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Magadiite and H-Magadiite: I. Sodium Magadiite and Some of Its Derivatives

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Abstract

Analytical composition, thermal analysis, and cation exchange reactions with organic cations are reported for the synthetic and natural layer silicate magadiite $Na_2Si_{14}O_{29} \cdot 11\ H_2O$. Thermal decomposition of magadiite depends upon the interlayer cation. With sodium ions a well crystallized tridymite is formed above 700°C. Decomposition of magadiite with organic interlayer cations leads to quartz.

The sodium interlayer cations of synthetic and natural magadiite can be quantitatively exchanged by alkylammonium-, dimethyldialkylammonium- and alkylpyridinium ions. With trimethylalkylammonium ions the exchange is not quantitative. Composition of the organic derivatives and their structures are discussed. Further types of organic derivatives can be prepared by base exchange reactions.

Introduction

In 1967 Eugster described the mineral magadiite, a new type of a sodium silicate with the composition $Na_2Si_{14}O_{29} \cdot 9H_2O$. Its synthesis has been reported by McCulloch (1952) and Lagaly, Beneke, and Weiss (1972a). McAtee, House, and Eugster (1967) and Brindley (1969) have shown that the spacing indexed as d_{001} by Brindley (1969) changes with the water content and that sodium ions are exchangeably bound. They concluded that magadiite has a layer structure with negatively charged silicate layers of still unknown structure, with exchangeable sodium ions between the layers and the capability of stepwise reversible hydration. Stability constants of magadiite have been determined by Bricker (1969); geological problems with magadiite formation are discussed by Rooney (1969) and Eugster (1973). The present paper deals with analytical composition, thermal dehydration, cation exchange with organic long chain cations, and organic intercalation compounds.

Materials and Methods

Magadiite

Natural magadiite from Trinity River, Trinity County, California (Minerals Unlimited, Calif.) and a synthetic magadiite have been used. The synthetic material has been prepared by heating mixtures of 9 moles SiO_2, 2 moles NaOH, and 75 moles H_2O at 100°C for 4 weeks. The reaction product, a white powder, was carefully washed with water, avoiding a decrease of pH below 9, and then dried at room temperature. Identity of this synthesized magadiite with the samples of Eugster (1967) and Brindley (1969) was checked by X-ray investigation and chemical analysis.

Organic Derivatives of Magadiite

Organic derivatives were prepared by reaction of magadiite with aqueous or aqueous-ethanolic solutions (maximum 10 percent ethanol) of alkylammonium chlorides, trimethylalkylammonium halogenides, dimethyldialkylammonium chlorides, alkylpyridinium chlorides, *etc.* at pH 7.5–8.0 at room temperature or 65°C, respectively. Detailed information is given by Lagaly *et al* (1972a). After several days the samples were separated from the mother liquid by filtration, then air-dried. Washing with water in general led to decomposition of the organic complexes and formation of H-magadiite.

X-ray diagrams were taken from the samples under the mother liquid and from the air-dried products.

Basal spacings at higher temperatures (25°C–120°C) were measured with a Philips Norelco diffractometer using a sample holder with electric heating (described by Lagaly, Fitz, and Weiss, 1975).

Analysis

The chemical composition of synthetic magadiite has been calculated from gravimetric SiO_2-analysis, photometric Na-determination, and potentiometric titration curves. Also measured for the organic derivatives were the C- and N-contents (by combustion) and the weight losses after heating to 900°C (formation of quartz). In some cases the data have been controlled by analysis of the equilibrium solutions. Both methods yielded similar results; minor differences arose from the adhering mother liquid or from negative adsorption in the suspension.

Results and Discussion

Composition of Synthetic Magadiite

Gravimetric SiO_2-analysis of the synthetic product gave 74.9 percent SiO_2. Problems arise in determining the Na_2O content due to adherent NaOH. Washing the product removes the sodium from the structure. In order to distinguish between sodium from adherent NaOH and from the structure, samples of about 1 g of synthetic product were washed x number of times with exactly 25 ml of water. In a plot of the sodium removed versus x, the curve showed no marked discontinuity. For $x \geqq 4$, however, the amount of sodium removed in each step became constant: 0.3 mg Na/g silicate. It may be assumed that at this point most of the excess of NaOH is removed. The total amount of sodium in the synthetic product is 4.90 percent; up to $x = 4$ 7.5 mg/g are leached so that the structural Na content is 4.15 percent.

During potentiometric titrations of the alkaline synthetic product with HCl at pH < 8, the pH increases with time. This may be considered as the start of the substitutions of structural sodium ions by protons. Up to this point 0.33 mval NaOH/g silicate—that is 7.7 mg Na/g—has been neutralized. The total Na content can be also taken from the titration curves to be 4.90 percent; thus the structural Na—4.90 minus 0.77— equals 4.13 percent. From Na = 4.13 percent and SiO_2 = 74.9 percent the ratio Na:Si is calculated to 0.144:1.0. The water content (H_2O:Si = 0.81:10) follows from the difference: 100 minus percent Na_2O (total) minus percent SiO_2, assuming the excess Na_2O (7.6 mg Na/g silicate) being in form of NaOH. It cannot be exactly determined from weight loss after heating as discussed below. Therefore

$$Na:Si:H_2O = 0.144:1:0.81$$

or, in comparison with data from McAtee *et al* (1968):

$$Na:Si:H_2O = 2.02:14:11$$

The natural magadiite from Trinity River which we used in our investigations yielded by direct determination of Na_2O and SiO_2:

$$Na : Si : H_2O = 2.09 : 14 : 11$$

These Na : Si ratios are very close to the data reported for other natural magadiites, ranging from 1.94 to 2.06. The H_2O content is larger than reported (8.8–9.6 H_2O/14 Si), probably due to different drying methods (Table 1).

Thermal Decomposition of Sodium Magadiite

The thermal behavior of sodium magadiite is summarized in Figure 1. Above 100°C the magadiite becomes dehydrated, and the basal spacing decreases to 11.5 Å. The dehydrated form is stable up to 500°C and can be completely rehydrated. In the narrow temperature range between 500°C and 700°C magadiite is decomposed and quartz (sometimes with cristobalite) is formed as the crystalline component. At 700°C a well-crystallized tridymite is developed, which is stable up to 1450°C (Table 2).

In the DTA diagram two large endothermic peaks indicate that the dehydration between 100 and 300°C occurs in two steps. A small broad endothermic peak at 600–700°C may be produced by the destruction of the magadiite lattice and formation of quartz; rear-

TABLE 1. Analytical Compositions (Main Components) of Synthetic and Natural Magadiites

Sample	Weight %			Atomic Ratios		
	Na_2O	SiO_2	H_2O	Na	Si	H_2O
Synthetic Magadiite [a]	5.58	74.9	18.19	2.02	14	11.3
Magadiite from Trinity County [a]	5.84	75.8	18.36	2.09	14	11.3
Magadiite Lake Magadite [b]	5.56	77.6	14.60	1.94	14	8.8
Alkali Valley Oregon [c]	5.74	77.78	15.42	2.01	14	9.26
Trinity County California [c]	5.82	76.13	13.98	2.06	14	8.51
Trinity County California [c]	5.61	77.36	15.17	1.97	14	9.16
Synthetic [d]	5.9	78.0	16.1	2.05	14	8.77

[a] this study [b] Eugster, 1967 [c] McAtee, House and Eugster, 1968
[d] McCulloch, 1952

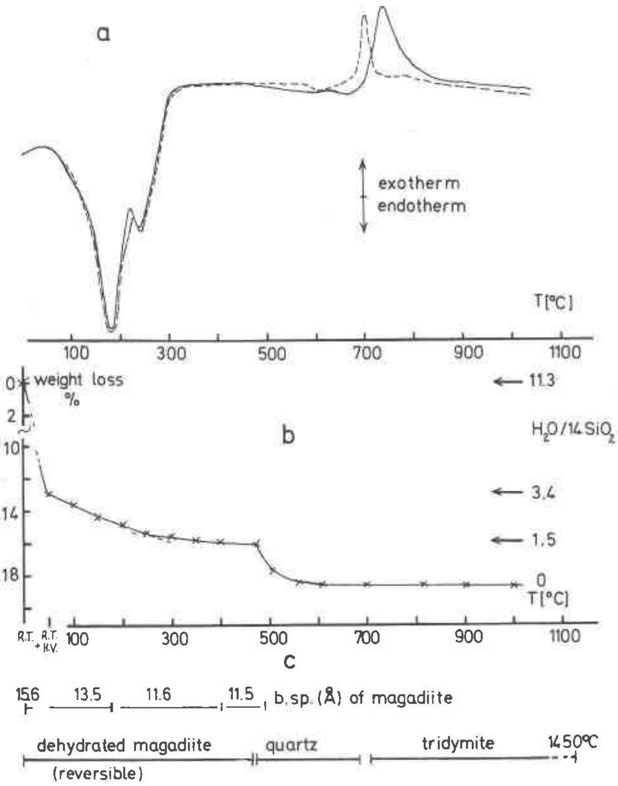


FIG. 1. Thermal behavior of magadiite. (a) DTA diagram (10°/min) of synthetic magadiite (—) and magadiite from Trinity River (---); (b) weight loss curve; (c) temperature ranges for reversible dehydration of magadiite and formation of quartz and tridymite.

rangement to tridymite is characterized by a sharp exothermic peak.

In high vacuum, 8 moles of H_2O are removed at room temperature. Two further molecules of water are removed up to about 450°C. The loss of the remaining H_2O between 500–600°C is not indicated in the DTA diagram. Perhaps the endothermic dehydration is superimposed upon the exothermic formation of quartz.

It is well known that tridymite is stabilized by Na_2O. Of the 1 mole of Na_2O per 14 of SiO_2 present in magadiite, only about 25 percent can be extracted with diluted HCl after formation of tridymite. The tridymite can be further stabilized by H_2O. The weight loss after heating is, therefore, often smaller for temperatures 700–1000°C than for 600–700°C, due to trapping of H_2O by tridymite. As a consequence, determination of water content by weight loss at these temperatures may lead to incorrect analytical data. A correct value can be taken from weight loss at 600–700°C.

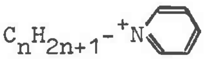
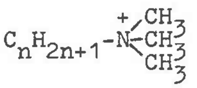
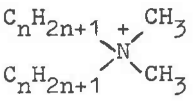
TABLE 2. Formation of Different SiO_2 Phases after Heating of Magadiite

	Phases after Heating to				
Interlayer Cation	500°C	600°C	700°C	800°C	1000°C
Na^+	Magadiite →	← quartz →	← tridymite →		
Organic Cations	Magadiite →		← quartz →		
H^+	← a new form of silica: $SiO_2 \cdot 0{,}1\ H_2O$ →				

Cation Exchange with Organic Cations

Formation of organic derivatives was assumed to be not possible with natural magadiite (McAtee *et al,* 1968). Under controlled experimental conditions, however, organic derivatives have been prepared with synthetic magadiite (Lagaly *et al,* 1972a). Because some of these compounds had unusual structural properties, more detailed investigations and complete chemical analysis seemed to be necessary. In addition, several investigations performed on natural magadiite showed no differences when performed on synthetic samples.

Organic derivatives are prepared by replacing the sodium ions by organic cations, namely the following long chain compounds:

n-alkylammonium ions (n = 1 - 18)	$C_nH_{2n+1}-NH_3^+$
N-n-alkylpyridinium ions (n = 1 - 18)	
N,N,N-trimethyl-N-n-alkyl-ammonium ions (n = 12, 14, 16, 18)	 $C_nH_{2n+1}-N^+(CH_3)_3$
N,N-dimethyl-N,N-di-n-alkyl-ammonium ions (n = 8, 10, 12, 14, 16, 18)	 $(C_nH_{2n+1})_2N^+(CH_3)_2$

The reactions proceed by cation exchange according to

$$Na_2Si_{14}O_{29} \cdot 11\,H_2O + x\,M^+ \rightarrow M_xNa_{2-x}Si_{14}O_{29} \cdot z\,H_2O + xNa^+ + (11-z)H_2O \quad (1)$$

The fraction x of sodium interlayer cations replaced depends upon the kind of the organic cations. Typical examples are listed in Table 3. With M^+ =

TABLE 3. Analytical Composition of Organic Derivatives of Magadiite $M_xNa_{2-x}Si_{14}O_{29} \cdot zH_2O$ (air dried samples)

Cation M^+ =	Analytical Composition x	z	CEC* a	b
$C_{12}H_{25}NH_3^+$ (n-dodecylammonium-)	2.0**	8	112	238
$C_{16}H_{33}NH_3^+$ (n-hexadecylammonium-)	2.0**	8	99	238
$(C_6H_5N^+)C_{14}H_{29}$ (N-n-tetradecylpyridinium-)	2.09	9	131	248
$(CH_3)_3N^+C_{12}H_{25}$ (trimethyl-n-dodecylammonium-)	1.65	10	116	196
$(CH_3)_3N^+C_{16}H_{33}$ (trimethyl-n-hexadecylammonium-)	0.59	9	48	70
$(CH_3)_2N^+(C_{14}H_{29})_2$ (dimethyldi-n-tetradecylammonium-)	1.86	7	104	221
$(CH_3)_2N^+(C_{18}H_{37})_2$ (Dimethyldi-n-octadecylammonium-)	1.83	8	91	218

* CEC: a mval M^+ per 100 g air dried material b mval M^+ per 100 g SiO_2

** and in addition 2.3 moles dodecylamin and 2.2 moles hexadecylamin, resp.

alkylpyridium ions or dimethyldialkylammonium ions, the exchange is nearly quantitative; with M^+ = trimethylalkylammonium ions the cation exchange is markedly reduced for very long chains.

With alkylammonium ions, the sodium ions are quantitatively exchanged, as determined by the sodium content of the samples. The C and N contents, however, correspond to about 4.3 moles alkylamine or alkylammonium ions per 14 SiO_2. Here the cation exchange reaction

$$Na_2Si_{14}O_{29} \cdot 11H_2O + 2C_nH_{2n+1}NH_3^+ \rightarrow (C_nH_{2n+1}NH_3^+)_2Si_{14}O_{29} \cdot z'H_2O + 2Na^+ + (11 - z')H_2O \quad \langle 2 \rangle$$

is followed by a complex formation

$$(C_nH_{2n+1}NH_3^+)_2Si_{14}O_{29} \cdot z'H_2O + 2C_nH_{2n+1}NH_2 \rightarrow (C_nH_{2n+1}NH_3^+)_2(C_nH_{2n+1}NH_2)_2Si_{14}O_{29} \cdot zH_2O + (z' - z)H_2O \quad \langle 3 \rangle$$

with free amine. (The free amine $C_nH_{2n+1}NH_2$ in aqueous solutions is produced by the amine-ammonium equilibrium:

$$C_nH_{2n+1}NH_3^+ + H_2O \rightarrow C_nH_{2n+1}NH_2 + H_3O^+$$

which becomes effective at $pH > 7$).

Thus, in addition to 2.0 alkylammonium ions, which are bound as cations, about two further alkylamine molecules are intercalated into the interlayer space forming 1:1 intercalation compounds. In attempts to leach out this excess of free amine, the alkylammonium ions are easily hydrolyzed so that the pure alkylammonium magadiite occurs only as an intermediate product.

Structure of Organic Derivatives

The exchange of the sodium ions against large organic cations is connected with a large increase in the basal spacing. In general the basal spacing increases most nearly linearly (Table 4) with the chain length of the cation. From the variation of the basal spacing with the chain length, models for the arrangement of the cations in the interlayer space can be deduced. It has been shown (Lagaly *et al*, 1972a) that different types of interlayer structures may be distinguished.

Alkylammonium-Magadiite

The high basal spacings of alkylammonium-magadiite have been interpreted by the following model: the alkylammonium ions are arranged in bilayers between the silicate layers, their chain axes orienting perpendicular to the silicate sheets (Fig. 2a). This structure is stable only if additional alkylamine molecules are intercalated according to reaction ⟨3⟩. This may be understood by a simple geometrical consideration. The unit cell ($Na_2Si_{14}O_{29} \cdot 11\ H_2O$) has a basal area of *ca* 54.7 Å². Since one alkyl chain in a monomolecular film requires an area of *ca* 25 Å² (perpendicular to its long axis), 4.4 alkyl chains per unit cell are at least necessary for a stable bimolecular arrangement. Thus about 2.4 alkylamine molecules per unit should be incorporated in addition to the two alkylammonium ions which are bound as cations. The experimental data lie at 2.3–2.4 moles alkylamine per 14 SiO_2.

From the above consideration a monomolecular arrangement (two chains per unit cell) should be stable without any incorporation of free alkylamine molecules. Under special experimental conditions (Lagaly *et al*, 1972a) such arrangements can be

TABLE 4. Basal Spacings of Organic Derivatives of Synthetic and Natural Magadiite

Cation	Basal Spacings (Å) (during the exchange reaction) for n = 8	10	12	14	16	18	$\Delta d/\Delta n$
$C_nH_{2n+1}NH_3^+$	37.8	42.9	48.0	53.2	59.0	64.0	2.6
$C_nH_{2n+1}N(CH_3)_3^+$			35.4	35.7	37.0	38.4	1.0
$(C_nH_{2n+1})_2N(CH_3)_2^+$	31.0	34.2	38.0	41.4	45.0	50.0	1.9
$C_nH_{2n+1}\overset{+}{N}$⬡	29.4	31.5	34.8	38.4	40.8	44.1	2.9

observed. The bimolecular arrangement, however, seems to be preferred in aqueous solutions, because the exchange reaction occurs at pH = 7–9. In this range the concentration of free alkylamine molecules due to the ammonium-amine equilibrium is enhanced and favors the bimolecular structure. Cation exchange in non-aqueous solutions of alkylammonium chloride—*e.g.* in dimethylsulfoxide—can lead to monolayer structures.

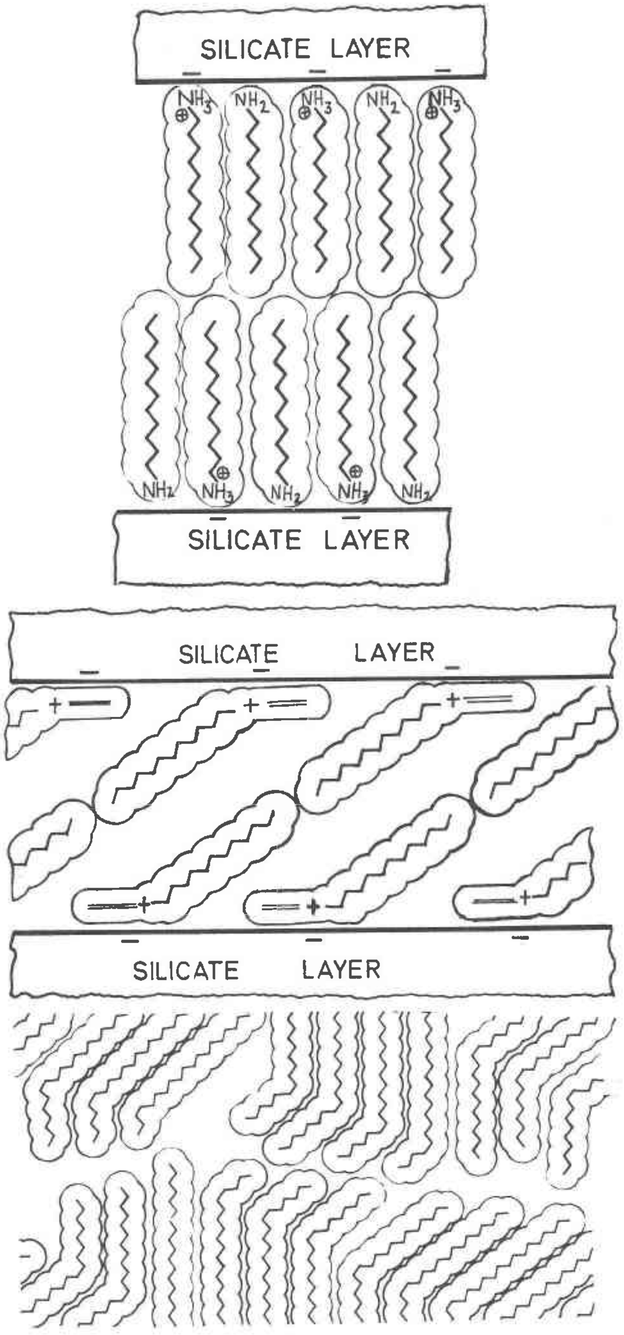


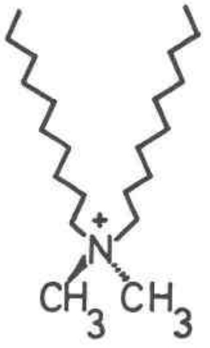
FIG. 2. Models for the interlayer structure of long chain magadiite derivatives. (a) arrangement of alkyl chains in alkylammonium magadiite; (b) arrangement of n-alkylpyridinium ions in n-alkylpyridinium magadiite; (c) gauche block structure of alkyl chains (α-phases of alkylammonium-alkylamine layer silicates; dimethylalkylammonium layer silicates—montmorillonites, beidellite, magadiite).

Alkylpyridinium-Magadiite

In alkylpyridinium-montmorillonite complexes, a characteristic orientation of alkylpyridinium ions in the interlayer space has been found (Lagaly *et al*, 1972b). The pyridinium ions lie flatly onto the silicate layers, so that the N–C_1 bond is parallel to the sheet. With all the C–C bonds of the chain in trans-conformation, the chains are directed away from the sheet in an angle of 35°. A similar arrangement has been tested for alkylpyridinium-magadiite. The best agreement between observed spacings and theoretical values for mono- and bilayer models with different tilting angles of the chains is reached for the bilayer model with the chains tilted at about 35° to the silicate layers (Fig. 2b). The holes between the chains are stabilized by water molecules probably organized into distinct water structures. Air drying reduces the water content and the basal spacings (Tables 4 and 6). A less regular variation of the basal spacings hints to a less regular structure in air-dried condition.

Dimethyldialkylammonium-Magadiite

With all C–C bonds in trans-conformation the two long alkyl chains of dimethyldialkylammonium ions are not parallel but form the sides of a "V" (I). This arrangement is less suitable for formation of stable mono- or bimolecular films. By some conformational changes in the alkyl chains near the N atom, however, the alkyl chains can be directed parallel to each other (II). It is this configuration which occurs in stable monomolecular films of dimethyldialkylammonium ions (Gaines, 1966).



I

II

* gauche bonds

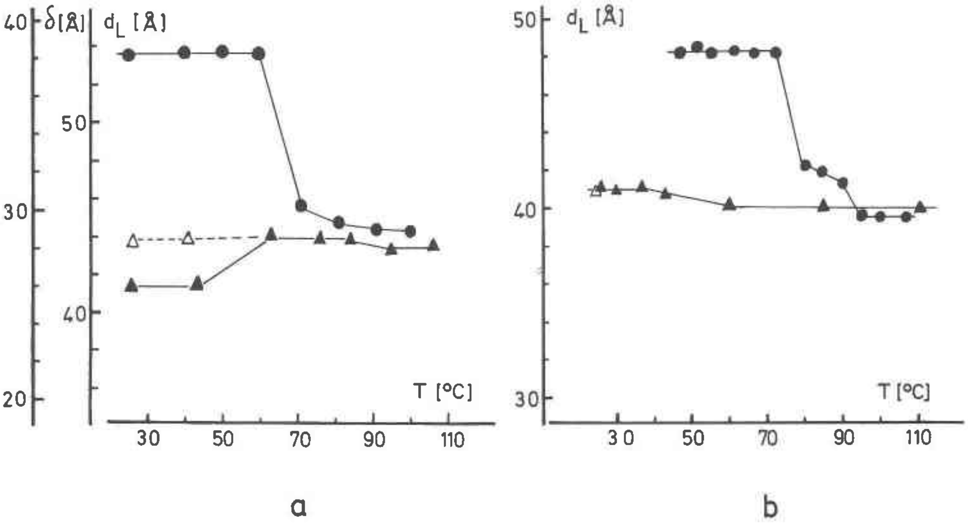


FIG. 3. Variation of the basal spacings d_L and interlayer spacings with temperature for tetradecylammonium-tetradecylamine complexes (●) and dimethylditetradecylammonium derivatives (▲, △): (a) magadiite from Trinity River, California; (b) beidellite from Unterrupsroth, Germany. (Interlayer spacing δ = basal spacing d_L minus layer thickness—15.4 Å for magadiite, 10 Å for beidellite; △: metastable spacings after cooling down).

In the case of dimethyldialkylammonium magadiite, bilayers of dimethyldialkylammonium ions are built up between the silicate sheets, since the basal spacings markedly exceed the theoretical spacings for a monolayer arrangement (alkyl chains parallel to each other and perpendicular to the silicate sheets). From the linear increase of the basal spacings with the chain length a tilting angle of 45° may be calculated. This angle is less comparable with the tilting angle of 70° which should occur for the "V" shaped structure of the ions. With the "V" shaped interlayer cations the space filling would be very poor.

Another interpretation is based on thermal phase transitions of long chain organic derivatives of layer compounds. As investigated with mica type layer silicates in detail (Lagaly *et al*, 1975; Lagaly and Weiss, 1971) the alkyl chains in the interlayer space rearrange at higher temperatures in special high temperature phases (α-phases). These phase transitions are connected with sharp decreases in the basal spacing. Figure 3 shows the variation of basal spacings with temperature for alkylammonium-alkylamine-magadiite and alkylammonium-alkylamine-beidellite (a mica-type layer silicate). Both compounds have the same interlayer structure at room temperature (Fig. 2a) and rearrange into high temperature forms above 60°C and 72°C, respectively, as indicated by the large decrease of the basal spacings. It is likely that in the α-phase the chains are arranged in gauche block structures (Fig. 2c), but other models with different chain conformations such as helices, *etc* cannot be distinctly excluded.

In Figure 3 the basal spacings for dimethyldialkylammonium-magadiite and -beidellite are inserted. These spacings coincide with the spacings of the α-phases of the alkylammonium-alkylamine-complexes so that similar types of gauche block structures can be postulated for the dimethyldialkylammonium derivatives. Table 5 shows that the basal spacings of dimethyldialkylammonium-magadiite at room temperature are comparable with spacings calculated for the idealized gauche block structure of type $\frac{n}{2}\perp$. The mean increase in the observed basal spacings (1.9 Å/$-CH_2-$) equals the

TABLE 5. Theoretical and Observed Basal Spacings for Different Structures of Chains in the Interlayer Space

chain length n =	Calculated Basal Spacings * (Å) chains perpendicular to the layers and arranged in			Observed Spacings (Å)	
	monolayers	bilayers	Gauche Blocks	Alkylammonium-Alkylamine-Magadiite	Dimethyldialkylammonium-Magadiite
10	31.1	43.8	34.9	42.9	34.2
12	33.6	48.8	39.1	48.0	38.0
14	36.2	53.9	41.8	53.2	41.4
16	38.7	59.0	46.0	59.0	45.0
18	41.3	64.1	48.7	64.0	50.0

Calculation: Monolayers: $d_L = 15.4 + 3 + 1.27\ n$ (Å); Bilayers: $d_L = 15.4 + 3 + 2 \cdot 1.27\ n$ (Å); Gauche Block: $d_L = 15.4 + 3 + \frac{x}{4} \cdot 1.45 + \frac{n}{2} \cdot 1{,}27$(Å)

($x = 3$ for $n = 8,12,16$; $x = 3n-2$ for $n = 10,14,18$)

(15.4 = b.sp. of NH_4-Magadiite, 3 = distance between the methyl end groups normal to the layers)

TABLE 6. Formation of Higher Hydrated Organic Complexes of $M^{+}{}_{x}Na_{2-x}Si_{14}O_{29}$ in the Solution during Cation Exchange in Comparison with the Air Dried Samples

Cation M^{+} =	x	Basal Spacing (Å) Air dried	under mother liquid	Δd	ΔV	additional water uptake moles $H_2O/Si_{14}O_{29}$
dodecylammonium	2.0	47.2	48.0	0.8	44	2
hexadecylammonium	2.0	57.7	59.0	1.3	71	3
tetradecylpyridinium	2.1	36.1	39.0	2.9	158	6
octadecylpyridinium		39.3	44.1	4.8	263	10
trimethyldodecyl-ammonium	1.65	29.7	31.8	2.1	115	4
trimethylhexadecyl-ammonium	0.59	29.2	37.2	8.0	438	17
dimethyldi-n-tetra-decylammonium	1.86	40.7	42.0	1.3	71	3
dimethyldi-n-octa-decylammonium	1.83	50.0	50.0	0	0	0

theoretical value for the idealized gauche block structure (1.7 Å/$-CH_2-$).

Trimethylalkylammonium-Magadiite

An interpretation of the basal spacings (Table 4) of the investigated samples is difficult because the mole fraction of the organic cations decreases with the chain length (Table 3). As a consequence the increase in the basal spacing from decyl- to octadecyl-complex is about 2 Å only. The spacings do not exceed the theoretical spacings for a monolayer arrangement of trimethylalkylammonium ions.

Water Content of Organic Derivatives

Long chain organic derivatives of montmorillonites and vermiculites in general have only minor water contents in the interlayer space after drying. In contrast, the water content of the air-dried magadiite derivatives is relatively high (Table 3). From the 7–10 moles of H_2O about 1.5 belong to the silicate layer; the rest are bound in the interlayer space, probably at the silicate surface. The $\geqslant$ Si–O groups project into the interlayer space, and may act as preferred adsorption sites.

TABLE 7. Basal Spacings of Magadiite-Amine-Complexes Prepared from Dodecylammonium-Magadiite by Amine Exchange Reaction

Amine	Basal Spacing (Å) of the Amine Complexes
n-hexylamine	29.8
diaminodecane	24.2
piperidine	23.0
pyridine	16.1
piperazine	19.0
pyrazine	18.2
cyclohexylamine	24.2
benzylamine	24.2
aniline	15.2

Under the reacting solutions during the cation exchange reactions, several samples have markedly higher basal spacings (Table 6) than in air-dried condition, hinting at more hydrated complexes. From the increase of the basal spacing (Δd_L) and the resulting volume increment $\Delta d_L \cdot 54.7$ Å³ (basal area of unit cell $a_0 b_0 = 54.7$ Å²), the amount of additionally intercalated water has been estimated using a molecular volume of 26 Å³ for H_2O (Table 6).

The complexes with primary alkylammonium ions and dimethylalkylammonium ions appear to be closely packed with large van-der-Waals interaction energies between the cations; they do not take up higher amounts of water. Higher hydration numbers, which increase with the chain lengths of the cations, are found for the alkylpyridinium- and trimethylalkylammonium derivatives. Particularly high amounts of water are intercalated in the trimethylhexadecyl compound with only 1/3 of the sodium ions being replaced by the organic cations. Probably the formation of distinct water clusters in the interlayer space plays an important part and contributes to the non-quantitative cation exchange. The free space between the alkyl chains in these samples is in the order of 7 × 9 × 25 Å³ and large enough for formation of distinct water structures.

Further Types of Organic Derivatives of Magadiite

Replacement of organic cations by free bases according to

$$(C_nH_{2n+1}NH_3^{+})_2Si_{14}O_{29}\cdot zH_2O + 2B \rightarrow (BH^{+})_2Si_{14}O_{29}\cdot z'H_2O + 2C_nH_{2n+1}NH_2 + (z - z')H_2O \quad \langle 5\rangle$$

offers a broad variety of organic derivatives. Some examples are listed in Table 7.

Proteins are strongly bound by magadiite. Since the basal spacing remains unchanged, it cannot be distinguished between external and interlayer sorption though the amounts adsorbed are quite high (at pH = 8: albumen 505 mval N/14 SiO_2, lysozyme 780 mval N/14 SiO_2, salmine 1860 mval N/14 SiO_2).

Different types of organic derivatives can be prepared from H-magadiite as described in detail in part II of this paper.

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