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IRREVERSIBLE COLLAPSE OF MONTMORILLONITE

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Abstract—A number of variable charge montmorillonites were prepared. One portion of each sample was extracted with ammonium chloride, while a second portion was first saturated with calcium chloride, washed, and then extracted with ammonium chloride. In both cases, the number of cations displaced by ammonium chloride was determined. The number of calcium ions displaced from Ca-saturated samples was higher than the sum of the number of lithium and calcium ions displaced from Li, Ca-mixed samples. The differences, increasing towards Li-rich end of the series are assumed to be due to protons liberated from the reaction of lithium ions with either structural hydroxyl groups or residual water molecules, as has been shown by other investigators. Supplementary X-ray and i.r. data lend support to this idea.

INTRODUCTION

SINCE IT was first observed that montmorillonite collapses irreversibly when heated at temperatures above 200°C (Méring, 1946; Gonzáles García, 1950) a great deal of work has been done on the subject using various techniques, and different opinions are held regarding the mechanism of the reaction. The two most important of these are: (i) migration of interlayer cations with small radius into vacant octahedral sites giving a pyrophyllite-like structure (Hofmann and Klemen, 1950; Greene-Kelly, 1953, 1955; Glaeser and Méring, 1967; Schultz, 1969); and (ii) migration of suitable cations into the hexagonal oxygen network (Tettenhorst, 1962; Russell and Farmer, 1964; Farmer and Russell, 1967; Calvet and Prost, 1971).

Russell and Farmer (1964) showed that the pyrophyllite-like structure did not develop during or following heat treatment, it did develop, however, if the mineral completely dehydroxylated by heating at 750°C and then rehydroxylated in steam (Heller *et al.*, 1962). They also pointed out that Li–, Mg–, and H–montmorillonite, the latter being formed from the decomposition of NH_4–montmorillonite, give similar spectra, and are acidic when treated with ethylene glycol. They suggested that the acidity resulted from the reaction of lithium or magnesium ions with either structural hydroxyl groups or residual water molecules to give protons. It was further proposed that if this were the case, collapsed samples could be completely re-expanded by treatment with ammonia vapour with the formation of ammonium ions in the interlayer space.

As a matter of fact, in a later work Farmer and Russell (1967) measured the number of ammonium ions formed by ammonia vapour treatment of collapsed samples, determined the cation exchange capacity, and the number of lithium ions displaced by ammonium acetate, and found that over half of the original lithium ions became non-exchangeable during heat treatment.

The present work has been undertaken in order to seek a relationship between the number of lithium ions in the interlayer prior to heat treatment, and the protons liberated from the reaction of lithium ions with either structural hydroxyl groups or residual water molecules during the course of heat treatment.

Experiments were carried out with a number of Li, Ca-mixed clay samples (Brindley and Ertem, 1971) heated at 220°∓5°C. It was assumed that upon heating three possibilities exist for the lithium ions occupying the interlayer space, namely,

(i) Some of them migrate into vacant octahedral sites and become non-exchangeable,

(ii) Some of them react with either structural hydroxyl groups or residual water molecules resulting in the formation of an equivalent number of exchangeable protons, and

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(iii) The remainder stay in the interlayer as exchangeable cations.*

EXPERIMENTAL

One of the three montmorillonites employed in this study, Mineral Colloid BP, was from Wyoming, U.S.A., and the other two were from Kursunlu, Turkey, and Sabanözü, Turkey. They are referred to as BP, T-1 and T-2, respectively, throughout this work. The empirical formula of each clay, derived from its chemical analysis, is given in the appendix.

Homoionic samples were prepared by saturating the clays with 1N solutions of corresponding salts. Washing was carried out first by centrifugation, then by dialysis technique at 60°–70°C. Subsequently, the $< 1\ \mu$ fraction was separated.

Cation exchange capacities were determined by displacing cations with 1N ammonium chloride solution at $pH = 5{\cdot}0–5{\cdot}5$, and determining the number of displaced cations by atomic absorption spectrophotometry (Table 1).

Table 1. CEC of homoionic clays

Clay	BP	T-1	T-2
CEC determined as Ca	125	103	115
CEC determined as Na	92	93	99

As will be noticed in the Table 1 the CEC of Ca–clays is higher than that of Na–clays, the latter corresponding to the values expected from the chemical formulae. High Ca-determined CEC values, lying outside the limits of experimental error, have been found throughout this study and since these values affect the results described herein the sources of the discrepancies are discussed below.

Sansom *et al.* (1968), in a recent work, have concluded that there are two different types of cation exchange sites on montmorillonites, one on the basal surfaces, arising from isomorphous substitution, the other on the edges associated with octahedral cations, where such cations are held less firmly and hydrolysed more readily. Their work confirmed the results obtained from various soil samples and kaolins by Okazaki *et al.* (1962, 1964) who showed that in exchange reactions performed without washing, the agreement between exchange capacities determined as different cations was good, discrepancies discovered on washing being attributed to the different hydrolysis rates of different cations.

In this study, CEC values of Ca-saturated clays exceeded the sum of lithium and calcium ions found by ammonium chloride exchange, and is believed to result from different hydrolysis rates discussed above.

Preparation of Li, Ca-mixed samples and cation exchange reactions

Equal volumes, 25 ml, of Ca–clay suspensions of a concentration of 20 mg/ml were treated with varying amounts of lithium chloride: 0·10 ml, 0·20 ml, 0·40 ml, 0·70 ml, 0·90 ml, 1·10 ml, 1·40 ml, 1·80 ml LiCl solutions of a concentration of 1 g/10 ml, and 0·20 g, 0·30 g solid LiCl. Mixtures were stirred 5 min, allowed to stand 2 hr and then centrifuged. The number of calcium ions displaced by lithium chloride were determined (Fig. 1). The lithium ions introduced were assumed to be equal to twice the number of calcium ions displaced from each sample. The number of calcium ions remaining on the clay was then calculated by subtracting the calcium ions displaced from the initial cation exchange capacity.

Using the curve in Fig. 1, mixed samples having desired numbers of lithium and calcium ions in the interlayer were prepared, washed free of excess salt. X-ray powder patterns of the oriented films prepared from each sample indicated interstratification when air-dried, however on heating at 110°C overnight well ordered reflections were recorded.

Each sample, the cation content prior to heat treatment now known (Table 2), was divided into two fractions, both of which were dried at 110°C overnight, and weighed. Subsequently, each fraction was heated at 220° ∓ 5°C for 24 hr and allowed to expand in ethyl alcohol at least 24 hr.

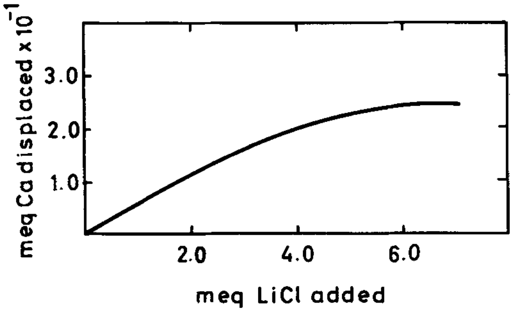

Fig. 1. Preparation of Li, Ca-mixed clays.

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*There are two viewpoints regarding the source of lithium ions exchangeable with ammonium chloride. While Green-Kelly (1955) considers them to be attached to external crystallite sites and to differ fundamentally from the interlamellar cations in their behaviour on dehydration, Quirk and Theng (1960) claim that the CEC values appear to be too large to be accounted for by exchange on the external surfaces of the crystals since the crystals would have a surface area in the region of $50\ m^2$.

Table 2. meq of cations/100 g clay

Clay	BP							T-1					T-2				
Sample No.	1	2	3	4	5	6	7	1	2	3	4	5	1	2	3	4	5
Before heating																	
Li introduced	8	21	31	40	56	67	81	7	30	39	54	66	25	39	49	61	74
After heating																	
(Li,Ca)NH_4Cl Li	0	0	1	2	2	7	9	0	1	4	5	7	0	tr	tr	tr	tr
(Li,Ca)NH_4Cl Ca	118	95	88	78	61	49	32	75	63	54	37	23	78	47	37	23	15
(Li,Ca)$CaCl_2$ Li	2	2	3	3	2	3	4	0	1	1	4	6	tr	tr	tr	tr	tr
(Ca)NH_4Cl Ca	103	92	91	86	88	93	89	99	100	82	97	99	105	97	96	94	99

(Li,Ca)NH_4Cl, cations displaced by NH_4Cl from Li,Ca-mixed clays.
(Li,Ca)$CaCl_2$, cations displaced by $CaCl_2$ from Li,Ca-mixed clays.
(Ca)NH_4Cl, cations displaced from Ca-saturated clays.

Fraction 1 of each sample, 0·3–0·4 g, was saturated with ammonium chloride solution, and the number of lithium and calcium ions displaced was determined.

Fraction 2, 0·5–0·6 g, was saturated with calcium chloride solution and washed, the supernatant liquor and the washings were collected for the determination of lithium ions displaced by calcium chloride. The Ca-saturated samples were dried at 110°C overnight, weighed, extracted with ammonium chloride, and the extracts analyzed for calcium ions in the expectation of finding the number of protons from the following equations, and lithium ions, if present:

$$\begin{array}{c}\text{CEC of}\\ \text{Ca-saturated}\\ \text{samples}\end{array} = \begin{array}{c}\text{Ca ions}\\ \text{remaining}\\ \text{on clay}\end{array} + \begin{array}{c}\text{Li ions}\\ \text{exchangeable}\\ \text{with } NH_4Cl\end{array} + \begin{array}{c}\text{Li reacted with}\\ \text{structural OH}\\ \text{or residual } H_2O\end{array}$$

$$\begin{array}{c}\text{Li reacted with}\\ \text{structural OH}\\ \text{or residual } H_2O\end{array} = \begin{array}{c}\text{CEC of}\\ \text{Ca-saturated}\\ \text{samples}\end{array} - \begin{array}{c}\text{Li ions}\\ \text{exchangeable}\\ \text{with } NH_4Cl\end{array} - \begin{array}{c}\text{Ca ions}\\ \text{remaining}\\ \text{on clay}\end{array}$$

The procedure just described for mixed clays was carried out with Li-saturated clays heated under the same conditions. The results are given in Table 3 together with the results obtained by Farmer and Russell (1967).

RESULTS AND DISCUSSION

Table 2 shows the number of cations introduced into the clay, displaced from the clay and remaining on the clay during lithium chloride treatment prior to heating. It shows also the number of cations,

(i) displaced by ammonium chloride from Li, Ca-mixed clays,
(ii) displaced by calcium chloride from Li, Ca-mixed clays,
(iii) displaced by ammonium chloride from Ca-saturated clays after heating.

A study of the data presented in Table 2 and Table 3 shows that Fraction 1 and Fraction 2 of each sample have undergone exactly the same changes until the end of heat treatment, that is to say, each fraction has the same number of lithium and calcium ions in the interlayer. Yet, when these samples were treated with, either ammonium chloride alone, or calcium chloride, followed by ammonium chloride the number of calcium ions displaced from Ca-saturated clays was higher than the sum of lithium and calcium ions displaced from Li, Ca-mixed clays. The differences, lying outside the limits of experimental error, are too high to be considered to result from washing processes. Neither could they result from different replacement cations, which has been suggested in a previous work (Brindley and Ertem, 1971), because the number of lithium ions displaced by calcium chloride from Li, Ca-mixed clays during Ca-saturation was also determined in this study and found to be either almost equal to or even lower than the number of lithium ions displaced by ammonium chloride.

The differences are attributed to protons as was suggested by Russell and Farmer (1964) and Farmer and Russell (1967). These protons formed on heating, were displaced both by ammonium chloride and calcium chloride, but determined only in the second case, indirectly, through calcium ions. The fact that the CEC values determined as calcium ions following Ca-saturation of mixed samples

Table 3. CEC of Li-clays after heat treatment

	CEC determined by saturating with		meq of Li displaced by	
	$CaCl_2$	NH_4-Ac	NH_4Cl	NH_4-Ac
BP	50		24	
T-1	34		13	
T-2	23		4	
Cheto-Wyoming*		45		39

*Results from Farmer and Russell (1967).

exceeded the initial values by the number of calcium ions attached to the crystal edges did not allow the establishment of a quantitative relationship. Results, however, indicated that the number of protons liberated increases with the number of lithium ions in the interlayer prior to heat treatment.

Supplementary experiments utilizing X-ray diffraction patterns of the samples did strengthen the viewpoint that cation(s) other than lithium and calcium ions were present, and i.r. spectra of heated clay films treated with urea solution gave characteristic bands indicating the protonation of urea, presumably by hydrogen ions on the clay (Mortland, 1966).

X-ray diagrams

In the previous work designed to study the solvation properties of liquids in conjunction with variable charge montmorillonites, containing both lithium and calcium ions in the interlayer, the liquid properties seemed to fall into two categories (Brindley and Ertem, 1971). Acetone, pentanone, and water brought about a "two step" expansion, namely 9–13 Å and 13–17 Å depending on the number of interlayer cations. Ethylene glycol and ethyl alcohol expanded the same samples up to 17 Å regardless of the number of lithium and calcium ions in the interlayer. The increase in expansion in the case of acetone, pentanone, and water with the increasing sum of lithium and calcium ions has been explained as resulting from cation–dipole interactions. An "additional mechanism", such as H-bonding, has been suggested to account for the behaviour of ethylene glycol and ethyl alcohol, the latter two expanding all samples to 17 Å, including those thought to have relatively few cations in the interlayer.

Similar experiments were carried out with the mixed Li, Ca-clays employed in this study. Air-dried oriented films, 2–3 mg/cm^2, prepared by pipetting mixed clay suspensions onto glass slides, were wrapped around both ends with aluminium foil strips in order to avoid curling up of the films, heated at 220°∓5°C for 24 hr, moistened with acetone, ethylene glycol, ethyl alcohol, and water, and allowed to stand in the saturated vapour atmosphere of the corresponding liquids for 24 hr (48 hr in the case of acetone). Acetone expanded samples of the same series to 13 Å in some cases, to 17 Å in other cases, as the experiments were repeated. The extent of expansion with acetone (Glaeser, 1949; Mortland, 1968) is controlled by the number of water molecule layers surrounding the cations in the interlayer. The number of water molecules around the cations is strongly influenced by the environmental conditions, where special care to exclude water is not taken.

Water, which will be discussed separately, ethylene glycol, and ethyl alcohol produced results similar to the previous work. As has been pointed earlier, interaction between an interlayer cation and ethyl alcohol (Bissada *et al.*, 1967; Dowdy and Mortland, 1967) ethylene glycol, (Bissada *et al.*, 1967), acetone (Bissada *et al.*, 1967; Parfitt and Mortland, 1968) is of cation–dipole type. Both in the present and in the previous work it is assumed that the number of interlayer cations is the sum of the lithium, calcium and hydrogen ions, the total either exceeding or equalling the number of cations necessary for swelling (Calvet and Prost, 1971) (Table 2). The further expansion to 17 Å for the samples with a lower sum of lithium and calcium ions is due to the solvation of hydrogen ions present in the interlayer. Actually, Gonzáles García and Gonzáles García (1953) have already shown that H-montmorillonite heated at 400°C is expanded to 16·4 Å and 9·9 Å when treated with ethylene glycol and water, respectively. In our experiments, H-clay prepared as described by Mathers *et al.* (1954) and heated at 220°∓5°C for 24 hr expanded to 17 Å when treated with ethylene glycol, ethyl alcohol, and acetone.

"Step-wise" expansion with water is in good agreement with previous results obtained by Johns and Tettenhorst (1959), who treated heated clays with ethylene glycol, glycerol, and water, and reported that the order of penetration was ethylene glycol > glycerol > water.

Calvet and Prost (1971) found out that the limiting value for exchangeable cations necessary to expand heated montmorillonites was 20% of the initial cation exchange capacity for ethylene glycol, 30% for glycerol and 50% for water.

I.R. spectra

Oriented clay films, 2–3 mg/cm², prepared by pipetting mixed clay suspensions onto glass slides were heated at 220° ∓ 5°C for 24 hr without being wrapped at the ends. Films that curled up during heat treatment, were transferred onto polyethylene films, treated with urea solution, approximately 150 m-moles/100 g clay, and allowed to equilibrate for 24 hr. The i.r. spectra were recorded as described by Mortland (1966). The appearance of bands at 2600 cm^{-1} and 1360 cm^{-1}, which has been attributed to the OH stretching vibration of the protonated carbonyl group, and to the hydrogen deformation mode, δ OH, respectively (Mortland, 1966), indicates that protonation of urea has occurred. Since protonation of urea ($pK = 13{\cdot}82$) only occurs in the presence of protons or aluminium ions, the latter have not been detected in the present exchange reactions, and does not occur with less electronegative alkali or alkaline earth cations (Mortland, 1968) then the protonation experiments lend support to the presence of interlayer protons.

CONCLUSIONS

The results obtained are in good agreement with those obtained earlier and cited above, and indicate that lithium ions occupying the exchange sites of a montmorillonite undergo two different reactions upon heating, namely,

(1) Some migrate into vacant octahedral sites and become non-exchangeable.

(2) Some react with either structural hydroxyl groups or residual water molecules to form protons and can be recognized indirectly through further reactions, such as the following: formation of ammonium ions on treatment with ammonia vapour; protonation of certain compounds, for example urea; displacement by other cations.

Exchange analyses carried out in the present study show that the number of protons formed on heating increases with number of lithium ions in the interlayer prior to heat treatment. Due to the fact that cation exchange capacity values deviate from the "real values" by the number of cations held on the crystal edges, a more quantitative relationship could not be established. The results, however, offer an explanation for a problem raised earlier (Brindley and Ertem, 1971) regarding high cation exchange capacity values of variable charge mixed montmorillonites after Ca-saturation. The differences between the number of calcium ions displaced from Ca-saturated samples and the sum of lithium and calcium ions displaced from Li, Ca-mixed samples arise from the displacement of protons during Ca-saturation of mixed samples. This is in addition to extra calcium ions held on crystal edges.

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REFERENCES

Bissada, K. K., Johns, W. D. and Cheng, F. S. (1967) Cation-dipole interactions in clay organic complexes: *Clay Minerals* **7**, 155–166.

Brindley, G. W. and Ertem, G. (1971) Preparation and solvation properties of some variable charge montmorillonites: *Clays and Clay Minerals* **19**, 399–404.

Calvet, R. and Prost, R. (1971) Cation migration into empty octahedral sites and surface properties of clays: *Clays and Clay Minerals* **19**, 175–186.

Dowdy, R. H. and Mortland, M. M. (1967) Alcohol-water interactions on montmorillonite surfaces—I. Ethanol: *Clays and Clay Minerals* **15**, 259–271.

Farmer, V. C. and Russell, J. D. (1967) Infrared absorption spectrometry in clay studies: *Clays and Clay Minerals* **15**, 121–142.

Glaeser, R. (1949) On the mechanism of formation of montmorillonite-acetone complexes: *Clay Min. Bull.* **1**, 88–90.

Glaeser, R. and Méring, J. (1967) Effet de chauffage sur les montmorillonites saturees de cations de petit rayon: *C.R. hebd Séanc. Acad. Sci. Paris* **265D**, 833–835.

Gonzáles García, F. (1950) Anales de Edafologia y Fisiologia vegetal: **9**, 149 (Ref. from Greene-Kelly, R. (1953) *Clay Min. Bull.* **2**, 52–56).

Gonzáles García, F. and Gonzáles García, S. (1953) Modificaciones en propiedades de silicatos. *An. Edafol. Fisiol. Veg.* **12**, 925–992. (Ref. from MacEwan, D. M. C. (1961) *The X-ray Identification and Crystal Structures of Clay Minerals* (Edited by Brown, G.) Chap. IV, p. 202, Mineralogical Society, London).

Greene-Kelly, R. (1953) Irreversible dehydration in montmorillonite—II: *Clay Min. Bull.* **2**, 52–56.

Greene-Kelly, R. (1955) Dehydration of the montmorillonite minerals: *Mineral. Mag.* **30**, 604–615.

Heller, L., Farmer, V. C., Mackenzie, R. C., Mitchell, B. D. and Taylor, H. F. W. (1962) The dehydroxylation and rehydroxylation of triphormic dioctahedral clay minerals: *Clay Min. Bull.* **5**, 56–72.

Hofmann, U. and Klemen, R. (1950) Verlust der Austauschfähigkeit von Lithiumionen an Bentonit durch Erhitzung: *Z. Anorg. Allg. chem.* **262**, 95–99.

Johns, W. D. and Tettenhorst, R. T. (1959) Differences in the montmorillonite solvating ability of polar liquids: *Am. Mineralogist* **44**, 894–896.

Mathers, A. C., Weed, S. B. and Coleman, N. T. (1954) The effect of acid and heat treatment of montmorillonoids: *Clays and Clay Minerals* **3**, 403–412.

Méring, J. (1946) Hydration of montmorillonite: *Trans. Faraday Soc.* **42B**, 205–219.

Mortland, M. M. (1966) Urea complexes with montmorillonite: An infrared absorption study: *Clay Minerals* **6**, 143–156.

Mortland, M. M. (1968) Protonation of compounds at clay mineral surfaces: *9th Int. Cong. Soil Sci.* Vol. I, 691–699.

Okazaki, R., Smith, H. W. and Moodie, C. D. (1962) Development of a cation-exchange capacity procedure with few inherent errors: *Soil Sci.* **93**, 343–349.

Okazaki, R., Smith, H. W. and Moodie, C. D. (1964) Some problems in interpreting cation-exchange-capacity data: *Soil Sci.* **97**, 202–208.

Parfitt, R. L. and Mortland, M. M. (1968) Ketone adsorption on montmorillonite: *Proc. Soil Sci. Soc. U.S.A.* **32**, 355–363.

Quirk, J. P. and Theng, B. K. G. (1960) Effect of surface density of charge on the physical swelling of Li-montmorillonite: *Nature* **187**, 967–968.

Russell, J. D. and Farmer, V. C. (1964) Infrared spectroscopic study of the dehydration of montmorillonite and saponite: *Clay Min. Bull.* **5**, 443–464.

Sansom, G. K., Smith, R. G. and White, D. (1968) The cation-exchange capacity of layer-lattice minerals – II. Two types of cation-exchange sites on montmorillonite and their determination: *Trans. of British Cer. Soc.* **67**, 93–103.

Schultz, L. G. (1969) Lithium and potassium absorption, dehydroxylation temperature and structural water content of aluminous smectites: *Clays and Clay Minerals* **17**, 115–149.

Tettenhorst, R. (1962) Cation migration in montmorillonites: *Am. Mineralogist* **47**, 769–773.

APPENDIX

Structural formulae of the clays employed

BP Clay

$(\mathrm{Si}^{4+}_{3\cdot 82}\mathrm{Al}^{3+}_{0\cdot 18})^{\mathrm{IV}}(\mathrm{Al}^{3+}_{1\cdot 52}\mathrm{Fe}^{3+}_{0\cdot 22}\mathrm{Fe}^{2+}_{0\cdot 01}\mathrm{Mg}^{2+}_{0\cdot 25})^{\mathrm{VI}}\mathrm{Na}^{+}_{0\cdot 35}\mathrm{K}^{+}_{0\cdot 01}\,\mathrm{O}_{10}(\mathrm{OH})_2\ 0\cdot 27\ \mathrm{H_2O}$

T-1 Clay

$(\mathrm{Si}^{4+}_{3\cdot 92}\mathrm{Al}^{3+}_{0\cdot 08})^{\mathrm{IV}}(\mathrm{Al}^{3+}_{1\cdot 49}\mathrm{Fe}^{3+}_{0\cdot 20}\mathrm{Fe}^{2+}_{0\cdot 06}\mathrm{Mg}^{2+}_{0\cdot 20})^{\mathrm{VI}}\mathrm{Na}^{+}_{0\cdot 27}\mathrm{K}^{+}_{0\cdot 03}\mathrm{Ca}^{2+}_{0\cdot 07}\mathrm{O}_{10}(\mathrm{OH})_2\ 1\cdot 08\ \mathrm{H_2O}$

T-2 Clay

$(\mathrm{Si}^{4+}_{3\cdot 96}\mathrm{Al}^{3+}_{0\cdot 04})^{\mathrm{IV}}(\mathrm{Al}^{3+}_{1\cdot 50}\mathrm{Fe}^{3+}_{0\cdot 07}\mathrm{Fe}^{2+}_{0\cdot 02}\mathrm{Mg}^{2+}_{0\cdot 41})^{\mathrm{VI}}\mathrm{Na}^{+}_{0\cdot 38}\mathrm{O}_{10}(\mathrm{OH})_2\ 1\cdot 07\ \mathrm{H_2O}$

Résumé – On a préparé un certain nombre de montmorillonites à charge variable. Une fraction de chaque échantillon a été extraite par le chlorure d'ammonium, tandis qu'une seconde fraction a été d'abord saturée par le chlorure de calcium, puis lavée et enfin extraite au chlorure d'ammonium. Dans les deux cas, on a dosé le nombre de cations déplacés par le chlorure d'ammonium. Le nombre d'ions calcium déplacés à partir des échantillons saturés par Ca est plus élevé que la somme des ions lithium et calcium déplacés à partir d'échantillons mixtes Li–Ca. On fait l'hypothèse que les différences qui augmentent au fur et à mesure qu'on se rappoche du terme extrême des séries constitué par un système riche en Li. sont dues aux protons libérés lors de la réaction des ions lithium avec, soit les groupes hydroxyle de constitution, soit les molécules d'eau résiduelle, comme cela a pu étre montré dans d'autres travaux. Des données supplémentaires obtenues en diffraction X et en spectrométrie i.r. s'accordent pour renforcer cette idée.

Kurzreferat – Eine Anzahl von Montmorilloniten verschiedener Ladung wurde hergestellt. Ein Teil jeder Probe wurde mit Ammonium–chlorid extrahiert während ein zweiter Teil zunächst mit Calciumchlorid gesättigt, gewaschen, und dann mit Ammonium–chlorid extrahiert wurde. In beiden Fällen wurden die durch Ammoniumchlorid ersetzten Kationen bestimmt. Die Anzahl der in den Ca-gesättigten Proben ersetzten Calciumionen war grösser als die Summe der aus gemischten Li, Ca-Proben ersetzten Lithium und Calciumionen. Es wird angenommen, dass die Unterschiede, die sich gegen das Li-reiche Ende der Reihe vergrössen, eine Folge der durch die Reaktion von Lithiumionen mit entweder strukturellen Hydroxylgruppen oder residuellen Wassermolekülen frei gewordenen Protonen sind, wie bereits durch andere Forscher festgestellt wurde. Zusätzliche Röntgen- und Infrarotdaten bekräftigen diese Idee.

Резюме — Приготовили несколько образцов монтмориллонита. Одна порция каждого образца подвергалась хлористоаммониевой вытяжке, в то время как вторая порция была сперва насыщена хлористым кальцием, отмучена, а затем экстрагирована хлористым аммонием. В обоих случаях определяли число катионов смещенных хлористым аммонием. Число ионов кальция смещенных в образцах насыщенных Са было выше, чем общее число ионов лития и кальция смещенных из смешанных образцов Li и Са. Предполагают, что разницы, повышающиеся по направлению к концу серии богатой Li, зависят от протонов выделившихся в свободном состоянии от реакции ионов лития либо с группами структурных гидроксилов либо с молекулами остаточной воды, как доказали другие исследователи. Добавочные рентгеновские и инфракрасные данные поддерживают эту гипотезу.