceux observés) semblent être en proportion inverse avec les étendues d'expansion intercouche par l'adsorption de molécules polaires dans les échantillons. Une "vraie montmorillonite," par conséquent, telle une bentonite du Wyoming <0,2 μm, ne contient que des couches à expansion complète avec des valeurs $-d(\Delta H_x)/dx$ entre 5,7 et 7,5 kJ/eq. De cette manière, elle est moins hétérogène et devrait avoir une beaucoup plus grande capacité de gonflement que la montmorillonite Camp Berteau qui a en plus des groupes avec des enthalpies d'échange de 8,7 et 10,3 kJ/eq. [D.J.]

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