THERMAL REACTIONS OF SYNTHETIC HECTORITE

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Abstract – The thermal reaction sequence of a synthetic hectorite (Laponite CP) was studied by X-ray diffraction, i.r. spectroscopy and thermal analysis. Although most of the interlayer water is removed at 200°C, a smally steady weight loss occurs until dehydroxylation is complete at about 700°C, indicating that an anhydrous intermediate phase is not formed prior to dehydroxylation. Immediately after dehydroxylation, enstatite and cristobalite can be identified, but lithium silicates are formed only from lithium-saturated hectorite. Around 1200°C a glass is formed by reaction of the alkalis with cristobalite, and removal of silica from the enstatite produces some forsterite. An inhomogeneous mechanism of dehydroxylation is postulated by analogy with that proposed for talc.

INTRODUCTION

HECTORITE is a trioctahedral smectite structurally related to saponite, montmorillonite and talc. The composition of the ideal mineral is such that there is no tetrahedral substitution but some octahedral magnesium is replaced by lithium. The interlayer cation is predominantly sodium and the ideal formula is $(Mg_{5.33}Li_{0.67})Si_8O_{20}(OH)_4Na_{0.67}nH_2O$.

Although the thermal reactions of some related montmorillonites (Bradley and Grim, 1951; Grim and Kulbicki, 1961) and talc (Nakahira and Kato, 1964) have been studied, little is known about the high temperature reactions of lithium-containing smectites except for DTA curves of natural hectorite (Bradley and Grim, 1951; Schmidt and Heystek, 1953).

Recently a synthetic hectorite marketed as "Laponite CP" has become available. The constitution and properties of this material closely approach those of the ideal mineral and the freedom from impurities inherent in its synthetic origin makes it suitable for a study of the thermal reactions. The purpose of this work was to determine the reaction sequence and final products of Laponite, particularly with respect to the role of lithium and sodium.

EXPERIMENTAL

Materials. The synthetic hectorite (Laponite CP) was supplied by Laporte Industries Limited, Surrey, England, and is one of the reference minerals in the OECD project on non-metallic minerals. It has been described by Fripiat (1969) as a very pure specimen containing traces of carbonate and soluble salts. The manufacturer's analysis is shown in Table 1, column 1.

The analysis leads to the atomic ratios for Laponite CP shown in Table 1, column 3. However, it is shown below that to distinguish between interlayer and structural water is very difficult; it seems probable that the revised figure for H_2O based on the weight loss obtained between 220°C and 1000°C after heating to constant weight at 220°C is a better measure of the structural water content. The revised analysis is shown in Table 1, column 2, and the revised atomic ratios in column 4. Atomic ratios for ideal hectorite and the type mineral from Hector (Deer, Howie and Zussman, 1962) are shown in columns 5 and 6 for comparison. Clearly Laponite CP has a composition extremely close to that of ideal hectorite. It is likely that the potassium, calcium and excess sodium are associated with the small amounts of CO_2 and SO_3 detected. Natural hectorite invariably has some tetrahedral substitution, and replacement of hydroxide ions by fluoride is also common. In other respects Laponite CP is similar to natural hectorite, although being synthetic it is less crystalline. A related synthetic hectorite, Laponite S, has been shown to occur as spherical particles rather than the characteristic laths of natural hectorite (Jennings *et al.*, 1969).

A sample in which the interlayer sodium is replaced by lithium was prepared by washing Laponite CP three times with a concentrated solution of lithium bromide, centrifuging and drying at 100°C.

Experimental techniques. Differential thermal analysis (DTA) was performed in nitrogen on a

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Table 1. Chemical analysis and atomic ratios for Laponite CP, ideal hectorite and natural hectorite

	1	2		3	4	5	6
SiO_2	60·4	62·38	Si	7·52	8·01	8·00	7·78
MgO	26·6	27·47	Mg	4·96	5·26	5·33	5·57
Li_2O	1·1	1·14	Li	0·56	0·59	0·67	0·71
Na_2O	3·4	3·51	Na	0·83	0·87	0·67	0·85
K_2O	0·06	0·06	H	6·62	3·97	4·00	4·00
CaO	0·2	0·21	O	24·00	24·00	24·00	24·00
Fe_2O_3	0·04	0·04					
CO_2	0·5	0·52					
SO_3	0·1	0·10					
H_2O (structural)							
	7·9	4·63					
Total	100·3	100·06					

1. Chemical analysis of Laponite CP % of oxide on dry weight basis.
2. Chemical analysis (of LaponiteCP) based on revised figure for H_2O^{+220} (see text).
3. Atomic ratios calculated from column 1, excluding trace impurities, based on O = 24.
4. Atomic atios calculated from column 2, based on O = 24.
5. Atomic ratios ideal hectorite.
6. Atomic ratios hectorite from Hector (Deer, Howie and Zussman, 1962).

Netzsch apparatus at a heating rate of 5°C/min. Thermogravimetry (TG) was performed on a Stanton TRI thermobalance in nitrogen with a heating rate of 4°C/min.

Qualitative X-ray and i.r. analyses were made of samples heated in a platinum muffle furnace to various temperatures selected from the thermal analysis data. X-ray phase identification was by powder diffraction using Ni-filtered CuKα radiation. I.R. spectra were obtained from a Perkin-Elmer 337 spectrophotometer in the range from 400 to 4000 cm^{-1} using samples suspended in KBr discs.

RESULTS

TG, DTG and DTA curves of synthetic hectorite are shown in Fig. 1. There is a broad low-temperature endotherm corresponding to loss of loosely bound inter-layer water, followed by a steady and progressive weight loss up to 600°C, corresponding to the removal of the last of the inter-layer water and the less tightly bound structural water. A distinction between the two types of water is impossible under dynamic conditions, but under isothermal conditions the loss of loosely bound inter-layer water is substantially complete at 220°C. This temperature was selected as the drying temperature to obtain a reliable figure for the water content for the chemical analysis (Table 1).

The second entotherm (680°C) is associated with dehydroxylation and is followed immediately by a sharp exotherm (710°C) corresponding to rapid recrystallization of the product(s).

X-ray diffraction patterns of samples heated to various temperatures and quenched to room temperature are shown in Fig. 2. The unheated material has the hectorite pattern (ASTM card 9-031) but with rather broad peaks due to poor crystallinity or small crystallite size. A slight contraction in the (220) spacing was observed after heating to 600°C, but no attempt was made to avoid rehydration since the broadness of the peaks makes precise measurement difficult.

The X-ray patterns of the phases formed in the temperature range from 700 to 1100°C correspond to orthorhombic enstatite, which became progressively more crystalline, and cristobalite. After firing at 1250°C, the sample melted, cristobalite disappeared and forsterite was detected, presumably formed by removal of silica from enstatite. Since no traces of crystalline sodium or lithium silicates were observed in these samples at any temperature, the sole action of the alkalis was apparently to act as fluxing agents.

The thermal behavior of lithium-saturated hectorite at 850°C is different from that of the sodium-saturated sample. The X-ray diffraction data listed in Table 2 show that two crystalline lithium silicates, Li_2SiO_3 and $Li_2Si_2O_5$, were formed in addition to well-crystallized enstatite.
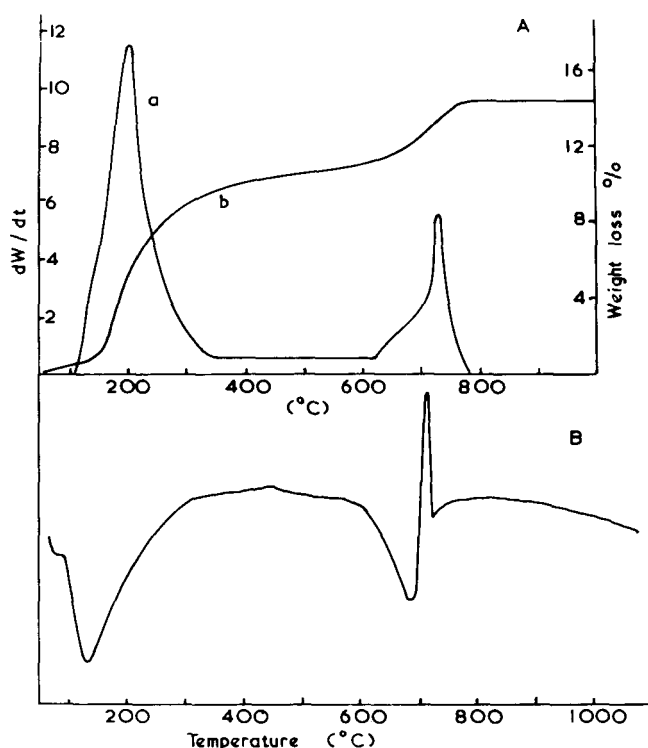
Fig. 1. (A) Curve a: Derivative thermogram of synthetic hectorite; Curve b: Weight-loss curve of synthetic hectorite. (B) Differential thermal analysis trace of synthetic hectorite.

No trace of cristobalite was observed. This is believed to be the first reported observation of lithium silicates in the firing products of lithium-containing smectites.

I.R. spectra corresponding to the X-ray diffraction patterns are shown in Fig. 3. The spectrum of the unheated material is identical with that of natural hectorite (Farmer, 1958). The spectra are little changed on heating to 700°C, but above this temperature fine structure develops which can be correlated with the spectrum of enstatite (Saksena, 1961). In the spectrum of the sample heated to 1250°C the intensity ratios of some enstatite peaks alter, probably due to the formation of forsterite which has a much simpler spectrum (Launer, 1952).

The i.r. spectrum of lithium-exchanged hectorite heated at 850°C (Fig. 3) contains additional bands at 760, 615 and 520 cm⁻¹ which can be attributed to the lithium silicates present.

DISCUSSION

The results obtained from X-ray diffraction, i.r. spectroscopy, DTA and TG, all confirm that Laponite CP is a typical, albeit poorly crystalline, hectorite whose thermal behaviour is comparable with that of the natural mineral, but uncomplicated by substitutions of aluminium for silicon and fluorine for hydroxyl.

The DTA curve of natural hectorite (Bradley and Grim, 1951; Schmidt and Heystek, 1953) differs from that of synthetic hectorite (Fig. 1B) in that the exotherm at about 900°C in the former is much broader and two additional endotherms are observed at about 1150°C. Bradley and Grim (1951) attribute these to transformation to clino-enstatite caused by the mineralizing action of fluoride ions. If this explanation is correct, the 1150°C endotherms would not be expected in the synthetic sample.

The i.r. spectra of unheated samples have a broad band due to water at 3400 cm⁻¹ and two sharp hydroxyl stretching frequencies at about 3630 and 3680 cm⁻¹. By analogy with hydroxyl assignments in micas (Vedder and Wilkins, 1969) and a lithium amphibole (Addison and White, 1968), the two hydroxyl bands in synthetic hectorite are probably associated with hydroxyl groups
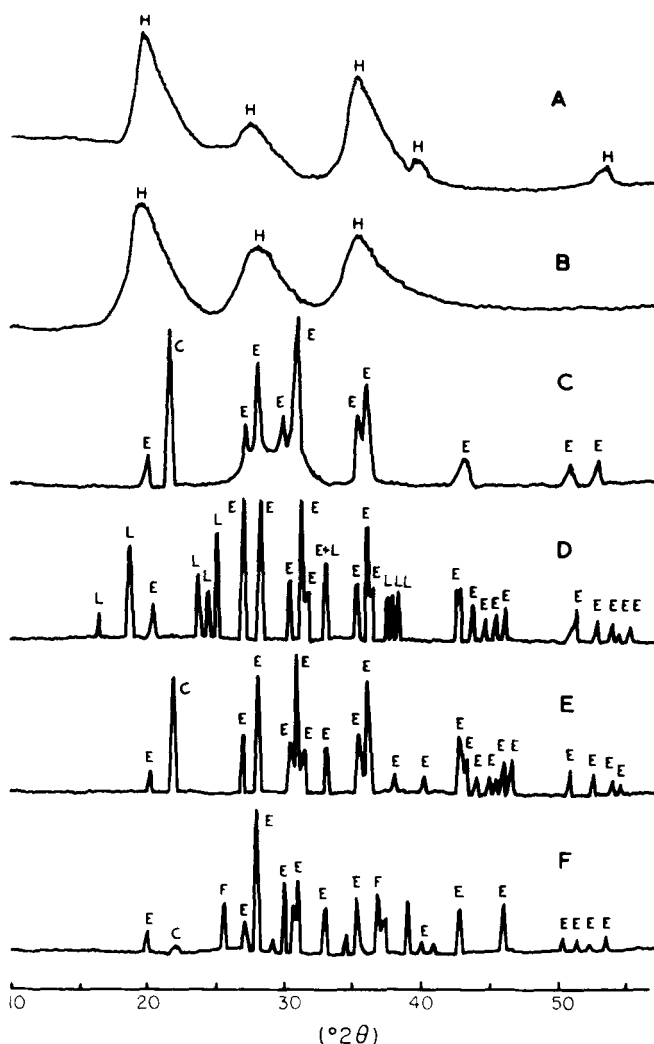
Fig. 2. X-ray powder patterns of synthetic hectorite heated to various temperatures for ~ 3 hr in air: (A) Unheated; (B) 600°C; (C) 800°C; (D) Li-treated sample at 850°C; (E) 1000°C; (F) 1250°C. Key:-
H = hectorite, E = enstatite, C = cristobalite, L = lithium silicate, F = forsterite.

coordinated to $3Mg^{2+}$, and $2Mg^{2+}+1Li^+$, respectively.

The spectrum of samples heated to 600°C indicates that dehydroxylation has become appreciable; the $3630 \, cm^{-1}$ peak has been lost and the higher peak shifted to $3670 \, cm^{-1}$. This behaviour is similar to that reported for kaolinite (Fripiat and Toussaint, 1960), in which the onset of dehydroxylation is marked by the temporary disappearance of two lower hydroxyl bands, which reappeared on cooling (the "predehydroxylation"

state). When true dehydroxylation sets in the two lowest bands do not reappear and only the band at $3695 \, cm^{-1}$ remains (associated in kaolinite (Wolf, 1963) with the hydroxyl groups in the layer common to the octahedral and tetrahedral sheets and nearly normal to the basal plane). Frequency shifts and loss of intensity of hydroxyl bands observed in other hydroxysilicates during heating, e.g. micas (Fripiat, Rouxhet and Jacobs, 1965), have been interpreted in terms of proton delocalization or tunneling through the potential energy

Table 2. X-ray diffraction data (d spacings, $d > 2$ Å) for Na
and Li saturated Laponite CP, fired at 850°C

Na-Satd.	Li-satd.	Li_2SiO_3[a]	$Li_2Si_2O_5$[b]	$MgSiO_3$[c]
	5·42		5·39	
	4·72	4·70		
4·39	4·40			4·41
4·07[d]				
	3·73		3·74	
			3·67	
	3·59		3·59	
3·28	3·30	3·32		3·30
3·16	3·15			3·17
2·94	2·94		2·90	2·94
2·86	2·86			2·87
	2·82			2·83
	2·71	2·72		2·71
		2·66		
2·53	2·53			2·53
2·49	2·48			2·49
	2·47			2·47
	2·39		2·40	
	2·35	2·35		2·36
	2·33		2·30	⎰2·28
				⎱2·25
				⎱2·23
2·11	2·11			2·11
	2·09			2·10
	2·05			2·06
2·01	2·02			2·02

[a]ASTM card number 4-723.
[b]ASTM card number 14-322.
[c]ASTM card number 7-216.
[d]Indicates presence of cristobalite.

barrier, a process necessary for dehydroxylation. The behaviour of the hydroxyl bands in the spectra of synthetic hectorite suggests that a similar process is involved in the initial formation of hydroxyl water.

Changes in the i.r. spectra between 400 and 1200 cm⁻¹ during the reaction can be explained in terms of the frequency assignments given for natural hectorite by Farmer (1958). The three broad bands in an unoriented specimen ($\sim$ 1000, 650 and 500 cm⁻¹) are associated with the Si–O (ν_1 and ν_3), Si–O (ν_2 and ν_4) and Mg–O (ν_6 and ν_7) vibrations, respectively. If the sample is oriented the spectra are only slightly sharpened, since the irregular replacement of Mg by Li leads to poorly defined perpendicularly polarized bands (Farmer, 1958).

The spectra of synthetic hectorite after heating above 700°C show these three broad groups, which have, however, developed fine structure (Fig. 3). The peaks at 1070, 1010, 930, 850, 725, 690, 565 and 545 cm⁻¹ have been attributed to the silicon–oxygen configuration of pyroxene

(Saksena, 1961). The peak at 795 cm⁻¹ is attributed to a silicon stretching vibration of cristobalite (Lippincott *et al.*, 1958), so that the remaining peaks must be associated with magnesium. This seems to be confirmed by the appearance in the lithium-rich sample of three new bands in close proximity to the proposed magnesium bands. Further heating causes only slight changes in the spectra.

The thermal reactions of synthetic hectorite are very similar to those of talc (Nakahira and Kato, 1964), which is similar in structure and also forms enstatite immediately on dehydroxylation. The presence of alkalis in hectorite does not interfere with this transformation; even when extra lithium is introduced in the interlayer positions, the formation of lithium silicates proceeds at the expense of cristobalite rather than enstatite. Sodium tends to enter a glassy phase rather than form crystalline silicates.

An inhomogeneous reaction mechanism has been proposed for the dehydroxylation of talc (Brindley, 1963; Nakahira and Kato, 1964), in
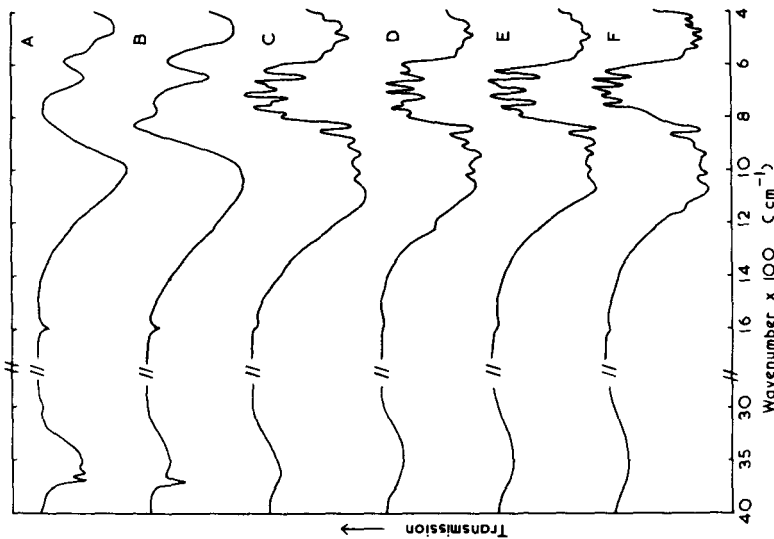
Fig. 4. Schematic diagram of the proposed inhomogeneous reaction mechanism for synthetic hectorite.

Fig. 3. I.R. spectra of synthetic hectorite heated to various temperatures for ~ 3 hr in air: (A) Unheated; (B) 600°C; (C) 800°C; (D) Li-treated sample at 850°C; (E) 1000°C; (F) 1250°C.
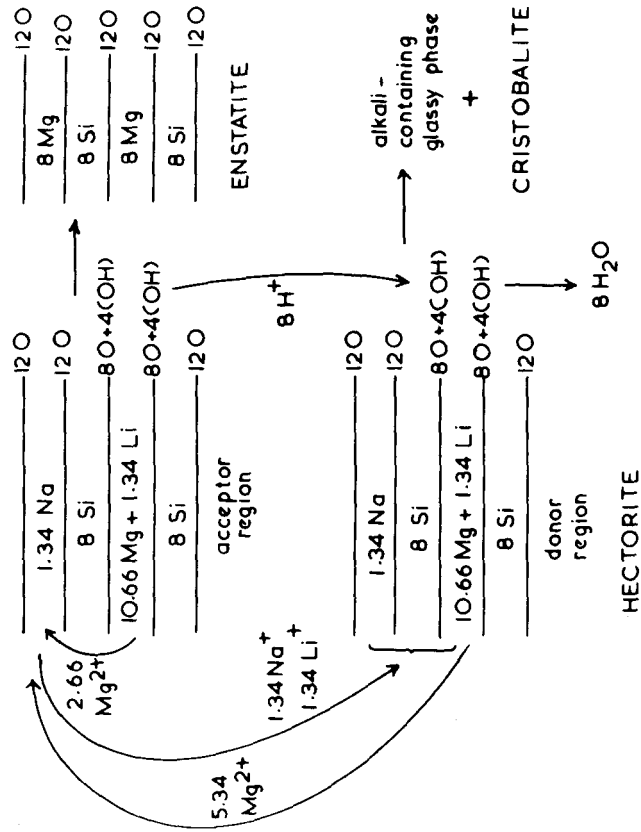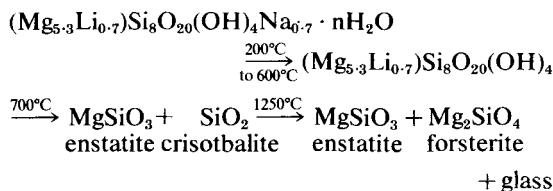
which acceptor regions lose 8 protons compensated by the gain of 4 Mg^{2+} to become enstatite. The donor regions, from which all the water is lost, become silica-rich. The principal evidence for this mechanism is the observed topotaxy between talc and enstatite. Unfortunately single crystals of synthetic hectorite were not available, although it seems feasible to postulate an inhomogeneous mechanism by analogy with talc. It is suggested that lithium and sodium may be associated with the silica-rich regions, since the enstatite formed is well crystallized. Lithium silicates are formed in the donor regions only when the lithium concentration is sufficient to form a separate phase. Similarly, sodium must be present in the donor regions to satisfy charge requirements, but it does not form a separate crystalline compound.
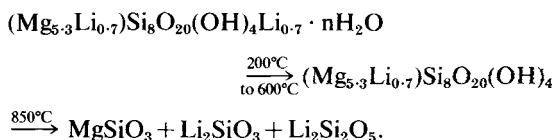
Thus, if the inhomogeneous mechanism proposed for the dehydroxylation of talc is accepted, the schematic representation of the analogous mechanism for the dehydroxylation of synthetic hectorite is as shown in Fig. 4.

CONCLUSIONS

Synthetic hectorite (Laponite CP) loses the bulk of its interlayer water at about 200°C, but continues to lose weight until dehydroxylation is complete at about 700°C. The reaction sequence for synthetic sodium-saturated hectorite can be summarized as

$$(Mg_{5.3}Li_{0.7})Si_8O_{20}(OH)_4Na_{0.7} \cdot nH_2O$$

$$\xrightarrow[\text{to }600°C]{200°C} (Mg_{5.3}Li_{0.7})Si_8O_{20}(OH)_4$$

$$\xrightarrow{700°C} \underset{\text{enstatite}}{MgSiO_3} + \underset{\text{crisotbalite}}{SiO_2} \xrightarrow{1250°C} \underset{\text{enstatite}}{MgSiO_3} + \underset{\text{forsterite}}{Mg_2SiO_4}$$

$$+ \text{glass}$$

whereas that for synthetic lithium-saturated hectorite is

$$(Mg_{5.3}Li_{0.7})Si_8O_{20}(OH)_4Li_{0.7} \cdot nH_2O$$

$$\xrightarrow[\text{to }600°C]{200°C} (Mg_{5.3}Li_{0.7})Si_8O_{20}(OH)_4$$

$$\xrightarrow{850°C} MgSiO_3 + Li_2SiO_3 + Li_2Si_2O_5.$$

Dehydroxylation is followed by immediate recrystallization. Structural similarities between hectorite and talc suggest a similar, probably inhomogeneous, mechanism of dehydroxylation for both minerals.

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Résumé – La séquence de réaction thermique d'un hectorite synthétique (Laponite CP) a été étudiée par diffraction des rayons X, spectroscopie à l'infra-rouge et analyse thermique. Bien que la plus

grande partie de l'eau entre les couches intermédiaires disparaisse à 200°C, il se produit une petite
perte régulière de poids jusqu'à ce que la déshydroxylation soit complète à environ 700°C, ce qui
indique qu'une phase intermédiaire anhydre ne s'est pas formée avant la déshydroxylation. Immédiate-
ment après la déshydroxylation, on peut identifier de l'enstatite et de la cristobalite, mais les les silicates
de lithium sont formés seulement à partir d'hectorite saturé au lithium. A environ 1200°C, un verre se
forme par réaction de l'alkali avec la cristobalite et la disparition de silice de l'enstatite produit de la
forsterite. Un méchanisme non homogène de déshydroxylation est postulé par analogie avec celui
proposé pour le talc.

Kurzreferat — Die thermische Reaktionsfolge eines synthetischen Hektorits (Laponit CP) wurde
durch Röntgenbeugung, Ultrarot-Spektroskopie und thermische Analyse studiert. Obgleich der Gros-
steil des Zwischenschichtwassers bei 200°C bereits entfernt ist, so findet doch ein geringer, stetiger
Gewichtsverlust statt bis die Dehydroxylierung bei ungefähr 700°C komplett ist, was darauf hindeutet,
dass es vor der Dehydroxylierung nicht zur Bildung einer wasserfreien Zwischenphase kommt.
Unmittelbar nach der Dehydroxylierung können Enstatit und Cristobalit identifiziert werden, während
sich Lithiumsilikate nur aus mit Lithium gesättigtem Hektorit bilden. Um 1200°C findet durch die
Reaktion von Alkalien mit Cristobalit Glasbildung statt, und die Entfernung von Silizium dioxyd as
dem Enstatit liefert Forsterit. Für die Dehydroxylierung wird ein inhomogener Mechanism, analog
dem für Talk, vorgeschlagen.

Резюме — Поведение синтетического гекторита при нагревании изучено методами рентгено-
графии, ИК-спектроскопии и термического анализа. Хотя большая часть воды удаляется
при 200°, небольшая, но постоянная потеря веса все же имеет место вплоть до полной
дегидроксилизации при температуре примерно 700°; это указывает на то, что до завершения
дегидроксилизации не происходит образования никакой промежуточной безводной фазы.
Немедленно после дегидроксилизации в остаточном продукте обнаруживаются энстатит и
кристобалит, литиевые силикаты образуются только из Li-насыщенного гекторита. При
температуре примерно 1200° в результате взаимодействия щелочных ионов с кристобалитом
образуется стекло, а удаление кремнезема из энстатита приводит к образованию небольших
количеств форстерита. Предполагается, что обнаруженный негомогенный механизм дегидрокси-
лизации аналогичен подобному механизму для талька.