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MONTMORILLONITE–ALKALI HALIDE INTERACTION: A POSSIBLE MECHANISM FOR ILLITIZATION

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Abstract—The reaction products obtained when montmorillonites react with potassium halide at elevated temperatures, which were described in a previous publication, are further characterized. On the basis of their X-ray powder diffraction patterns, i.r. spectra, CEC and chemical composition they could be regarded as montmorillonite–illite interstratifications. Changes in morphology of various montmorillonites heated with and without K halide are related to the size, charge and position of interlayer cations. Scanning electron-micrographs of samples heated with KBr resemble those of well-crystallized illite. It is speculated that reactions of clay minerals with halides or other proton acceptors may account for some diagenetic processes in nature, e.g. the conversion of montmorillonite to illite on deep burial.

INTRODUCTION

Heating montmorillonites with alkali halides causes changes in the structure of the clay layers. Chemical, i.r. and Mössbauer analyses indicated that alkali ions can enter the clay interlayers in excess of the exchange capacity of the clay, the charge balance being maintained by deprotonation of hydroxyl groups (Heller-Kallai, 1975). The reaction of Wyoming montmorillonite with KBr can be represented by

$$(Si_{7.69}Al_{0.31})(Al_{3.07}Fe^{3+}_{0.36}Fe^{2+}_{0.05}Mg_{0.51})O_{20}(OH)_4M^{+}_{0.90} + (x+y)KBr \rightarrow$$

$$(Si_{7.69}Al_{0.31})(Al_{3.07}Fe^{3+}_{0.41}Mg_{0.51})O_{(20+x)}(OH)_{(4-x)}M^{+}_{(0.85-y)}K_{(x+y)} + xHBr + yMBr.$$

Small interlayer cations initially present are mostly retained by the clay, while larger ones are at least partially exchanged. The exchange may occur as a solid state reaction or, more probably, take place in the process of washing out excess salt. The reactions described occur in the laboratory at relatively low temperatures—appreciable changes can be achieved at 300°C within several days. It thus seems possible that such reactions may occur in nature under conditions of mild metamorphism.

The purpose of the present study is to investigate the nature of the reaction products of montmorillonite–KBr mixtures. It is pertinent also to enquire how material of this type would be classified if encountered in the course of a routine laboratory examination of a clay mineral mixture. The samples used in this study were prepared with KBr for convenience. However, as previously shown, the products obtained with KCl are identical. With NaCl similar reactions occur but the amount of alkali sorbed under corresponding conditions differs.

EXPERIMENTAL

The samples of montmorillonite are the same as those used in the previous investigation (Heller-Kallai, 1975):

Wyoming (W) $(Si_{7.69}Al_{0.31})(Al_{3.07}Fe^{3+}_{0.36}Fe^{2+}_{0.05}Mg_{0.51})M^{+}_{0.90}O_{20}(OH)_4$*

Camp Berteaux (CB) $(Si_{7.74}Al_{0.26})(Al_{2.91}Fe^{3+}_{0.30}Fe^{2+}_{0.06}Mg_{0.78})M^{+}_{0.93}O_{20}(OH)_4$*

Skyverdalen (S) $(Si_{7.74}Al_{0.26})(Al_{3.24}Fe^{3+}_{0.04}Mg_{0.72})(Ca_{0.46}Na_{0.02})O_{20}(OH)_4$†

Fortun (F) $(Si_{7.68}Al_{0.32})(Al_{3.10}Mg_{0.84}Fe^{3+}_{0.08})(Ca_{0.52}Na_{0.02})O_{20}(OH)_4$†

* Analyst: Z. Shohat
† Rosenquist (1959)

Analar KBr was ground, mixed with monoionic samples of montmorillonites and heated at different temperatures for various periods of time. Excess KBr was removed by washing six times with distilled water. The products were designated "KBr treated samples". Cation exchange of the "KBr treated samples" was effected by washing three times with a 1 N NaCl solution. X-ray powder diffraction patterns of the samples were recorded in the air-dried state and after saturation with glycol. I.r. spectra were recorded under ambient conditions. Aliquots of the samples were dissolved in H_2SO_4–HF–HCl solutions and analysed by atomic absorption spectroscopy. Scanning electron micrographs were obtained using a Cambridge S-4-10 instrument.

BASAL SPACINGS AND CATION EXCHANGE

Table 1 shows the basal spacings recorded for some of the montmorillonites after heating at 520°C, with

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Table 1. Basal spacings and interlayer cations of montmorillonites heated at 520°C without (-) and with (+) KBr

Sample	Time of heating, hrs	KBr	NaCl exchanged	d_{001} (Å) air dried	d_{001} (Å) saturated with glycol	Int.* cation retained, meq/100g	K sorbed meq/100g	Σ (7)+(8)	cations exchanged, meq/100g int.*	K	Σ(10)+(11)
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)	(12)
Li(W)	1	-	-	12.8	14.7	114					
Li(W)	1	+	-	12.1	13.4	107	124	231			
Li(W)	1	+	-	12.4	17.0				5	85	90
Mg(W)	1	-	-	9.7	9.7	102					
Mg(W)	1	+	-	12.6 } d 14.7 } d	15.5 br	89	109	198			
Mg(CB)	1	+	-	12.3	17.0 9.7 (br)	81	113	194			
Mg(S)	1	+	-	12.3	17. 9.7 br	131	82	212			
Mg(W)	72	+	-	12.3	13.8	96	270	366			
Mg(W)	72	+	+	12.3	17 } 13.2 } d				-	44	44
Ca(W)	1	-	-	9.8	17.0	110					
Ca(W)	1	+	-	12.2	17.0	23	109	132			
Ca(W)	1	+	+	12.4	17.0				15	103	118
Ca(W)	72	+	-	12.3	14.2	100	180	280			
Ca(W)	72	+	+	12.2	17.0				33	84	117
Ca(CB)	1	+	-	12.6	17.0	40	132	172			
Ca(CB)	1	+	+	12.6	17.0				23	101	124
Ca(F)	1	+	-	12.6 br	17.0	80	65	145			
Ca(F)	72	+	-	12.3	13.6	85	190	275			
Ca(F)	72	+	+	12.0	16.3 br				27	58	85
Na(W)	1	-	-	14.2	17.0						
Na(W)	1	+	-	12.3	16.7	13	120	133			
Na(W)	192	+	-	12.3	diffuse	10	236	246			

* = interlayer

and without KBr, for various periods of time. Some of the samples were subsequently treated with a NaCl solution and the basal spacings were again recorded. After heating without KBr for 1 hr, samples saturated with large cations remained completely expandable with glycol, while those saturated with smaller cations collapsed to about 10Å and did not expand. Air dried "KBr treated samples" showed a basal spacing of about 12·3Å, resembling K montmorillonite. They expanded completely or partially with glycol. On more prolonged heating with KBr the tendency to expand decreased.

Table 1 also shows the amount of interlayer cations retained and of K sorbed by the "KBr treated samples". To remove excess KBr these samples had been washed with water, and had thus been exposed to concentrated KBr solutions. It is reasonable to assume that any cations replaceable by K were exchanged in the course of this treatment. Subsequent washing of the samples with NaCl caused partial displacement of K by Na. Some of the interlayer cations which had been retained against K exchange were also replaced.

The ability of the clay to expand depends on various factors. It appears from Table 1, and from additional data, that "KBr treated samples" expand completely with glycol, provided that the sum of the cations retained and of K sorbed does not exceed 130–190 m-equiv/100g of clay, the exact amount depending on the nature of the montmorillonite. Of the four montmorillonites examined, (W) is the least expandable after KBr treatment. Na exchange increases the ability of all the clays to expand (Table 1). The sum of the cations displaced by Na is either equivalent to the initial exchange capacity of the clay, or lower. If it is close to the exchange capacity, the Na exchanged samples expand completely. As the amount of exchangeable cations decreases, so also does the capacity of the samples to sorb two layers of glycol.

When the "KBr treated samples" were subsequently heated at temperatures lower than that at which KBr treatment had been carried out, the ability of the clay to expand decreased, air-dried specimens collapsed to 10Å, but even samples containing more than 200 m-equiv. K/100 g clay tenaciously retained some tendency to expand with glycol. However, on more prolonged heating this is considerably reduced, as shown for selected samples in Table 2 and Fig. 1.

On the basis of their X-ray powder diffraction patterns the "KBr treated samples", if encountered in the course of a routine analysis, would be identified as montmorillonite, partially expanding mixed layer material, or, after contraction caused by further heating, as illitic clay. The cation exchange capacity is compatible with this conclusion.

Table 2. Basal spacings of "KBr treated samples". (A)

Sample	(1) Air dried	(1) Saturated with glycol	(2) Air dried	(2) Saturated with glycol	(3) Air dried	(3) Saturated with glycol
Ca(W)	12.4	17	10.4	10.5	10.1	10.5
Mg(W)	12.3	13.8	10.6	11-14.7	10.4	10.7
Al(W)	12.3	13.6	10.8	11-14.7	10.5	10.7

(1) Sample heated with KBr for 72 hours at 520°C, washed to remove KBr

(2) Sample (1) heated 96 hours at 300°C

(3) Sample (2) heated 48 hours at 400°C

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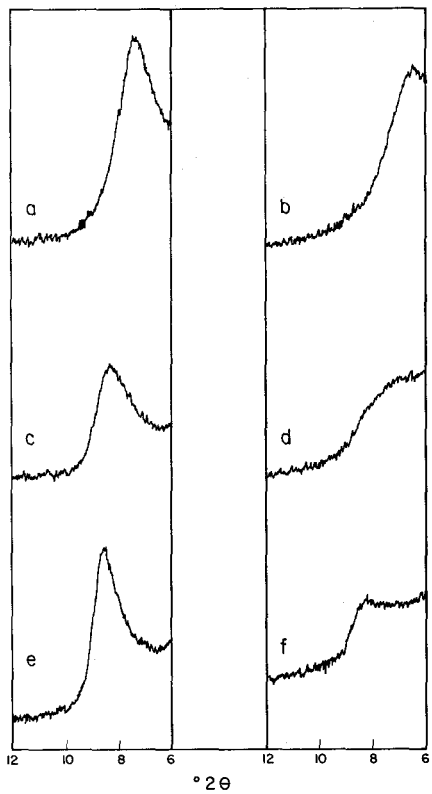


Fig. 1. Diffractometer traces, CuKα radiation.
a) "KBr treated Mg(W)"*, 72 hr at 520°C, air dried.
b) Sample a, saturated with glycol.
c) Sample a, after 96 hr at 300°C.
d) Sample c, saturated with glycol.
e) sample c, after 48 hr at 400°C.
f) Sample e, saturated with glycol.
* for definition, see text.

INFRARED PATTERNS

The spectra of "KBr treated samples" resemble those of other layer silicates. The 800–1000 cm^{-1} region was previously studied in some detail (Heller-Kallai, 1975). It was shown that the 880 cm^{-1} band, assigned to Al–OH–Fe^{3+} bending, is weak or absent. Mössbauer spectra showed that Fe^{3+} ions are neither expelled nor reduced and the attenuation of the i.r. absorption at 880 cm^{-1} was attributed to deprotonation of OH groups. In addition, the frequency of the main Si–O stretching vibration at about 1040 cm^{-1} was reduced, probably due to changes in the symmetry of the tetrahedral layers.

The hydroxyl stretching vibrations of montmorillonite are, at present, less diagnostic than the bending vibrations and require further investigation. With most of the samples they were preserved, though modified, throughout the KBr treatment under the conditions employed, which ranged up to 72 hr heating at 520°C. The spectrum in that region is dominated by a band centered at 3630 cm^{-1}, with small shoulders at higher frequencies.

Some of the "KBr treated samples" developed a shoulder at about 3540 cm^{-1}, e.g. Li(W) after heating for 1–2 hr at 500–550°C and Na(W) after heating at 520°C for 72 hr. Similar absorption was previously reported by Russell and Farmer (1964) and Calvet and Prost (1971) for samples of Ca montmorillonite heated at 200°C or above and for Mg montmorillonite heated briefly at 220–300°C. They attributed the band to perturbation of OH groups by cations retained in hexagonal holes. While this interpretation could also apply to the "KBr treated samples", the absorption feature seems to be problematic. Not only could no rules be established for the "KBr treated samples", but even with heated powders its appearance was erratic. Thus, after one hour's heating at 520°C Ca(W) and Ca(S) gave rise to the band, while Ca(CB) and Ca(F) did not.

Hunt (1950) noted that "the spectra of illite are similar to the spectra of montmorillonite except for some minor peaks... The strongest illite band forms a peak at 9·7μ (1030 cm^{-1}), whereas in montmorillonite it forms at 9·6μ (1041 cm^{-1}). Bands at 11·4 and 11·85μ (878 and 845 cm^{-1}) in montmorillonite do not appear in illite, but unfortunately they are too weak in some spectra of the former mineral to be used for comparison". Hunt studied reference illites from Fithian and Morris, Illinois. Similar features were observed in an i.r. study of illitic material from Paleozoic formations in the Negev, Southern Israel (unpublished).

On the basis of a routine examination of the i.r. spectra, the "KBr treated samples" would be classified as layer silicates, probably illites. The band at about 3540 cm^{-1}, if detected at all, might be regarded as indicative of the presence of trioctahedral Fe^{3+} in the octahedral layer (Farmer and Russell, 1964).

CHEMICAL ANALYSIS

Heating montmorillonites with alkali halides, e.g. KBr, results in changes in the composition of the clay. Depending upon the heat treatment, K may be sorbed in considerable excess of the exchange capacity. Interlayer Li and Mg ions are readily fixed, probably in the hexagonal holes, Ca becomes nonexchangeable on more prolonged heat treatment while most of the Na remains exchangeable. Charge balance is maintained by loss of protons. Structural Fe^{3+} is preserved in the trivalent state and the minor amounts of Fe^{2+} initially present are oxidised (Heller-Kallai, 1975).

In the course of the KBr treatment the Al:Mg ratio remained unchanged, unless the samples were initially Al or Mg saturated. It was therefore concluded that no selective dissolution occurred. The concentration of Si, Fe and of structural Al and Mg can thus be deduced for any analysed sample of montmorillonite, if the concentration of one of these components is known, provided that this component was not also initially present in the interlayers. To determine the chemical composition of e.g. KBr treated Ca montmorillonite, it is therefore necessary to determine only two components: K and either Si, Al, Fe^{3+} or Mg.

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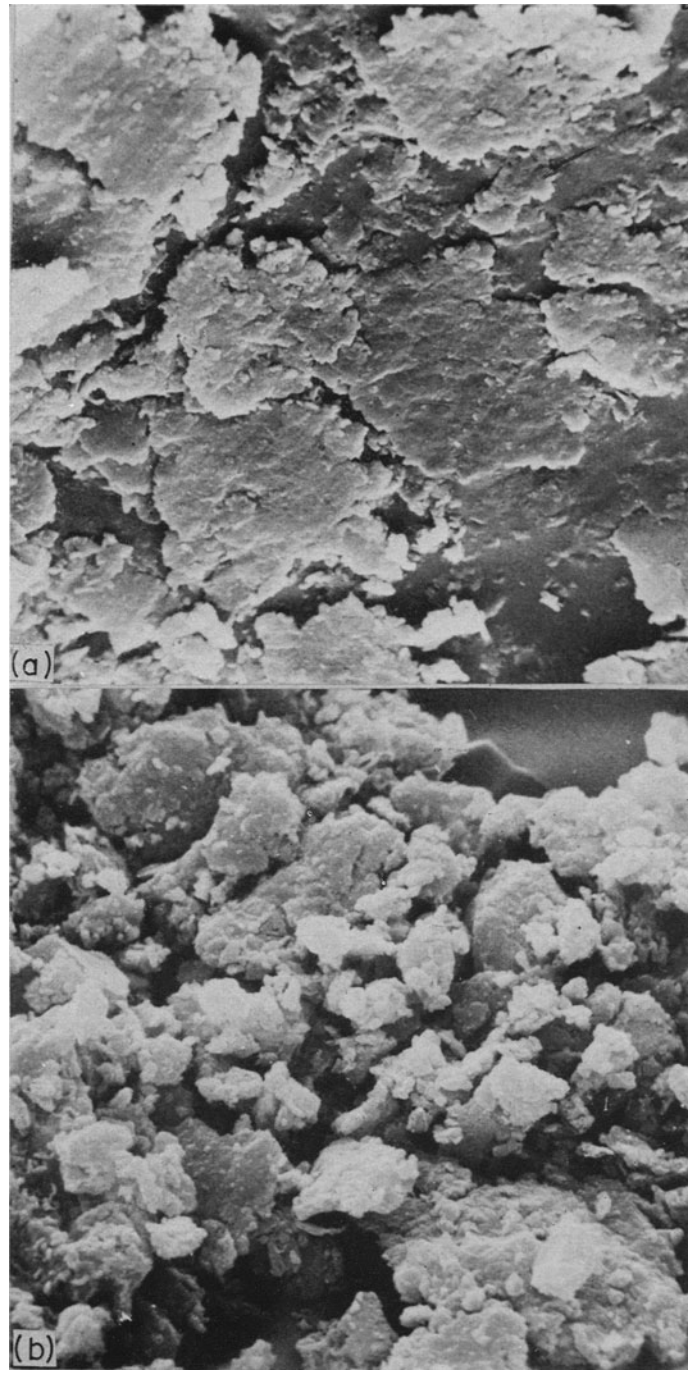


Fig. 2. Scanning electron micrographs of samples heated 1 hr at 520°C (original magnification × 2400). (a) Li(W); (b) Mg(W); (c) Al(W); (d) Na(W); (e) Mg(W) + KBr (excess KBr removed by washing); (f) Li(W) + KBr (excess KBr removed by washing).

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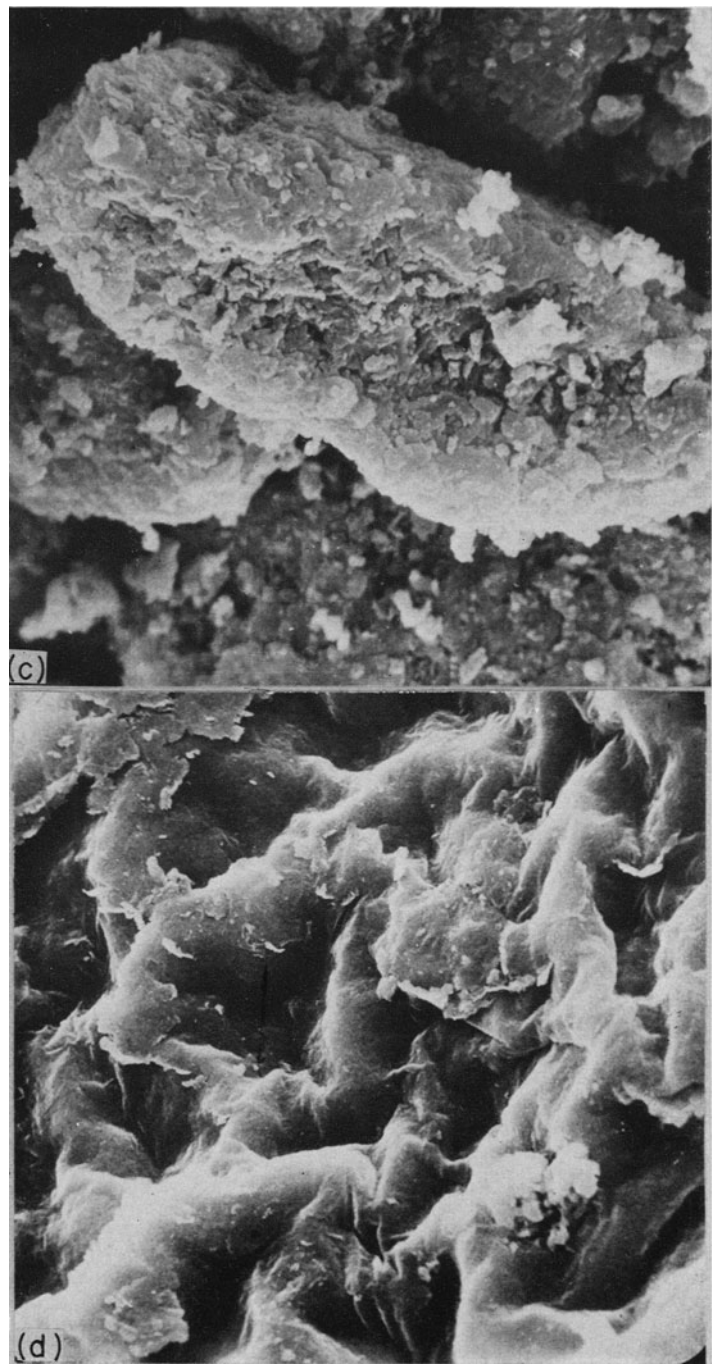


Fig. 2 (c)–(d).

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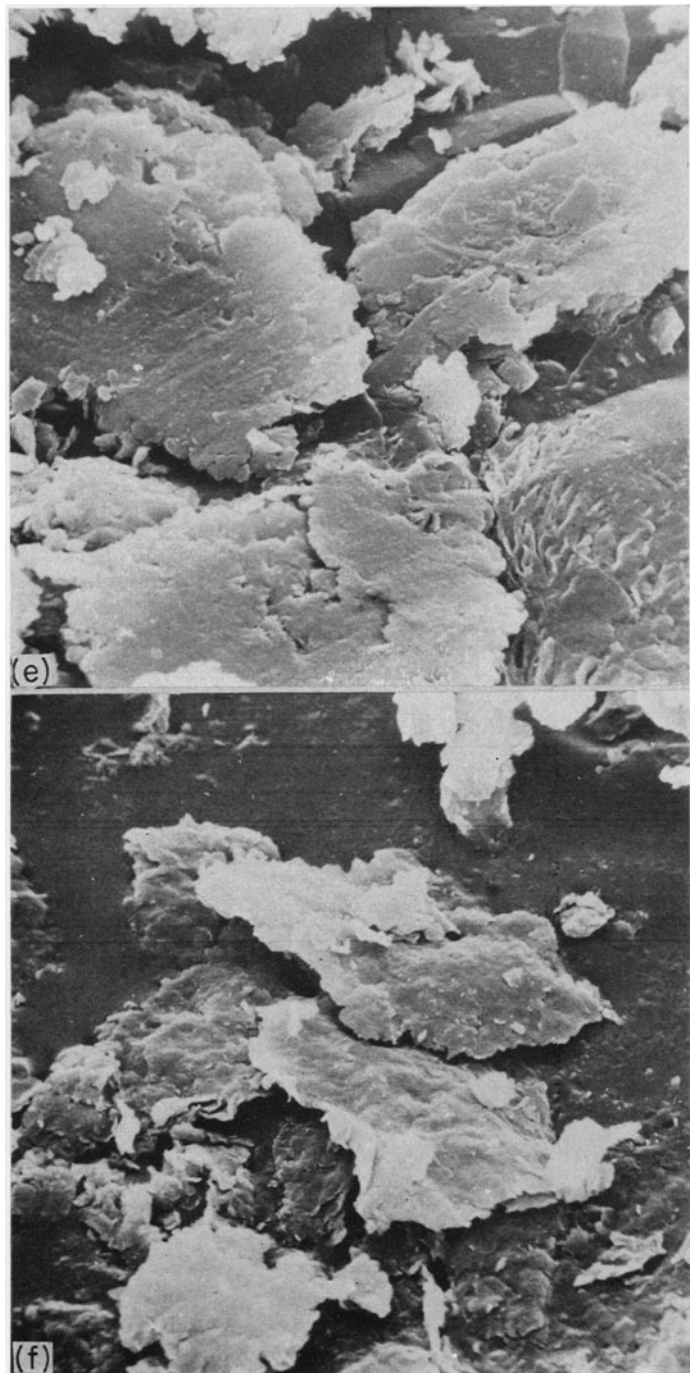


Fig. 2 (e)–(f).

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Table 3. Chemical analyses and structural formulae of Al(CB)

	Original material (without exchangeable cations)		Heated with KBr 1 hr at 520°C		
	Chemical analysis %	Structural formula	Chemical analysis %	Structural formula**	Structural formula***
	(1)	(2)	(3)	(4)	(5)
Si	24.49	7.74 tet.	25.95+	7.74 tet.	7.49 tet.
Al		0.26		0.26	0.51
	9.67	2.91	11.41	2.91	2.92
Mg	2.17	0.78 oct.	2.30	0.79 oct.	0.77 oct.
Fe^{3+}	1.89	0.30	3.07+	0.36	0.32
Fe^{2+}	0.13	0.06			
K			5.97	1.27	1.21
Al *				0.41	
O		20		21.51	20
OH		4		2.49	4

\+ calculated
* Al in hexagonal holes
** calculated assuming deprotonation
*** calculated on basis of $O_{20}(OH)_4$

To deduce the chemical composition of Al or Mg montmorillonites, at least three analyses are required, e.g. Al(CB) heated with KBr for 1 hr at 520°C was analysed for K, Al and Mg. The amount of Si and Fe associated with the Mg determined (2·30%) was deduced from the chemical composition of the original sample (column 1, Table 3). The chemical composition shown in column 3 was thus obtained.

Structural formulae can then be calculated by two methods: either on the assumption that the composition of the layers remains unchanged except for deprotonation or by using the conventional method of Ross and Hendricks (1945). In the first alternative, the amount of structural Al associated with 2·30% Mg is derived from the Al:Mg ratio of 4·4 of column 1. The amount of Al originating in the interlayers can then be calculated from the total Al content (column 3) and the structural formula I (column 4) is inferred. If, on the other hand, the chemical analysis is interpreted according to the method of Ross and Hendricks, the structural formula II (column 5) is obtained.

The Al(CB) studied was an aged sample which had been stored in aqueous suspension at room temperature. It contained 150 m-equiv. Al/100 g heated clay. This exceeds the exchange capacity and is probably due to the presence of polymerised Al hydroxide. The sum of K and interlayer cations retained by this specimen is greater than that observed with any other sample under corresponding conditions. It is probable that protons are formed in the interlayers by hydrolysis and that these react with the alkali halides. Differences were observed between corresponding samples of Al(W) and Al(CB) which require further investigation. If calculations similar to those shown for KBr treated Al(CB) are carried out for two KBr treated Mg(W) samples heated for different periods of time, the alternative structural formulae shown in Table 4 are obtained.

It is evident from Tables 3 and 4 that the conventional method of calculation leads to structural formulae with greater Al for Si substitution, which increases with the duration of the KBr treatment. This apparent increase is greater for Al saturated samples but occurs also if there is no increase in the total Al content. Thus, with KBr treated Mg montmorillonite it is the Mg and not the Al content of the sample that is increased and yet structural formulae calculated by the conventional method show greater Al for Si substitution than in the original clay. In general, fixation of K and increased Al for Si substitution are regarded as characteristic of illitization. It appears, therefore, that KBr treatment leads to products which, on the basis of their chemical analyses, could be regarded as illitic.

SCANNING ELECTRON MICROSCOPY

Scanning electron micrographs of various clay minerals have been described in the literature, but

Table 4. Structural formulae of Mg(W)

Sample	Structural formula I calculated on assumption of deprotonation	Structural formula II calculated on basis of 44 anionic charges
Mg(W) heated 1 hr 520°C	$(Si_{7.69}\ Al_{0.31})(Al_{3.07}\ Fe^{3+}_{0.40}\ Mg_{0.51})$ $Mg_{0.34}\ K_{0.90}\ O_{20.70}(OH)_{3.30}$	$(Si_{7.63}\ Al_{0.37})(Al_{2.95}\ Fe^{3+}_{0.40}\ Mg_{0.76})$ $K_{0.84}\ O_{20}(OH)_4$
Mg(W) heated 72 hrs 520°C	$(Si_{7.69}\ Al_{0.31})(Al_{3.07}\ Fe^{3+}_{0.40}\ Mg_{0.51})$ $Mg_{0.42}\ K_{2.39}\ O_{22.35}(OH)_{1.65}$	$(Si_{7.40}\ Al_{0.60})(Al_{2.67}\ Fe^{3+}_{0.38}\ Mg_{0.80})$ $K_{2.10}\ O_{20}(OH)_4$

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the effect of heat treatment on the morphology of montmorillonite particles does not seem to have been studied.

Air dried samples of any particular montmorillonite saturated with different cations resemble each other closely. However, when these samples were heated, striking differences were observed. Mg and Al montmorillonite, and, to a lesser degree, Li montmorillonite, developed a fluffy, porous texture (Fig. 2a, b, c) while Na and Ca montmorillonite appeared as thin, warped sheets (Fig. 2d). The corresponding KBr treated samples, except Li montmorillonite, differed fundamentally from the samples heated without KBr, but resembled each other, whatever the interlayer cation originally present. Up to 72 hr heating at 520°C, at least, the duration of the KBr treatment does not affect the morphology significantly. The samples are composed of small, irregular flakes in a turbostratic arrangement as shown in Fig. 2(e). KBr treated Li(W) resembled heated Li(W) rather than the other KBr treated samples (Fig. 2f).

The observed changes in morphology are compatible with the reactions postulated. Migration of small cations into the octahedral layers, which occurs when Li, Mg or Al montmorillonites are heated, causes the flakes to disintegrate into small, porous fragments. Since the effect is more pronounced with Al and Mg than with Li montmorillonite, it appears that the ionic size determines whether or not such migration occurs, but the degree to which the crystals are disrupted depends on the charge. With larger interlayer cations, which do not migrate into the octahedral layers on heating, the clay sheets are preserved, but they are curled, probably due to loss of interlayer water.

Except with Li montmorillonite, the presence of KBr inhibits both warping of the sheets and their disintegration, irrespective of the interlayer cations initially present. Previously, it has been inferred from i.r. spectra that interlayer cations other than Li do not migrate into the octahedral layers when montmorillonites are heated with alkali halides (Heller-Kallai, 1975). Accordingly, the particles are preserved intact and their surfaces are much less eroded than those of similar specimens heated without alkali halides. It seems that the presence of intercalated alkali halides inhibits curling of the sheets. The symmetry of the octahedral and tetrahedral sheets is altered (Heller-Kallai, 1975), which may also affect the morphology. The amount of K sorbed appears to have only a minor effect.

KBr treated Li montmorillonite is composed of small perforated fragments, resembling the sample heated without KBr. It was previously shown that some of the Li ions penetrate into octahedral holes before appreciable deprotonation and sorption of K occur (Heller-Kallai, 1975). The particles are eroded at an early stage and subsequent reaction with KBr cannot convert the porous, disintegrated fragments into coherent flakes.

Scanning electron micrographs of clays are not used routinely for mineralogical analysis. However, comparison of micrographs of KBr treated montmorillonites with those reported in the literature reveals a striking similarity between the morphology of these samples and the well-crystallized illite from Beavers Bend State Park described by Borst and Keller (1969).

POSSIBLE APPLICATIONS TO CLAY DIAGENESIS

In view of the relative ease with which montmorillonite reacts with potassium halides in the laboratory and the apparent similarity of the products to mixed layer montmorillonite–illite, the question arises whether reactions of this type could account for some of the material described as illite in nature. The problem of the characteristics and mechanism of formation of illite has occupied clay mineralogists for some time. It is generally agreed that illite can be formed on land by degradation of micas and felspars, or diagenetically, from montmorillonite. Weaver (1967) and Weaver and Beck (1971) have summarized the evidence against the hypothesis that diagenesis proceeds in the sea by extraction of K from sea water, and in support of the theory that it occurs after deep burial of the sediments.

All the mechanisms proposed presuppose that the alumino–silicate layers are preserved throughout the diagenetic process. Disintegration of montmorillonite followed by recrystallization of illite would undoubtedly require energies higher than those actually encountered.

Powers (1959) introduced the concept of the equivalence level, below which K is preferentially sorbed and illitization occurs. Burst (1969) and Perry and Hower (1970) found a monotonic decrease in expandability of montmorillonite/illite mixed layer material with increasing depth of subsurface samples of Gulf Coast sediments. They stressed that the decrease in expandability is proportional to the geothermal gradient rather than to the depth of burial. Various mechanisms have been proposed to account for the loss of expandability and concomitant changes in structure of the clays. Powers suggested that on deep burial Mg migrates into the octahedral layer, where it replaces Al, which in turn displaces tetrahedral Si, thus causing an overall increase in layer charge. This mechanism seems improbable in view of the high energy which would be required for direct Al for Si substitution. Burst (1969) attributed the loss of expandability to irreversible loss of interlayer water. Perry and Hower (1970) pointed out that this would require temperatures far higher than those encountered. They enumerated three possible mechanisms for converting expanding into nonexpanding clay: substitution of Al for Si, substitution of Mg and/or Fe^{2+} for Al and/or reduction of Fe^{3+}. They concluded, however, that there is insufficient evidence to decide which chemical reactions are involved.

Pollard (1971) proposed a semi-displacive mechanism for structural changes occurring in the

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course of conversion of montmorillonite into illite layers. In the first stage interlayer Al enters hexagonal holes. Subsequently, under conditions of low grade metamorphism, temperatures become sufficient to permit switching of Si–O to Al–O bonds, accompanied by rotation of the tetrahedra, geometric adjustment of the octahedral layers and migration of protons from OH groups to apical oxygens. The layers are regarded as activated complexes requiring a critical concentration of Al for the rotation to become irreversible. This mechanism, though sterically possible, involves stretching of Si–O bonds, followed by expulsion of Si from tetrahedral positions, which would undoubtedly require relatively high energies. Moreover, samples at the first stage of the reaction could be identified by their i.r. absorption spectra. Yet, to date, no natural occurrence of such samples has been reported.

The possibility that partial deprotonation of the clay, with associated minor changes in the symmetry of the octahedral and tetrahedral layer, may account for the diagenetic processes, does not seem to have been considered. Yet, in view of the observation of Fripiat *et al.* (1965) that mobility of protons in micas is appreciable at 200°C, it seems reasonable to infer that irreversible deprotonation may occur in the presence of proton acceptors at the temperatures encountered in the early stages of metamorphism. The experiments here described showed that reactions of this type readily occur with alkali halides. It may be significant that a survey of the mineralogy of clays from the Negev, Southern Israel, shows a close correlation between diagenetically formed illite and a hypersaline environment of deposition (Bentor, 1966).

Weaver and Beck (1971) discussed the geochemical processes leading to an overall enrichment of K and Al in montmorillonite on deep burial. Their reasoning would apply equally to the processes envisaged here. The difference lies in the postulated reaction mechanism and in the interpretation of the chemical analyses.

Preliminary experiments indicate that similar reactions occur between salts and other silicates, e.g. chlorite, palygorskite, kaolinite and biotite. It therefore appears that reactions of silicates with halides or other proton acceptors could account for diagenetic changes other than illitization in nature. Reactions between clay minerals and proton acceptors at elevated temperatures also may be of importance in ceramics. The products resemble well characterized clay minerals or clay mineral mixtures and could thus easily escape correct identification.

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