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# Intercalation and Pillaring Reactions of

# Layered Alkali Metal Silicates

presented by

James Steven Dailey

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degree in Chemistry Ph D

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# INTERCALATION AND PILLARING REACTIONS OF LAYERED ALKALI METAL SILICATES

bу

James Steven Dailey

### A DISSERTATION

## Submitted to Michigan State University in partial fulfillment of the requirements for the degree of

#### DOCTOR OF PHILOSOPHY

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#### ABSTRACT

#### INTERCALATION AND PILLARING REACTIONS OF LAYERED ALKALI METAL SILICATES

bу

James Steven Dailey

The goal of this work was to design and synthesize pillared microporous materials from intercalation complexes of the layered alkali metal silicates. By extrapolating knowledge gained from other layered silicate clays to the alkali metal silicates, new classes of silicate intercalation compounds have been developed. Two routes were used to intercalate robust pillars between the layers of the layered alkali metal silicates, direct ion exchange of pillar cations for alkali cations, and the intercalation of siloxane reagents within preintercalated derivatives of H<sup>+</sup>-magadiite.

The cationic metal cage complex (1,3,6,8,10,13,16,19)octaazabicyclo[6.6.6]eicosane)cobalt(III), Co(sep)<sup>3+</sup>, has been investigated as a potential pillaring reagent for Na<sup>+</sup>-magadiite  $(Na_{1.7}Si_{14}O_{27.9}(OH)_{1.9}7.6H_20)$  a synthetic layered sodium silicate. Reaction of Na<sup>+</sup>-magadiite with aqueous solutions of Co(sep)Cl<sub>3</sub> at 25°C resulted in the binding of Co(sep)<sup>3+</sup> cations to the external crystallite surface of the layered silicate. In contrast, an intercalated product exhibiting a 17.6 Å basal spacing was generated by reaction at 100°C. <sup>29</sup>Si MAS NMR and FT-IR spectroscopy indicate that  $Co(sep)^{3+}$  intercalated reaction products retain the magadiite layer structure. Moreover, scanning electron micrographs of the reaction products showed retention of the original particle morphology, suggesting a topotactic intercalation. However, during intercalation, some of the  $Co(sep)^{3+}$  underwent an unusual demetalation reaction leaving a combination of Co(II) and  $Co(sep)^{3+}$  between the layers. Nitrogen surface area analysis showed that only a small amount of microporous surface existed in the  $Co(sep)^{3+}$  intercalated derivative, suggesting that most of the interlayer space is "stuffed" with cobalt species.

Reaction of the silicic acid H<sup>+</sup>-magadiite, H<sub>3.1</sub>Si<sub>14</sub> O<sub>29.5</sub>•H<sub>2</sub>O, with an excess of an n-alkylamine such as octylamine afforded high basal spacing derivatives in which the silicate layers were separated by layers of solvated alkylammonium cations  $(d_{001} = 34 \text{ Å})$ . The properties of the alkylammonium silicate as a precursor for the intercalation of hydrolyzable reagents such as tetraethylorthosilicate, TEOS, has been investigated. Neat TEOS readily intercalates at room temperature and partially polymerizes in a molecularly regular fashion in the H<sup>+</sup>-magadiite galleries, giving rise to ordered basal spacings in the range 23.3-28.1 Å. The mechanism for polymerization appears to occur by a topochemical process. Calcination of the TEOS hydrolysis products yielded layered magadiite derivatives regularly intercalated by silica pillars. Silica pillared derivatives exhibited gallery heights of 9.5-14.5 Å and microporous surface areas of 480-670  $m^2/g$  depending on the TEOS reaction stoichiometry. The silica pillared products contain interior

surface silanol groups of the type  $Q^3$  HOSi(OSi)<sub>3</sub> and  $Q^2$  (HO)<sub>2</sub>Si(OSi)<sub>2</sub> as confirmed by proton cross polarization <sup>29</sup>Si magic angle spinning NMR spectroscopy. These surface silanol groups should prove to be useful as grafting sites for metal centers for catalysis or sensor applications. In memory of my father, William J. Dailey.

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#### **CHAPTER I**

Layered Alkali Metal Silicates: An Overview

#### A. Introduction

A large number of naturally occuring alkali metal silicate minerals with layered structures have been discovered in alkaline lakes around the world over the last 25 years. They include the anhydrous sodium silicate natrosilite  $(Na_2Si_2O_5)$  (1) and the hydrous silicates kanemite (NaHSi<sub>2</sub>O<sub>5</sub> $\cdot$ 5H<sub>2</sub>O) (2), makatite sodium  $(Na_2Si_4O_8(OH)_2 \cdot 4H_2O)$  (3), magadiite  $(Na_2Si_{14}O_{29} \cdot 11H_2O)$ , and kenyaite  $(Na_2Si_{20}O_{41} \cdot xH_2O)$  (4). Also a naturally occuring crystalline silicic acid, silhydrite, was discovered in a Trinity county (CA) magadiite deposit (5,6). Synthetic forms of these and other alkali metal silicates are readily obtainable. These layered silicates also possess interesting ion exchange and intercalation properties. Bv extrapolating knowledge gained from other layered silicate clays to the alkali metal silicates, it should be possible to design new classes of silicate intercalation compounds with novel catalytic properties. The proton exchange forms of the alkali silicates represent new families of crystalline silicic acids with layered structures. Owing to the presence of interlamellar SiOH groups, the layered silicic acids may prove to be excellent hosts for the immobilization of metal complexes. In anticipation of the future catalytic application of these

1

materials, we review here the synthesis, structure, and intercalation properties of the layered alkali metal silicates and their corresponding layered silicic acid forms.

#### B. Syntheses

Alkali silicates have been synthesized by two general methods, namely, by high temperature reaction of  $SiO_2$  with alkali metal carbonate melts, or by hydrothermal reaction of aqueous alkali hydroxide solutions with  $SiO_2$ . Both the molten salt and hydrothermal routes can generate anhydrous or hydrous alkali silicates, depending on the reaction conditions. Table I.I. lists the compositions of typical alkali metal silicate phases and their acid exchange forms, where known.

 $\alpha$  and  $\beta$  phase sodium disilicates have been synthesized by fusing Na<sub>2</sub>CO<sub>3</sub> and SiO<sub>2</sub> in a 1:2 molar ratio at 500°C-860°C. The lower temperature polymorph  $\beta$ -Na<sub>2</sub>Si<sub>2</sub>O<sub>5</sub> forms between 600-700°C, while  $\alpha$ -Na<sub>2</sub>Si<sub>2</sub>O<sub>5</sub> crystallizes in its pure form between 750°C and 860°C (7-9). Potassium disilicate, K<sub>2</sub>Si<sub>2</sub>O<sub>5</sub>, was readily prepared at 800°C by fusing K<sub>2</sub>CO<sub>3</sub> and SiO<sub>2</sub> in a 1:2 molar mixture (10). The more silicious K<sub>2</sub>Si<sub>4</sub>O<sub>9</sub> can be synthesized by heating a K<sub>2</sub>O•4SiO<sub>2</sub> glass (10) at 400°C in the presence of small amounts of H<sub>2</sub>O (9).

The hydrothermal synthesis of layered alkali silicates has been accomplished by the reaction of aqueous NaOH, KOH or LiOH with SiO<sub>2</sub> between 60°C and 300°C. The higher reaction temperatures, 200°C-350°C resulted in anhydrous alkali silicates such as Na<sub>2</sub>Si<sub>2</sub>O<sub>5</sub> (11). Wey et. al (12) synthesized KHSi<sub>2</sub>O<sub>5</sub> by reaction of a ternary mixture

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	Crystal Structure	Reference	59,48	60	61	ı	ı	65	12,64	ı	16	30	17	19	18
Forms.	Silicic Acid Form		H <sub>2</sub> Si <sub>2</sub> O <sub>5</sub> , I, II	H <sub>2</sub> Si <sub>2</sub> O <sub>5</sub> , IV	H <sub>2</sub> Si <sub>2</sub> O <sub>5</sub> , I, II, III	AA	NA	AN	H <sub>2</sub> Si <sub>2</sub> O <sub>5</sub> , III	AN	H <sub>2</sub> Si <sub>8</sub> O <sub>17</sub> •xH <sub>2</sub> O	H <sub>2</sub> Si <sub>14</sub> O <sub>29</sub> •xH <sub>2</sub> O	H <sub>2</sub> Si <sub>20</sub> O <sub>41</sub> •xH <sub>2</sub> O	H <sub>2</sub> Si <sub>20</sub> O <sub>41</sub> •xH <sub>2</sub> O	NA
ı Exchange	Crystal Structure	Reference	62	63	1	1	23	65	60	22	I	ı	ı	1	•
their Protor	Synthetic Reference		1,2	8,9	N	10	9,10	65	9,12	11,15,17	15-17	13,14,17	14,17	19	18
Silicates and	Synthetic Method		melt	melt	hydroth.	melt	hydroth.	melt	hydroth.	hydroth.	hydroth.	hydroth.	hydroth.	hydroth.	hydroth.
Table I.I. Layered Alkali Metal S	Alkali Silicate		αNa <sub>2</sub> Si <sub>2</sub> O <sub>5</sub>	βNa <sub>2</sub> Si <sub>2</sub> O <sub>5</sub>	NaHSi <sub>2</sub> O <sub>5</sub> •3H <sub>2</sub> O(kanemite)	K <sub>2</sub> Si <sub>2</sub> O <sub>5</sub>	K <sub>2</sub> Si <sub>4</sub> O <sub>9</sub>	Li <sub>2</sub> Si <sub>2</sub> O <sub>5</sub>	KHSi <sub>2</sub> O <sub>5</sub>	Na <sub>2</sub> Si <sub>4</sub> O <sub>8</sub> (OH) <sub>2</sub> •4H <sub>2</sub> O (makatite)	Na <sub>2</sub> Si <sub>8</sub> O <sub>17</sub> •xH <sub>2</sub> O	Na <sub>2</sub> Si <sub>14</sub> O <sub>29</sub> •11H <sub>2</sub> O (magadiite)	Na <sub>2</sub> Si <sub>20</sub> O <sub>41</sub> •xH <sub>2</sub> O (kenyaite)	K2Si20041•xH2O	K <sub>2</sub> Si <sub>14</sub> O <sub>29</sub> •8H <sub>2</sub> O

of KOH, SiO<sub>2</sub>, and H<sub>2</sub>O in a 1.1:2:20 molar ratio at 300°C. The naturally occuring hydrous sodium disilicate kanemite (NaHSi<sub>2</sub>O<sub>5</sub>•5H<sub>2</sub>O), has been obtained as an alteration product of other sodium silicates such as Na<sub>2</sub>Si<sub>2</sub>O<sub>5</sub>, makatite (Na<sub>2</sub>Si<sub>4</sub>O<sub>9</sub>•5H<sub>2</sub>O) or magadiite (Na<sub>2</sub>Si<sub>14</sub>O<sub>29</sub>•11H<sub>2</sub>O) (2). Kanemite has also been derived from NaOH-SiO<sub>2</sub> mixtures prepared in methanol subsequently dried, heated to 700°C and dispersed in H<sub>2</sub>O (2). The other hydrous layered alkali metal silicates were formed most readily at temperatures between 60°C and 175° (13,14).

A layered sodium octosilicate  $(Na_2Si_8O_{17} \cdot xH_2O)$  has been prepared by heating a mixture of 30% "Ludox" colloidal silica solution and NaOH (s) in sealed glass bottles at 100°C for one to three weeks (15,16). Mixtures with a SiO<sub>2</sub>/Na<sub>2</sub>O molar ratio of 4.6:1 resulted in an opaque crystalline material with an empirical formula of  $8SiO_2:Na_2O:9H_2O$ . A layered tetrasilicate with a compositional range close to that of makatite has been synthesized by Baker et al. (11). The material produced at 70°C from a 1:2:17 Na<sub>2</sub>O:SiO<sub>2</sub>:H<sub>2</sub>O reaction mixture exhibited a final composition of  $3Na_2O \cdot 13SiO_2 \cdot 11H_2O$ . Another synthetic preparation reported in the literature, utilized a ternary system with a NaOH:SiO<sub>2</sub>:H<sub>2</sub>O ratio of 2:4:20, but no other details were given (17).

Synthetic Na<sup>+</sup>-magadiite  $(Na_2Si_{14}O_{29}\cdot 11H_2O)$ , was first prepared by the crystallization of sodium silicate solutions at 100°C over a three to four week period (15). Lagaly et.al. (13) studied in detail the range of ternary compositions that resulted in crystalline samples of Na<sup>+</sup>-magadiite (13). Na<sup>+</sup>-magadiite forms over a range of

reaction compositions, but the best samples were obtained by reaction of a 2:9:75 molar ratio of NaOH:SiO<sub>2</sub>:H<sub>2</sub>O at 100°C in sealed glass ampules. At certain compositions magadiite was formed in combination with kenyaite  $(Na_2Si_{20}O_{41} \cdot xH_2O)$  (17). The phase boundary between these two products has also been investigated (14). Reaction mixtures with SiO<sub>2</sub>/NaOH  $\leq$  16 yielded Na<sup>+</sup>-magadiite as an intermediate in the formation of kenyaite. These mixtures result in quartz formation at longer reaction times, indicating a magadiite to kenyaite to quartz transformation most likely occurs (17). The alkali cation also has an effect on which silicate will form. Sodium ions favor the formation of Na<sup>+</sup>-magadiite, while potassium ions favor K<sup>+</sup>-kenyaite formation (17). More recently, a new potassium silicate hydrate with a composition, K<sub>2</sub>O • 14SiO<sub>2</sub> • 8H<sub>2</sub>O, similar to K<sup>+</sup>-magadiite was prepared which possesses enhanced intracrystalline reactivity (18). Various other alkali-kenvaite materials containing Li, Cs, and Sr were also prepared under special conditions (19). The effect of high levels of anions other than OH- on the synthesis of magadiite and kenyaite indicated that the kenyaite/magadiite ratio decreased with an increase in the atomic number of the halide used. The presence of F<sup>-</sup> increased the conversion to kenyaite but also enhanced the conversion of kenyaite to quartz (14). The increase of hydrothermal reaction temperatures, from 100°C to between 125° - 175°C, dramatically decreased reaction times for the synthesis of magadiite and kenyaite(14).

#### C. Structures of the Alkali Metal Silicates

In general, layered alkali silicates are composed of silicate layers separated by alkali cations. Hydrated forms may also contain  $H_2O$  between the layers usually as a hydration sphere around the interlayer cation. Adjacent layers are held together by electrostatic interactions between the layer and cation or by hydrogen bonding with interlayer  $H_2O$ .

The crystal structures of certain alkali silicates have been determined (cf. Table I.I.). The layered structures of the alkali disilicates, Li<sub>2</sub>Si<sub>2</sub>O<sub>5</sub>,  $\alpha$ -Na<sub>2</sub>Si<sub>2</sub>O<sub>5</sub>,  $\beta$ -Na<sub>2</sub>Si<sub>2</sub>O<sub>5</sub>, and KHSi<sub>2</sub>O<sub>5</sub> are composed of continuous sheets of SiO<sub>4</sub> tetrahedra which corner share with oxygens from adjacent tetrahedra to form six membered rings. Each SiO<sub>4</sub> tetrahedron shares three oxygens with adjacent tetrahedra. The remaining apical oxygen of the tetrahedron is directed above or below the plane of bridging oxygens in an alternating fashion, as shown in Figure I.1. Since each SiO<sub>4</sub> tetrahedron in the  $Si_2O_5$  layer carries a negative charge, one monovalent cation or a proton is required to satisfy layer charge neutrality. Due to the flexibility of layers formed by corner sharing of  $SiO_4$  tetrahedra a change in cation size or charge can alter the degree of layer folding. For instance, Figure I.2. illustrates the decrease in folding of the tetrahedral layer as the cation size increases from Li<sup>+</sup>< H<sup>+</sup>< Na<sup>+</sup>< K<sup>+</sup>. It appears that the smaller cations are more enfolded within the tetrahedral layer.

A layered structure was corroborated for  $\text{KHSi}_2\text{O}_5$  and kanemite (NaHSi<sub>2</sub>O<sub>5</sub>•3H<sub>2</sub>O), by <sup>29</sup>Si MAS NMR spectroscopy. The <sup>29</sup>Si



I.1. Schematic representation of a silicate layer which is composed of continuous sheets of  $Q^3$  corner sharing tetrahedra. Structure derived from the crystal structure of  $H_2Si_2O_5$ , I (64).





I.2. Variation in the folding of  $Si_2O_5$  units with cation charge to radius ratio in a)  $Li_2Si_2O_5$ , b)  $H_2Si_2O_5$ -I, c) a-Na\_2Si\_2O\_5, and d) KHSi\_2O\_5-II (9).

MAS NMR spectrum of  $\text{KHSi}_2O_5$  indicated one resonance characteristic of a Q<sup>3</sup> OSi(OSi)<sub>3</sub> type environment (20). The hydrous sodium disilicate kanemite exhibited two resonances, one at -99 ppm relative to TMS characteristic of a Q<sup>3</sup> OSi(OSi)<sub>3</sub> type environment and a weaker resonance near -110 ppm assigned to the presence of a Q<sup>4</sup> Si(OSi)<sub>4</sub> type environment (21). The Q<sup>4</sup> resonance grew in intensity with sample age and this was thought to result from the condensation of adjacent layers.

The layered structure of synthetic makatite  $(Na_2Si_4O_8(OH)_2 \cdot 4H_2O)$  was found to be based on a continuous sheet of Q<sup>3</sup> tetrahedra condensed to form six membered rings. But instead of unbranched zweier chains as in the disilicates, makatite was built up of unbranched vierer single chains. In addition, the makatite structure was found to be composed of highly folded  $[Si_2O_4(OH)]_n^n$ layers which contain six membered rings of Q<sup>3</sup> tetrahedra, as shown in Figure I.3. (22). More highly condensed alkali silicates such as  $K_2Si_4O_9$ , although still built up of unbranched zweier single chains, have layers composed of both four and six membered rings of  $SiO_4$ Both  $O^3$  and  $O^4$  type tetrahedra, as illustrated in Figure I.4. tetrahedra were present in this structure in an equal ratio (23).

The crystal structures for magadiite  $(Na_2Si_{14}O_{29} \cdot 11H_2O)$ , octosilicate  $(Na_2Si_8O_{17} \cdot xH_2O)$ , and kenyaite  $(Na_2Si_{20}O_{41} \cdot xH_2O)$ , are unknown. Structural information has been obtained using various techniques such as thermal analysis, X-ray powder diffraction, infrared spectroscopy, <sup>1</sup>H, <sup>23</sup>Na MAS NMR, and especially, <sup>29</sup>Si MAS NMR spectroscopy.



I.3. Polyhedral representation of the crystal structure of synthetic makatite (22).



I.4. Polyhedral representation of the crystal structure of  $K_2Si_4O_9$ . a) view perpendicular to the layer, b) view parallel to the layer.(23)

The X-ray powder diffraction pattern of octosilicate vacuumdried at 30°C indicated a basal spacing of 11.0 Å. <sup>29</sup>Si MAS NMR spectroscopy of sodium octosilicate indicated the layer was composed of  $Q^3$  OSi(OSi)<sub>3</sub> and  $Q^4$  Si(OSi)<sub>4</sub> type silicon environments (24, 25). Cross polarization resulted in an enhancement of the  $Q^3$  silicon environment which confirmed the presence of  $O^3$  silanol HOSi(OSi)<sub>3</sub> groups (25). Infrared spectroscopy was used to elucidate structural similarities between sodium octosilicate and various zeolites (24). This study indicated the presence of structural blocks in sodium octosilicate which contain five membered rings of tetrahedra. Two models for the layer structure of octosilicate were proposed (24,25). For instance, Schwieger et al. (25) condensed two makatite layers to produce a model with the correct  $Q^3/Q^4$  ratios and approximate basal This model unfortunately did not contain the five spacing. membered ring blocks shown present by the IR study. Garces et al. (24) proposed that sodium octosilicate has layers which consist of six membered ring sheets of SiO<sub>4</sub> tetrahedra and structural blocks composed of four, five, and six membered rings which protrude from these sheets. The calculated layer thickness for this model would be approximately 11Å, close to the basal spacing of the hydrated form of sodium octosilicate.

X-ray powder diffraction studies of natural and synthetic samples of Na<sup>+</sup>-magadiite indicated a basal spacing of 15.6 Å (26-28). The basal spacing was consistent with silicate layers =11.2 Å thick plus a layer of hydrated sodium cations which fill the gallery space (26,29). The X-ray diffraction patterns of synthetic Na<sup>+</sup>-

magadiite samples heated to between 25°C and 300°C showed that the interlayer  $H_2O$  is lost by 120°C. Also, Na<sup>+</sup>-magadiite heated to 165°C reversibly re-hydrates. Above 165°C there is a loss of structural integrity (28). New structural information has been obtained from thermally treated samples of naturally occurring Trinity Center magadiite using a combination of <sup>1</sup>H NMR spectroscopy and infrared spectroscopy (30). Both techniques indicated the presence of a large concentration of silanol groups in Na<sup>+</sup>-magadiite =2Na+/3OH. <sup>23</sup>Na MAS NMR spectroscopy of these samples also indicated two Na environments, which were assigned to interlayer Na<sup>+</sup> and NaOH (28). The proposed interlayer structure, as shown in Figure I.5A., indicates that the negative charge of the layer is balanced in part by either Na<sup>+</sup> ions or protons. In addition, a bilayer arrangement of H<sub>2</sub>O and ion pairs of Na<sup>+</sup> OH<sup>-</sup> were thought to coexist within the interlayer. An earlier <sup>29</sup>Si MAS NMR study of proton exchanged natural Trinity County Na<sup>+</sup>-magadiite, (31), indicated a ratio of 1.7:1 for the  $O^4:O^3$  environments of silicon, corresponding to 5.2 Q<sup>3</sup> HOSi(OSi)<sub>3</sub> groups per Si<sub>14</sub> unit cell.

The reported ratios for the Q<sup>4</sup>:Q<sup>3</sup> silicon environments, deduced from <sup>29</sup>Si NMR spectroscopy for synthetic and natural magadiite samples varies greatly. As shown by the data in Table I.II. the quantitative use of <sup>29</sup>Si MAS NMR data requires that values for the spin-lattice relaxation times, T<sub>1</sub>, be known in order to avoid saturation due to insufficient spin relaxation between pulses. Spinlattice relaxation times are especially long for synthetic Na<sup>+</sup>magadiite with values of 160 seconds and 280 seconds, being



I.5. Schematic representation of the interlayer space of A)  $Na^+$ -magadiite and B) H<sup>+</sup>-magadiite (30).

Magadiite	Q4/Q3	Q <sup>3</sup> sites/unit cell	ref
Sample			
Na <sup>+</sup> ,Synthetic	2.0	4.6	26
Na <sup>+</sup> , Synthetic	1.0	7.0	25
Na <sup>+</sup> , Synthetic	2.5	4.1	25
Na <sup>+</sup> , Synthetic	3.0	3.5	24
Na <sup>+</sup> , Synthetic	2.9	3.6	32
H <sup>+</sup> , Synthetic	3.6	3.0	32
H <sup>+</sup> ,Synthetic	3.0	3.5	24
Na+, Natural	1.2	6.3	25
H+, Natural	1.7	5.2	31

Table I.II. <sup>29</sup>Si MAS NMR Data for Various Samples of Na<sup>+</sup>-magadiite and H<sup>+</sup>-magadiite

observed, for the Q<sup>3</sup> and Q<sup>4</sup> silicon environments respectively (32). The differences in Q<sup>3</sup> and Q<sup>4</sup> silicon relaxation times for synthetic Na<sup>+</sup>-magadiite in this case were attributed to <sup>29</sup>Si-<sup>1</sup>H dipolar relaxation of the Q<sup>3</sup> silicon environments due to coupling to interlayer H<sub>2</sub>O (32). On the basis of thermal analysis (weight loss) and Na<sub>2</sub>O content, the empirical formula for this synthetic Na<sup>+</sup>-magadiite sample was found to be Na<sub>1.7</sub>Si<sub>14</sub>O<sub>27.9</sub>(OH)<sub>1.9</sub>\*7.6H<sub>2</sub>O (32). The <sup>29</sup>Si MAS NMR spectra of this synthetic sample reveals a Q<sup>4</sup>:Q<sup>3</sup> ratio of 2.85:1 which is equivalent to 3.6 Q<sup>3</sup> sites per Si<sub>14</sub> unit. This agreed closely with the empirical formula for Na<sup>+</sup>-magadiite which indicated 3.6 [Na<sup>+</sup>, OH] Q<sup>3</sup> groups per Si<sub>14</sub> unit. Experiments performed with delay times < 5 T<sub>1</sub> in this case resulted in spectra which exhibited artificially enhanced Q<sup>3</sup> silicon resonances. Previous <sup>29</sup>Si MAS NMR studies, Table I.II., were performed with delay time

values between 4 and 20 seconds, much to short for complete relaxation of Si environments subjected to pulse widths of 90°. This may explain the discrepancies in  $Q^4:Q^3$  ratios observed by various authors. The presence of paramagnetic impurities in natural samples of magadiite may provide a mechanism for more efficient relaxation but synthetic samples require careful relaxation studies.

Two models for the layer structure of Na<sup>+</sup>-magadiite have been reported (24, 25). The model proposed by Garces et al. (24) combines information obtained from X-ray powder diffraction, infrared spectroscopy and <sup>29</sup>Si MAS NMR. The model consists of five membered ring blocks of tetrahedra protruding from both above and below a continuous sheet of six membered ring  $O^3$  tetrahedra, as shown in Figure I.6. The model put forward by Schweiger et al. (25) was based on X-ray basal spacing and <sup>29</sup>Si MAS NMR data. In this latter model the layer is formed by connecting three makatite-type layers to form an  $(Si_{12} O_{26})_n^{4n}$  unit cell (25). The proposed structure resulted in a framework composed of four, six and eight membered ring blocks of tetrahedra. This model is incompatible with infrared results reported by Garces et al. (24) which indicated the presence in Na<sup>+</sup>-magadiite of five and six membered ring tetrahedral blocks, similar to those reported present in pentasil zeolites.

Two orders of basal plane X-ray reflections at 19.8 Å and 9.9 Å have been reported for synthetic and natural Na<sup>+</sup>-kenyaite samples (17). Synthetic K<sup>+</sup>-kenyaite also is reported to exhibit basal reflections near these values (17,25). Thermal treatment of synthetic Na<sup>+</sup>-kenyaite at 120°C under vacuum resulted in a


I.6. Postulated layer structure for  $Na^+$ -magadiite. a) vertices of the magadiite layer represent silicon positions; oxygen positions are between adjacent silicon pairs. The fourth coordination position of silicon is not shown. b) Polyhedral representation of the layer structure of magadiite; vertices represent oxygen positions (24)

decrease in basal spacing to 17.7 Å. This decrease in basal spacing was attributed to the loss of a monolayer of  $H_2O$ . Synthetic Na<sup>+</sup>kenyaite remained crystalline to 600°C, but a transformation to quartz occured at 700°C. The retention of the 17.7 Å basal reflection for hydrous Na<sup>+</sup>-kenyaite suggested that the van-der Waals thickness of the layer was near this value (17). As stated previously, the synthesis of kenyaite resulted in the formation of magadiite as a byproduct (14). This suggested that magadiite was a possible intermediate for kenyaite formation. The possibility that layers of magadiite condense to form the kenyaite layer was discussed previously (17). This mechanism is not likely because X-ray diffraction studies of suspensions taken from kenyaite syntheses show no phase intermediate between magadiite and kenyaite (17).

The <sup>29</sup>Si MAS NMR spectra of synthetic Na<sup>+</sup>-kenyaite indicated silicon resonances characteristic of Q<sup>3</sup> OSi(OSi)<sub>3</sub>-type and Q<sup>4</sup> Si(OSi)<sub>4</sub>type environments (25). The observed Q<sup>4</sup>:Q<sup>3</sup> ratio of 4.1:1 for kenyaite supports the evidence that kenyaite contains more highly condensed layers than Na<sup>+</sup>-magadiite. Unfortunately, spin-lattice relaxation times for synthetic kenyaite were not determined and this puts into question the reported Q<sup>4</sup>:Q<sup>3</sup> ratio. On the basis of basal spacing, chemical composition, and Q<sup>4</sup>:Q<sup>3</sup> ratios a model structure was derived by Schweiger and co-workers for synthetic kenyaite (25,28,33). The combination of 5 makatite layers resulted in a theoretical thickness of 25.1 Å and a Q<sup>4</sup>:Q<sup>3</sup> ratio of 4:1. The <sup>23</sup>N a MAS NMR spectrum of synthetic kenyaite with proton to sodium cross polarization revealed the presence of two Na environments (34). As in synthetic Na<sup>+</sup>-magadiite, these environments were assigned to the presence of Na<sup>+</sup> interlayer cations and to physisorbed NaOH ion pairs.

### D. Morphology

Scanning electron micrographs of synthetic Na<sup>+</sup>-octosilicate indicate a crystallite morphology composed of rectangular plates, 3-4  $\mu$ m on a side and ~ 400 Å thick (15,16,24). The crystallites of magadiite and kenyaite, both natural and synthetic derivatives, show a more unusual particle morphology composed of intergrown plates which form rosette-like spherical nodules (17,24,32). Variations in synthetic reaction conditions, such as changes in the temperature of crystallization from water glass or in the alkali metal cation caused alterations in the particle morphology of kenyaite (17,19).

E. Intercalation Properties

### **1.** Cation Exchange Properties

In general, the alkali cations of layered alkali metal silicates can be replaced by three classes of cations: (i) hydrated alkali metal, alkaline earth or transition metal cations, (ii) organic cations and (iii) hydronium ions. The proton exchange forms in most cases retain the layered structure of the parent alkali metal silicate and, in addition, possess interesting intercalation and ion exchange properties. The various ion exchange and intercalation reactions are depicted in Figure 1.7.

#### Alkali Metal Silicate



I.7. Representation of some intercalation chemistry of the layered alkali metal silicates (47).

The ion exchange of Na<sup>+</sup> ions for NH<sub>4</sub><sup>+</sup>, Li<sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>, Pb<sup>2+</sup>, Ag<sup>+</sup>, Co<sup>2+</sup>, Ni<sup>2+</sup> and Cu<sup>2+</sup> in synthetic sodium octosilicate produced the corresponding alkali, alkaline earth or transition metal silicate. Also the exchange reactions were 85-100% complete and no change in crystallite shape or size occurred upon exchange, indicating the reactions were topotactic (16). Synthetic Na<sup>+</sup>-magadiite also exchanges sodium ions for other inorganic ions such as Ca<sup>2+</sup>, NH<sub>4</sub><sup>+</sup> and Ni<sup>2+</sup> (35). Owing to its ion exchange capability, synthetic Na<sup>+</sup>-magadiite is an effective builder for low phosphate detergents (36).

KHSi<sub>2</sub>O<sub>5</sub> (37), kanemite NaHSi<sub>2</sub>O<sub>5</sub>•5H<sub>2</sub>O (2), Na<sup>+</sup>-magadiite Na<sub>2</sub>Si<sub>14</sub>O<sub>29</sub>•9H<sub>2</sub>O (13,38), kenyaite Na<sub>2</sub>Si<sub>20</sub>O<sub>41</sub>•xH<sub>2</sub>O (17), and sodium octosilicate  $Na_2Si_8O_{17} \cdot xH_2O$  (16) all reacted with aqueous alkylammonium chloride solutions to produce intercalated derivatives composed of silicate layers expanded by RNH<sub>3</sub>+ ions. For instance, KHSi<sub>2</sub>O<sub>5</sub> reacted exclusively with aqueous solutions of nalkylammonium chlorides,  $RNH_3^+$  with (R=CH<sub>3</sub> to C<sub>8</sub>H<sub>17</sub>), to produce intercalated onium ion derivatives with expanded basal spacings (37). Kanemite, magadiite and kenyaite intercalated quaternary cations such dimethyldialkylammonium ammonium as and trimethylalkylammonium, in addition to n-alkylammonium cations. Na<sup>+</sup>-magadiite, in particular, reacted with n-alkylpyridinium  $(R=C_{10}H_{21}-C_{18}H_{37})$  cations. Iler found that sodium octosilicate intercalates both small and large chain quaternary ammonium cations, but only a monolayer of cation formed between the layers (16).

In general the basal spacing varies with the size, shape and spatial orientation of the interlayer cation. In addition, the configuration or conformation of the alkyl chain also effects the basal spacing. The effect of chain conformation on basal spacing has been studied previously for kanemite, magadiite and other layered systems (2,38-41). The general orientation of the chains within the interlayer depends on various factors such as the area of the alkyl chain and the charge on the layer. A monolayer of cations oriented parallel to the silicate layer will result if one half the unit cell basal area, UBA/2  $\geq$  CA, where CA=(the cross sectional area of the cation) X (# of cations /unit cell). If CA exceeds UBA/2 the orientation of the alkyl chains will change from parallel to perpendicular or some tilt angle in between. Figure I.8. illustrates the change in interlayer orientation for the alkylammonium ions as the alkyl chain length and, hence the area of the intercalated ion, increases. After perpendicular monolayers, further enlargement of the alkyl chain results in a bilayer arrangement. Analogous interlayer structural orientations were observed if the layer charge changed while keeping the alkyl chain length constant.

For example, basal spacings for n-alkylammonium derivatives of KHSi<sub>2</sub>O<sub>5</sub>, kanemite, magadiite and kenyaite increase linearly as the alkyl chain length increases. Figure I.9. shows a plot of basal spacing versus alkyl chain length for these silicates with various types of cations. N-alkylammonium intercalates of KHSi<sub>2</sub>O<sub>5</sub> and kanemite with carbon chain length between 7-10 exhibited basal spacings characteristic of bilayer arrangements with tilt angles less than 90°.



I.8. Arrangements of n-alkylammonium cations within a layered silicate. Cation chain length was varied while keeping layer charge constant. a)  $C_2H_5NH_3^+$ , b)  $C_8H_{17}NH_3^+$ , and c)  $C_{12}H_{25}NH_3^+$ .



I.9. Basal spacing of n-alkylammonium derivatives of layered silicates vs number of carbon atoms in the alkyl chain for kanemitex (2),  $\text{KHSi}_2\text{O}_5 \square$  (37), magadiite O (13), and kenyaite  $\diamondsuit$  (17). All spacings were determined for derivatives in equilibrium with  $\text{RNH}_3^+$  solutions.

For kanemite, a change in chain length from 10 to  $\geq 12$  resulted in perpendicular bilayer formation, as shown in Figure I.9. Dimethyldialkyl ammonium derivatives of kanemite exhibit swelling or enhanced basal spacings to bilayer arrangements when brought into contact with alkanol or alkyl amine reagents (2). Analogous bilayer arrangements were observed for n-alkylammonium montmorillonite derivatives solvated by n-alkylalcohols and nalkylamines (39). More recently, Fripiat et al. (20) have shown that intercalation of either ethylammonium or heptylammonium ions within KHSi<sub>2</sub>O<sub>5</sub> resulted in the hydrolysis and partial condensation of adjacent layers yielding an interstratified structure. The possibility that similar hydrolysis reactions have occurred in alkylammoniumkanemite intercalates has not been investigated previously.

The basal spacings of n-alkylammonium intercalates of magadiite, when ploted versus carbon chain length, as shown in Figure I.9., indicated an increase of 2.6 Å of basal spacing per carbon atom in the chain. This result is indicative of a bilayer structure within the interlayer with the alkyl chains oriented perpendicular to the layer in an all trans configuration (13). When the kenyaite basal spacings were normalized with respect to layer thickness, it became apparent that the interlayer structure of kenyaite (17.7 Å layer thickness) was composed of bilayers with tilt angles < 90°.

### 2. Alkylammonium Derivatives as Reaction Precursors

Various long chain alkylammonium exchange forms of alkali metal silicates have been used as precursors for subsequent

intercalation reactions. For instance, ethylammonium and heptylammonium ion intercalated derivatives of KHSi<sub>2</sub>O<sub>5</sub> have been exchanged with  $Al_{13}O_4(OH)_{24}(H_2O)_{12}^{7+}$  solutions (42). The pillared materials which resulted, although of low crystallinity, exhibited BET surface areas in the range of 400  $m^2/g$ . Approximately two thirds of this surface was attributed to micropores. Fripiat et al. further postulated that this material was composed of an interstratified network of open pillared galleries and siloxane-bridged galleries. In addition, a dodecyltrimethylammonium exchange form of magadiite has been utilized as a precursor for the intercalation of acrylonitrile Heat treatment of the resultant acrylonitrilemonomer (43). C<sub>12</sub>H<sub>25</sub>N(CH<sub>3</sub>)<sub>3</sub>-magadiite complex at 1300°C in flowing Ar produced  $\beta$ -SiC (43). Treatment of the same material at 1400°C under flowing N<sub>2</sub> resulted in  $\beta$ -Si<sub>3</sub>N<sub>3</sub> formation (44). The interlayer SiOH groups in alkylammonium derivatives of magadiite and kenyaite were found to be reactive centers for the derivatization by silane reagents (45). For example, dodecyltrimethylammonium complexes of magadiite and kenvaite reacted readily with trimethylchlorosilane 10 diphenylmethylchlorosilane to form intercalated derivatives (45,46). <sup>29</sup>Si MAS NMR and <sup>29</sup>Si CP-MAS NMR of these derivatives indicated the presence of  $O^1$  R<sub>3</sub>Si-O type environments.

3. H+-Silicates

Many layered alkali metal silicates reversibly exchange interlayer cations for protons by ion exchange to form layered silicic acids. In some cases the proton exchange form is favored even at high pH (47). The reversibility of the proton exchange reaction also allows for cation exchange of other alkali cations for protons (47).

The stability of alkali metal silicates towards acid has been related to the size and charge of the alkali metal cation. For instance, treatment of  $Li_2Si_2O_5$  with acid did not result in loss of Li<sup>+</sup> from the silicate structure (48). Other layered silicates were found to be unstable under acidic conditions. For example, the layer structures of  $BaSi_2O_5$  and  $K_2Si_2O_5$  were altered to X-ray amorphous products with general composition  $2SiO_2 \cdot H_2O$  by acid treatment (48). In most cases, however, the proton exchange form is stable and the layer structure is retained ( cf. Table I.I.).

### 4. Intercalation Complexes of H<sup>+</sup>-Silicates.

Layered silicic acids intercalate various polar organic guest molecules. Table I.III. summarizes the various families of organic molecules that have been found to intercalate in the galleries of  $H_2Si_2O_5$ , H<sup>+</sup>-makatite, and H<sup>+</sup>-magadiite. However, not all silicic acids possess the same reactivity. For instance, although all silicic acids intercalate alkylamines, only the more highly condensed forms such as H<sup>+</sup>-makatite, H<sup>+</sup>-magadiite, and H<sup>+</sup>-kenyaite imbibe other polar organic molecules. The mechanism of intercalation involves disruption of the hydrogen bonds which hold the layers together. In order for this to occur the guest compound must possess a high molecular dipole moment  $\geq 3.5$  Debyes (47). In addition, the polar organic guest compound must have strong acceptor sites for hydrogen bond formation.

Group	Examples	Gallery Height (Å)				
-	•	H <sub>2</sub> Si <sub>2</sub> O <sub>5</sub>	H-makatite	H-magadiite		
Short chain	formamide	3.3	1.7	2.4		
amides	dimethyl formamide	4.9	3.6	5.5		
	acetamide	3.8	3.8	2.9		
	diethyl acetamide	6.1	5.4	5.9		
Urea and	urea			4.3		
derivatives	N.N-dimethyl urea		5.2	5.3		
	N,N'-diethyl urea		6.3	4.3		
S-oxides	dimethylsulfoxide	3.6	6.7	4.6		
N-oxides	trimethylamine-N-oxide		3.7	4.7		
	pyridine-N-oxide	4.9	3.7	4.6		
	3-picoline-N-oxide	5.1	4.3	5.6		
Aromatic	pyridine	4.7	6.8	5.3		
bases	imidazole		6.1	3.2		
	pyrazine		3.5			
	quinoline		10.7	6.1		
Alkylamines	hexylamine	17.1	18.4	18.4		
•	decylamine	26.9	29.3	29.0		
	benzylamine			12.7		

Table I.III. Possible guest molecules for interlamellar adsorption by crystalline silicic acids and the gallery height (47).

--:no reaction

Another group of molecules which preferentially intercalate into silicic acids are organic bases with  $pK_b < 9$ . In this case the orientation of the interlayer molecules was discussed elsewhere (2,17,37,38,47,49).

The layered silicic acids derived from, kanemite, KHSi<sub>2</sub>O<sub>5</sub>,  $\alpha$ -Na<sub>2</sub>Si<sub>2</sub>O<sub>5</sub> and Na<sup>+</sup>-magadiite all intercalate n-alkylamine molecules to form structures similar to the n-alkylammonium derivatives The basal spacings for these derivatives also discussed earlier. increases in a linear fashion as the alkyl chain length increases. Figure I.10. indicates that all the layered silicic acid forms possess approximately the same interlayer onium ion structures. The interlayer structure in each case corresponds to bilayers of alkylamine molecules with tilt angles of  $\geq 60^{\circ}$ . H<sup>+</sup>-magadiite preintercalated with dimethylsulfoxide reacted with excess nalkylamines to form bilayer structures. Derivatives with alkyl chain length  $\leq$  10 resulted in chain tilt angles of 56° relative to the silicate layer. Longer chains,  $\geq 12$ , arrange themselves perpendicular to the layer. The H<sup>+</sup>-magadiite intercalation complexes also retained  $\approx 2$ moles of DMSO/ 14SiO<sub>2</sub> (38). Lagaly et al. (38) have reported previously that the direct reaction of alkylamines and H<sup>+</sup>-magadiite without preintercalation by dimethylsulfoxide resulted in only a small increase in basal spacing  $(d_{001}=14 \text{ Å})$ . The presence of interlayer  $H_2O$  in the H<sup>+</sup>-magadilte phase  $(d_{001}=13.2 \text{ Å})$  used by Lagaly et al. (38) may impede the intercalation of n-alkylamines. However, related work reported that reaction of H<sup>+</sup>-magadiite. dehydrated phase  $(d_{001}=11.2 \text{ Å})$ , with excess octylamine resulted in



I.10. Basal spacing (d001 Å) versus number of carbon atoms (N<sub>c</sub>) in the alkyl chain for n-alkylamine derivatives of H<sup>+</sup>-Kanemite  $\Box$  (2), H<sub>2</sub>Si<sub>2</sub>O<sub>5</sub>-I  $\Diamond$ (37), H<sub>2</sub>Si<sub>2</sub>O<sub>5</sub>-II × (49), and H<sup>+</sup>-magadiite O (38). All basal spacings were derivatives under mother liquid.

an intercalated derivative with 34 Å basal spacing (50).

### 5. Structure of H<sup>+</sup>-silicates

In layered silicic acids, adjacent layers are connected by hydrogen bonds between silanol groups or between silanol groups and interlayer water molecules (51). Strong chemical bonding in the two dimensions, which make up the layer, in combination with the inert nature of the silicate layer towards acid allow for retention of the layer structure during proton exchange. Crystal structures of various disilicic acid exchange forms indicate, (c.f. Table I.I.), that the structures change only slightly after proton exchange. <sup>29</sup>Si MAS NMR data for acid-hydrolyzed KHSi<sub>2</sub>O<sub>5</sub> (20) and kanemite, NaHSi<sub>2</sub>O<sub>5</sub>•3H<sub>2</sub>O (21) indicated that both materials were sensitive to hydrolysis. In both cases Q<sup>3</sup> SiOH groups from adjacent layers condensed to form Q<sup>4</sup> Si(OSi)<sub>4</sub> type environments. Similar NMR results were obtained for H<sub>2</sub>Si<sub>2</sub>O<sub>5</sub> derived from  $\alpha$ -Na<sub>2</sub>Si<sub>2</sub>O<sub>5</sub> (52).

More highly condensed acids such as those derived from makatite, octosilicate, magadiite and kenyaite have unknown structures. The X-ray powder patterns for these silicic acids were indexed by comparison with the parent alkali silicate (47). Small changes in the a- and b- axes after proton exchange were revealed, indicating some distortion of the silicate layers.

The X-ray powder diffraction pattern for H<sup>+</sup>-magadiite vary depending on preparation. Both hydrated  $(d_{001}=13.2 \text{ Å})$  and dehydrated  $(d_{001}=11.2 \text{ Å})$  forms of H<sup>+</sup>-magadiite have been obtained by altering the titration conditions. H<sup>+</sup>-magadiite, like its sodium analogue, exhibited <sup>29</sup>Si MAS NMR spectra indicative of both Q<sup>3</sup> HOSi(OSi)<sub>3</sub>-type and O<sup>4</sup>-Si(OSi)<sub>4</sub> type environments (27,31). Various workers have published  $O^4:O^3$  ratios for H<sup>+</sup>-magadiite that range from 1.7-3.6, as shown in Table I.II. The differences in  $O^3:O^4$  ratios can be attributed to inadequate relaxation of the spins associated with the  $O^4$  silicon environment as compared to the  $O^3$  environment (32). The characterization of H<sup>+</sup>-magadiite by infrared spectroscopy and <sup>1</sup>H NMR spectroscopies has indicated the presence of two types of OH groups. As shown in Figure I.5B. one set of SiOH groups is believed to be involved in strong hydrogen bonds between adjacent layers (OH<sub>B</sub>) and the second set of SiOH have been attributed to weakly hydrogen bonded groups  $(OH_A)$  (53). The  $(OH_A)$  groups point towards tetrahedral ring holes in the adjacent layer. <sup>1</sup>H NMR indicated that the average distances between neighboring protons was  $\sim 2.5$  Å. This small H-H distance required that the protons be from adjacent lavers. Thermal analysis of H<sup>+</sup>-magadiite in combination with <sup>29</sup>Si MAS NMR suggested that interlayer siloxane bond formation occured even at 230°C (27). This contradicted an earlier thermal study that indicated the onset of Si-O-Si bond formation to be 400°C (29).

The titration of Na<sup>+</sup>-kenyaite suspensions with dilute acid (0.1 M HCl) resulted in exchange of Na<sup>+</sup> by protons (17). The basal spacing of the Na<sup>+</sup>-kenyaite, decreased from an initial value of 19.8 Å to 17.6 Å following proton exchange. A comparison of layer thickness for H<sup>+</sup>-magadiite and H<sup>+</sup>-kenyaite indicated that kenyaite possessed a thicker silicate layer, 11.2 Å versus 17.6 Å respectively.

### 6. Silylation of Interlamellar Silanol Groups

The interlayer SiOH groups of H<sup>+</sup>-magadiite, H<sup>+</sup>-kenyaite, and  $\alpha - H_2Si_2O_5$  are accessible, for reaction, with silane grafting reagents when the galleries were preintercalated by polar organic molecules (54). Preintercalation of the silicic acid separates individual layers, thus allowing the organosilane access to the interlayer SiOH groups. Direct reaction of layered silicic acids with trimethylchlorosilane resulted in grafting of  $(CH_3)_3$ -Si groups to the external surfaces only. However, as illustrated in Figure I.11., preintercalation of the layered silicic acid by either dimethylsulfoxide (DMSO), N-methylformamide, or N,N-dimethylformamide followed by reaction with either hexamethyldisilazane or trimethylchlorosilane results in the silvlation of interlayer SiOH groups. X-ray powder diffraction of these materials indicated gallery heights of - 8 Å. Infrared spectroscopy and chemical analyses indicated that the silylation reaction was accompanied by displacement of the preintercalated polar organic molecules (55). The <sup>29</sup>Si MAS NMR spectra of Hmagadiite treated in this fashion indicated the presence of (CH<sub>3</sub>)<sub>3</sub>Sienvironments. Also, from these data it was estimated that 30% of the SiOH groups present in H<sup>+</sup>-magadiite had reacted with organosilane (31).

### 7. Pillared Layered Silicates

Various authors have tried to generate pillared materials by utilizing the intercalation chemistry and intracrystalline reactivity of



I.11. Interlamellar grafting of trimethylsilyl groups into the intracrystal surface of silicic acids by reaction of trimethylchlorosilane (TMCS) with the N-methylformamide (NMF) solvated form of the silicic acid. The unsolvated silicic acid is unaccessable for reaction with TMCS (55).

the layered silicic acids. For example, Sprung et al. (56) reported on the pillaring of H<sup>+</sup>-magadiite with polyhedral silicate species. The polyhedral three dimensional silicate species used as pillaring reagents were synthesized by cyclic polymerization of either phenyltrichlorosilane or cyclohexyltrichlorosilane. The direct reaction of H<sup>+</sup>-magadiite with these pillaring reagents resulted in partially pillared materials. The resultant products when calcined at  $350^{\circ}$ C exhibited surface areas between 100-200 m<sup>2</sup>/g and basal spacings of ~ 15.6 Å.

More recently Landis et. al. (57,58) expanded on Rojo and Ruiz-Hitzkys work (54,55) and produced pillared microporous derivatives of H<sup>+</sup>-magadiite, H<sup>+</sup>-makatite and H<sup>+</sup>-kenyaite. The pillaring procedure they employed utilizes a pre-swelling step which separates the layers and expands the interlayer space allowing access for siloxane pillaring reagents. For example, preintercalation of H<sup>+</sup>-magadiite by octylammonium ions or octylamine molecules solutions followed with from aqueous by treatment tetraethylorthosilicate, TEOS, resulted in the intercalation and hydrolysis of TEOS between the layers of H<sup>+</sup>-magadiite. After calcination at 538°C in air for several hours this material exhibited a nitrogen BET surface area of 530  $m^2/g$ .

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### **CHAPTER II**

# Intercalative Reaction of a Cobalt(III) Cage Complex, $Co(sep)^{3+}$ , with Magadiite, a Layered Sodium Silicate.

### A. Introduction

Pillared layered materials have attracted widespread interest recently due in part to their potential utility as catalysts and molecular sieving adsorbents [1,2]. Normally, pillared microporous solids are derived from materials with ion exchange capabilities. Examples of layered ionic materials that have been examined previously for their pillaring properties include, 2:1 phylosilicate clays, layered double hydroxides and zirconium phosphates[1]. Another class of ionic layered minerals, namely, the hydrous sodium silicates have been identified as having intercalation properties suitable for producing pillared derivatives [2]. In an effort to broaden the diversity of pillared materials, we have been investigating the pillaring reactions of lamellar hydrous sodium Examples of this unique family of silicates include, silicates. magadiite  $(Na_2Si_{14}O_{29}\cdot 9H_2O)$ , kenyaite  $(Na_2Si_{20}O_{41}\cdot 10H_2O)$ , and kanemite (NaHSi<sub>2</sub>O<sub>5</sub> $\cdot$ 3H<sub>2</sub>O). All are naturally occurring minerals first found in lake beds at Lake Magadi, Kenya [3]. These compounds also can be conveniently prepared in the laboratory via hydrothermal synthesis [4-6]. It has been shown that the hydrated interlayer sodium ions of these materials can be exchanged by large alkylammonium cations to form organic derivatives [5-7]. These alkylammonium derivatives of magadiite and kenyaite have been used as precursors for reaction of interlayer silanols by organo silanes [8].

Certain alkylammonium exchange forms of smectites show considerable promise as selective adsorbents for the removal of priority pollutants from contaminated ground waters [9,10]. Similar adsorption properties might be expected for organo cation exchange forms of layered silicates. However, in contrast to smectite clays, layered sodium silicates have a relatively high layer charge and are not easily swellable. The highly charged layers require highly charged cations to induce porosity. No examples of magadiite intercalated by a robust cation of charge 3<sup>+</sup> or larger have been reported previously.

In this work, we examine the possibility of preparing a pillared derivative of magadiite using a high charged cation of known dimension. The cation chosen for this purpose was cobalt sepulchrate,  $[Co(sep)]^{3+}$ , a highly stable cobalt cage complex derived from the capping of trisethylenediaminecobalt(III) cation [11]. The structure of this complex is illustrated in Figure I.1.

### B. Experimental

## 1. Preparation of Na<sup>+</sup>-magadiite

Synthetic  $Na^+$ -magadiite was prepared by the reaction of NaOH and SiO<sub>2</sub> under hydrothermal conditions according to a previously



II.1. Schematic representation of the cobalt sepulchrate complex.

described method [4]. A suspension of Davisil 62 SiO<sub>2</sub> (12.0 g, 0.20 mol) in 60 mL of 1.11 <u>M</u> NaOH (0.067 mol) was allowed to digest at 150°C for 46 hours in a Teflon-lined stainless steel bomb. The solid Na<sup>+</sup>-magadiite reaction product was separated by centrifugation, washed twice with 200 mL of deionized H<sub>2</sub>O in order to remove excess NaOH and air dried at 40°C.

### 2. Preparation of Co(sep)Cl<sub>3</sub>

synthesis of (1, 3, 6, 8, 10, 13, 16, The 19 octaazabicyclo[6.6.6]eicosane)cobalt(III) chloride, [Co(sep)]Cl<sub>3</sub>, was accomplished by using the method described by Creaser et al. [11]. To a stirred suspension of [Co(en)]Cl<sub>3</sub>•H<sub>2</sub>O (18.0 g, 0.05 mol) and  $Li_2CO_3$  (25 g, 0.34 mol) in deionized H<sub>2</sub>O (125 mL) were added 37.9% aqueous formaldehyde (550 mL, 7.5 mol) and 30% aqueous  $NH_4OH$ (157.4 mL, 2.5 mol diluted to 550 mL). The solutions were added separately by addition funnel over a period of three hours. The mixture was allowed to stir for an additional 30 minutes, and  $Li_2CO_3$ was filtered from the red solution. The pH of the filtrate was adjusted from 9 to 2.5 by the addition of concentrated  $HClO_4$ , and the  $LiClO_4$  that formed was filtered from the solution. The filtrate was passed through a Dowex 50W-X8 column (100-200 mesh), and the column was washed with five liters of 0.2 M trisodium citrate. The resin was then washed with  $H_2O$  and 1 <u>M</u> HCl to remove Na<sup>+</sup>. The resultant orange Co(sep)<sup>3+</sup> cation was eluted from the column with 3 <u>M</u> HCL (= 4 liters). The orange solution was reduced to dryness on a rotoevaporator and recrystallized from water by the addition of acetone. Anal Calcd for: CoC<sub>12</sub>N<sub>8</sub>H<sub>30</sub>Cl<sub>3</sub>: Co, 13.05; C, 31.91; N, 24.81; H, 6.69; Cl, 23.54. Found: Co, 12.41; C, 30.76; N, 23.72; H, 6.96.

## 3. Co(sep)<sup>3+</sup>-magadiite Reactions

 $Co(sep)^{3+}$  exchange forms of magadiite were prepared by the addition of synthetic Na<sup>+</sup>-magadiite (0.50 g,  $4.7x10^{-4}$  mol) in 10 mL of deionized H<sub>2</sub>O to Co(sep)Cl<sub>3</sub> (0.914 g,  $2.02x10^{-3}$  mol) in water (40 mL). Reaction mixtures were maintained either at 25°C for 72 hours or at 100°C for 24 hours. After each reaction period, the solid was centrifuged and reexchanged with 50 mL of fresh 0.04 <u>M</u> Co(sep)Cl<sub>3</sub> solution. The exchange solutions were replaced up to four times. Each reaction product was recovered by centrifugation and washed with deionized H<sub>2</sub>O until the orange solid was Cl<sup>-</sup> free.

### 4. Physical Measurements

Basal spacings were determined from 001 X-ray reflections using a Rigaku Rotaflex diffractometer equipped with Cu K $\alpha$ radiation. Samples were prepared by depositing a suspension of the washed solid on a glass microscope slide and allowing the suspension to air dry at 40°C. The extent of intercalation was followed after each exchange by measuring the change in basal spacing.

<sup>29</sup>Si MAS NMR experiments were performed on a Varian 400 VXR solid state NMR spectrometer operated at 79.5 MHz. A Doty multinuclear MAS probe equipped with zirconia rotors was used for all measurements. <sup>29</sup>Si spin lattice relaxation times were determined experimentally by inversion recovery experiments. The <sup>29</sup>Si relaxation time and 90° pulse width for Na-magadiite were found to be 280 seconds and 5.8  $\mu$ s respectively. The Q<sup>3</sup> and Q<sup>4</sup> silicon environments exhibited relaxation times of 160 seconds and 280 seconds respectively. A total of 12 scans were recorded for each sample. The sample spinning rate was approximately 5 kHz. A delay time five times as large as T<sub>1</sub> for the Q<sup>4</sup> sites was used in order to obtain quantitative results.

Nitrogen adsorption isotherms at liquid  $N_2$  temperature were determined on a Quantachrome Quantasorb Jr. using ultra pure  $N_2$ .as the adsorbate and Helium as the carrier gas. All samples were outgassed at 120°C under flowing He for 12 hrs. Surface areas were determined using the BET equation and the t-plot method [12].

FTIR spectra were obtained by use of an IBM IR44 spectrometer and the KBr pressed pellet technique. All pellets contained 2% sample by weight.

Thermogravimetric analyses were performed using a Cahn TG system 121 analyzer. All samples were heated to 1000°C at a heating rate of 5°C/min.

### C Results and Discussion

### 1. Preparation of Na<sup>+</sup>-magadiite

Base hydrolysis of silica gel at 150°C under autogenus pressure produced a well crystallized Na<sup>+</sup>-magadiite product. The X-ray diffraction pattern for an air dried film sample, shown in Figure II.2., exhibited 001 reflections corresponding to a basal spacing of 15.6 Å.



II.2. X-ray diffraction pattern (Cu-K $\alpha$ ) of an oriented film sample of Na<sup>+</sup>-magadiite.

Despite the planar structure of Na<sup>+</sup>-magadiite and efforts to produce well oriented films, several hkl reflections with  $h \neq k \neq 0$  were observed due to the rosette-like morphology of the aggregated platelets. The broad hump in the X-ray pattern centered near 20 degrees 2 $\Theta$  (d=4.43 Å) may be indicative of a quasi-crystalline silica impurity. The peak positions for this synthetic product agreed closely with values reported previously for synthetic and natural magadiite [3,13-15].

The sodium content of synthetic Na<sup>+</sup>-magadiite depended in part on the extent of hydrolysis that occured during the washing procedure. Initial washes removed excess NaOH associated with the material. However, repeated washes leached Na<sup>+</sup> cations from the interlayer and caused layer hydrolysis. The chemical composition of Na<sup>+</sup>-magadiite was obtained by combining the results of thermogravimetric analyses and chemical analyses. Air dried Na<sup>+</sup>magadiite that had been well washed to remove excess NaOH, Figure II.3a., lost 13% of its total weight as water below 200°C. An additional 1.6% was lost between 200°C- 1000°C. The weight loss above 200°C was assigned to the dehydroxylation of SiOH groups. The combination of Na<sub>2</sub>O content (4.98%) and weight loss provided empirical composition for synthetic Na<sup>+</sup>-magadiite of an  $Na_{1.7}Si_{14}O_{27.9}(OH)_{1.9}$  7.6 H<sub>2</sub>0. These data agreed well with those put forth by Lagaly et al. [7] and Garces et al. [14] that indicated an ideal unit cell of  $Na_2Si_{14}O_{29}$  9H<sub>2</sub>O. Other workers report compositions shown in Table II.I. that vary between 2.13 and 1.96 sodium cations per 14 silicon atoms. The samples synthesized in this work (cf., Table



II.3. Thermogravimetric analysis curves obtained under flowing argon for samples (A) Na<sup>+</sup>-magadiite, (B) Co(sep)<sup>3+</sup>-mag(25°C) and (C) Co(sep)<sup>3+</sup>-mag(100°C).

Sample	Weight Percent			Atomic Ratios			
	NacO	SiO	H <sub>2</sub> O	Total	Na	Si	H2O
Na <sup>+</sup> -magadiite, synthetic	6.58	75.8	15.5	97.88	2.35	14	10.9
unwashed, this work	(1.00)	(11.9)	(8.11)				
Na <sup>+</sup> -magadiite, synthetic	4.98	80.2	14.6	<b>99.78</b>	1.69	14	8.5
washed, this work	(1.00)	(16.6)	(10.0)				
Na <sup>+</sup> -magadiite, synthetic	5.58	74.9	18.2	98.68	2.02	14	11.3
Lagaly (1975)	(1.00)	(13.4)	(3.26)				
Na <sup>+</sup> -magadiite, natural	5.6	77.4	15.2	98.2	2.13	14	9.2
McAtee (1968)	(1.00)	(13.8)	(2.71)				
Na <sup>+</sup> -magadiite, synthetic	6.56	84.8	7.8	<b>99</b> .16	2.09	14	4.29
Garces (1988)	(1.00)	(12.9)	(1.19)				
Na <sup>+</sup> -magadiite, synthetic	6.31	87.0	8.1	101.4	1.96	14	4.35
Garces (1988)	(1.00)	(14.2)	(4.42)				
H <sup>+</sup> -magadiite, synthetic washed.this work	>.01	93.9	6.1	100	0	14	2.0

Table II.I. Analytical Composition of Synthetic and Natural Magadiite

II.I.) straddle these compositions, depending on post hydrothermal treatment of the product, especially the number of washings. The water content also varied dramatically depending on differences in drying conditions. The low sodium content of our washed product, 1.69 Na<sup>+</sup> per 14 Si, was a direct result of hydrolysis caused by the extensive washing with water.

## 2. Reaction with $Co(sep)^{3+}$

The basal spacings of the products obtained by ion exchange reaction of  $Co(sep)^{3+}$  with Na<sup>+</sup>-magadiite depended greatly on the reaction temperature. For reactions carried out at 25°C, there is little or no change in the basal spacing of the host material as shown by the XRD patterns in Figure II.4. After three treatments with 0.12N  $Co(sep)^{3+}$ , the magadiite basal spacing increased slightly from an initial value of 15.6 Å to ~15.9 Å. The 001 peak became less symmetric with a possible shoulder developing on the low angle side of the diffraction peak, and the hkl reflections in the region 24-30° 20 decreased in intensity.

The color of the reaction product obtained at  $25^{\circ}$ C was orange indicating that some Co complex was bound to the magadiite surface. Despite the change in diffraction pattern and the color change, it was unlikely that significant intercalation had occurred. The change in basal spacing was far too small to be directly attributed to intercalation of Co(sep)<sup>3+</sup>. The change in hkl intensities in the 24-30° region most likely was due to a breakdown in the rosette morphology of the magadiite as a result of prolonged stirring of the



II.4. X-ray diffraction patterns for oriented film samples of the reaction products obtained after successive exchange of Na<sup>+</sup>-magadiite with 0.12 N Co(sep)Cl<sub>3</sub> at 25°C.
crystals during the exchange reaction. Multiple exchange reactions at  $25^{\circ}$ C most likely resulted in the Co(sep)<sup>3+</sup> being bound at the external surfaces of the crystals. Chemical analysis, to be presented below, verified this conclusion.

In contrast to the results obtained at 25°C, the successive treatments of Na<sup>+</sup>-magadiite with fresh 0.12 N [Co(sep)]Cl<sub>3</sub> solutions at 100°C resulted in the steady increase in the basal spacing from 15.6 Å before exchange to 17.6 Å after the 3rd exchange reaction, as shown in Figure II.5. Further exchange did not result in additional expansion of the structure. The increase in basal spacing indicated intercalation of  $[Co(sep)]^{3+}$  between the layers of magadiite. On the basis of an 11.2 Å thickness for magadiite in the absence of hydrated Na<sup>+</sup> ions, the observed spacing corresponded to a gallery height of  $\sim$  6.4 Å. This value was in agreement with the gallery height reported for smectite clays pillared by  $Ir(diamsar)^{3+}$ , an oval-shaped metal cage complex with dimensions similar to  $Co(sep)^{3+}$  [16].

The compositions of the products obtained by ion exchange reaction of Na<sup>+</sup>-magadiite with Co(sep)<sup>3+</sup> at 25°C and 100°C were deduced from TGA and chemical analysis. TGA curves for the reaction products produced at 25°C and 100°C, henceforth designated  $Co(sep)^{3+}$ -Mag(25°C) and Co(sep)<sup>3+</sup>-Mag(100°C), respectively, are shown in Figure II.3b. and II.3c. Included in the Figure for comparison purposes are the TGA curves obtained for Na<sup>+</sup>-magadiite before exchange with Co(sep)<sup>3+</sup>. The product produced at 25°C exhibited an initial weight loss of 8.5 wt % between 20°C - 200°C assigned to adsorbed H<sub>2</sub>O. In addition, the 2.0 wt % loss from



II.5. X-ray diffraction patterns for oriented film samples of the reaction products obtained after successive exchange of  $Na^+$ -magadiite with 0.12 N Co(sep)Cl<sub>3</sub> at 100°C.

 $200^{\circ}C - 350^{\circ}C$  was attributed to dehydroxylation. Above  $350^{\circ}C$  the weight loss (4.5 %) was probably due to the oxidation by air of the sepulchrate ligands of  $Co(sep)^{3+}$ . Elemental analyses, given in Table II.II., indicated a total of 4.4 wt % percent carbon, and nitrogen, in good agreement with the TGA results.

The product prepared at 100°C exhibited a weight loss of 8.0 % below 350°C, which we assigned to the loss of  $H_2O$  and hydroxyl groups. The additional 10 % weight loss from 350°C-1000°C was probably due to the loss of sepulchrate ligand by desorption and/ or oxidation. Elemental analyses for total carbon and nitrogen was (9.8 wt %) in close agreement with the 10 % weight loss observed by TGA above 350°C.

On the basis of the data summarized in Table II.II. for Co(sep)<sup>3+</sup>-Mag(25°C), there were approximately 0.18 cobalt atoms per  $Si_{14}$  unit. The N/Co molar ratio was 6.63, in reasonable agreement with the expected N/Co molar ratio of 8 for  $Co(sep)^{3+}$ . A substantially lower N/Co ratio of 4.1 was obtained for Co(sep)<sup>3+</sup>-Mag(100°C). The C/N molar ratio was 1.6, in close agreement with the expected C/N molar ratio of 1.5 for  $Co(sep)^{3+}$ . This suggested that  $Co(sep)^{3+}$  cations and uncomplexed cobalt cations were present in this material. Cobalt(II), the most stable uncomplexed form of cobalt in aqueous solution, is known to form a blue complex with SCN<sup>-</sup> in ethanolic solution [17]. The supernatant recovered after leaching Co(sep)<sup>3+</sup>-Mag(100°C) with 6 M HCl became deep blue when ethanolic KSCN was added, indicating the presence of Co(II). However,  $Co(sep)^{3+}$ -Mag(25°C), gave a negative SCN<sup>-</sup> test for Co(II), indicating that

	Co(sep) <sup>3+</sup> -Mag(25°C)	Co(sep) <sup>3+</sup> -Mag(100°C)
Na <sub>2</sub> O	6.1	0.3
SiO <sub>2</sub>	82.7	80.5
Co	1.0	4.2
С	2.7	5.6
Н	1.97	2.35
Ν	1.6	4.2
H <sub>2</sub> O <sup>a</sup>	8.5	8.0
Total	102.6	103.3
Chemical	Α	В
Formula		

Table II.II. Compositions (wt %) of Products Prepared by Reaction of Na<sup>+</sup>-magadiite with Co(sep)<sup>3+</sup> at 25°C and 100°C.

A.  $H_{0.46}Na_{1.0}^{+}[Co(sep)]_{0.18}^{3+}Si_{14}O_{29} \cdot 1.1 H_2O$ ,

B.  $H_{0.10}Co_{0.36}^{2+}[Co(sep)]_{0.39}^{3+}Si_{14}O_{29}\cdot 1.4H_2O$ \*Weight loss below 200°C from TGA.

essentially all the cobalt was bound as the  $Co(sep)^{3+}$  complex. Thus, the composition of  $Co(sep)^{3+}$ -Mag(25°C) was consistent with  $Co(sep)^{3+}$ present mainly at the external surfaces of the layered silicate. Whereas  $Co(sep)^{3+}$ -Mag(100°C) was an authentic intercalation compound that contained a mixture of  $Co(sep)^{3+}$  and uncomplexed Co(II), formed as a result of demetalation of  $Co(sep)^{3+}$ .

The <sup>29</sup>Si MAS NMR spectra for Na<sup>+</sup>-magadiite,  $Co(sep)^{3+}$ -Mag(25°C) and  $Co(sep)^{3+}$ -Mag(100°C) are shown in Figure II.6. Na<sup>+</sup>-magadiite exhibited two general Si environments, namely Q<sup>3</sup> type HOSi(OSi)<sub>3</sub> or Na<sup>+</sup>[OSi(OSi)<sub>3</sub>] sites and Q<sup>4</sup> type Si(OSi)<sub>4</sub> sites [2]. A single Q<sup>3</sup> peak was centered at -99.8 ppm and three Q<sup>4</sup> resonances occured at -110.7 ppm, -111.7 ppm and -114.2 ppm respectively. The ratio of integral intensities for Na<sup>+</sup>-magadiite, Q<sup>3</sup>/Q<sup>4</sup>=0.35, corresponded to 3.63 Q<sup>3</sup> sites/Si<sub>14</sub>. These data were in close agreement with the Q<sup>3</sup>/Si<sub>14</sub>=3.6).

The Q<sup>3</sup> and Q<sup>4</sup> resonances in Co(sep)<sup>3+</sup>-Mag(25°C) exhibited chemical shifts similar to those found for Na<sup>+</sup>-magadiite, but the lines are somewhat broadened. For instance, the shoulder present at -110.7 ppm in Na<sup>+</sup>-magadiite was unresolved in Co(sep)<sup>3+</sup>-Mag(25°C) due to line broadening. The increase in linewidth was even more apparent in Co(sep)<sup>3+</sup>-Mag(100°C). The presence of paramagnetic Co<sup>2+</sup> in the latter product undoubtedly contributed to the spectral broadening. A comparison of relative integral intensities for the <sup>29</sup>Si resonances indicated that the Q<sup>3</sup>/Q<sup>4</sup> ratio was very similar for Na<sup>+</sup>-





II.6. <sup>29</sup>Si Magic Angle Spinning NMR spectra for (A) Na<sup>+</sup>-magadiite, (B) Co(sep)<sup>3+</sup>-mag(25°C), and (C) Co(sep)<sup>3+</sup>-mag(100°C).

magadiite  $(Q^3/Q^4=0.35)$ ,  $Co(sep)^{3+}$ -Mag(25°C)  $(Q^3/Q^4=0.27)$ , and  $Co(sep)^{3+}$ -Mag(100°C)  $(Q^3/Q^4=0.26)$ . These data confirmed that the layer structure of magadiite remained intact after intercalation of  $[Co(sep)]^{3+}$ . Earlier workers have published  $Q^3/Q^4$  ratios for Na<sup>+</sup>-magadiite that range from 0.25-1 [2,15,18]. However, a careful evaluation of the relaxation times for the various <sup>29</sup>Si environments has not been undertaken until now. We have found that the spinlattice relaxation times for the Q<sup>3</sup> site is 160 s and ~ 280 s for the Q<sup>4</sup> sites. The differences in Q<sup>3</sup> and Q<sup>4</sup> relaxation times can be attributed to the presence of H<sub>2</sub>O in the interlayer. The importance of <sup>29</sup>Si-<sup>1</sup>H dipolar relaxation via water molecules has been shown for other layered materials [19]. The close proximity of interlayer water to the Q<sup>3</sup> <sup>29</sup>Si sites of Na<sup>+</sup>-magadiite allows for their relaxation via <sup>29</sup>Si-<sup>1</sup>H dipolar relaxation and, in turn, reduces the relaxation time of the Q<sup>3</sup> site greatly as compared to the Q<sup>4</sup> site.

Infrared spectra for Na<sup>+</sup>-magadiite and the Co(sep)<sup>3+</sup> reaction products are shown in Figure II.7. The IR spectrum for Na<sup>+</sup>magadiite, Figure(II.7c), agreed well with those reported elsewhere [15,20]. The bands centered at 3500 cm<sup>-1</sup> and 1650 cm<sup>-1</sup> have been assigned previously to the stretching and bending frequencies, respectively, of intercalated water (20). The bands from 1500 cm<sup>-1</sup> - 400 cm<sup>-1</sup> have been attributed to the stretching and bending frequencies of the SiO<sub>4</sub> units that make up the layer (15). Garces et al. [15] have assigned the bands atabout 1225 cm<sup>-1</sup> to five membered rings of SiO<sub>4</sub> tetrahedra that are present in certain zeolites.



II.7. Infrared spectra (2% w/w KBr pellet) of (A) Na<sup>+</sup>-magadiite, (B)  $Co(sep)^{3+}$ -mag(25°C), and (C)  $Co(sep)^{3+}$ -mag(100°C).

The IR spectrum of  $Co(sep)^{3+}$ -Mag(100°C) exhibited all the peaks characteristic of magadiite, along with weak absorptions from  $Co(sep)^{3+}$ . Weak broad IR bands at 3100 cm<sup>-1</sup>, 2960 cm<sup>-1</sup> and 2850 cm<sup>-1</sup> were assigned to the C-H stretching frequencies of the ligand. Also, a weak absorption at 1465 cm<sup>-1</sup> was characteristic of the C-H asymmetric bending modes of  $Co(sep)^{3+}$ . The characteristic magadiite absorptions in the 1500 cm<sup>-1</sup> - 400 cm<sup>-1</sup> region remained unchanged upon intercalation of  $Co(sep)^{3+}$  cation, indicating that the layered structure was not changed during intercalation.

Nitrogen adsorption isotherms over the partial pressure range of  $0 < P/P_0 < 0.4$  were obtained at -196°C for Na<sup>+</sup>-magadiite, and the  $Co(sep)^{3+}$  reaction products. The data were treated by using the BET equation [12] in order to obtain surface area values. The equivalent surface areas were determined from the BET monolayer volume V<sub>m</sub> (BET), and the microporous volumes determined from the t-plots (see Table II.III.). A very small microporous surface area,  $(7 \text{ m}^2/\text{g})$ , was observed for  $Co(sep)^{3+}$ -Mag(25°C). The virtually non-existent microporosity was consistent with little or no Co(sep)<sup>3+</sup> intercalation for the reaction product obtained at 25°C. Somewhat more surprising was the low microporous surface area for  $Co(sep)^{3+}$ . Mag(100°C), (8.7  $m^2/g$ ). Although Co(sep)<sup>3+</sup> had been intercalated, apparently insufficient space was available to allow access to the nitrogen molecule (kinetic diameter 3.6 Å). That is, the mixed  $Co(sep)^{3+}$  and  $Co^{2+}$  intercalation product appeared to be "stuffed" with little free volume between the metal complex pillars.

Sample	S <sub>BET</sub> m²g-1	V <sub>m</sub> cm <sup>3</sup> liq g <sup>-1</sup>	Nonmicroporous Surface m <sup>2</sup> g <sup>-1</sup>
Na-magadiite	24	0	24
H-magadiite	45	0	45
Co(sep)-Magadiite 25°C	33	0.0025 (7 m <sup>2</sup> g <sup>-1</sup> )	24
Co(sep)-Magadiite 100°C	57	0.0031 (8.7 m <sup>2</sup> g <sup>-</sup> 1)	48

Na<sup>+</sup>-magadiite can adopt a particle morphology composed of silicate layers intergrown to form spherical nodules resembling rosettes [15]. The proton exchange form of magadiite also has this characteristic particle morphology [7]. Scanning electron micrographs of the Co(sep)<sup>3+</sup> reaction products, shown in Figure II.8b., and II.8c., revealed the same morphology as the starting Na<sup>+</sup>-magadiite, Figure II.8a., except that the size of the rosettes were reduced by the attrition caused by vigorous stirring during reaction. This result indicated that the Co(sep)<sup>3+</sup> in Co(sep)<sup>3+</sup>-magadiite(100°C) was intercalated in a topotactic fashion. Close inspection of the micrographs also indicated the absence of other crystalline phases.

The demetalation of  $Co(sep)^{3+}$  that occurred upon reaction of the complex with Na<sup>+</sup>-magadiite at 100°C is particularly noteworthy. Sargeson and his coworkers have reported previously that it was not possible to remove the metal from the Co(III) complex [11]. II.8A Scanning electron micrographs at X6600 and X1500 magnification for Na<sup>+</sup>-magadiite



X1500

II.8B. Scanning electron micrographs at X6600 and X1500 magnification for Co(sep)<sup>3+</sup>-mag(25°C)



II.8C. Scanning electron micrographs at X6600 and X1500 magnification for Co(sep)<sup>3+</sup>-mag(100°C)

•





X1500

 $Co(sep)^{3+}$  is very stable and remains intact even after prolonged treatment in boiling 12 M HCl. Elemental analyses suggested that during the intercalation of  $Co(sep)^{3+}$ , one half of the metal centers were no longer complexed by the sepulchrate ligand and was confirmed by qualitative analysis for Co(II). The stability of Co(sep)Cl<sub>3</sub> was tested in basic solution under reaction conditions identical to those used to obtain the 100°C intercalation product. Under these conditions no Co(II) was detected using the SCN<sup>-</sup> qualitative test. Demetalation seemed to be a direct result of the interaction of  $Co(sep)^{3+}$  with magadiite. Treatment of  $Co(sep)^{2+}$  with acid leads to release of Co(II) from the sepulchrate ligand [11], but an analogous reaction does not occur for the 3<sup>+</sup> cation. The mechanism of decomplexation on the magadiite surface may have involved reduction of the Co(sep)<sup>3+</sup> complex by water followed by rupture of the cage and release of Co(II). The ovalshaped  $Co(sep)^{3+}$  is oriented with with its long axis parallel to the silicate sheet, as judged from the 6.4 Å gallery height obtained by X-ray diffraction. Magadiite might facilitate the reduction of  $Co(sep)^{3+}$  by distorting the bicyclic complex in the intercalated state.

The relatively sharp X-ray diffraction pattern observed for  $Co(sep)^{3+}$ -magadiite(100°C) indicated that the material was regularly intercalated. That is, both the  $Co(sep)^{3+}$  and  $Co^{2+}$  cations appear to be mixed within each interlayer in a uniform manner. A previously proposed model structure for Na<sup>+</sup>-magadiite suggested that the magadiite layer has a corrugated surface [15]. A plausible arrangement in this case could involve placement of the larger

 $Co(sep)^{3+}$  cations between the pleated folds of the layer with the Co<sup>2+</sup> cations adopting positions at the ridges as illustrated in Figure II.9. Confirmation of this structure will have to await future studies of the magadiite structure.

# D. Conclusions

The reaction of Co(sep)<sup>3+</sup> with Na<sup>+</sup>-magadiite at 25°C resulted in a product that contained  $Co(sep)^{3+}$  cations bound to the external crystallite surfaces of the layered silicate. In contrast, reaction at 100°C resulted in penetration of the metal complex between the layers of magadiite. The magadiite structure was retained even after prolonged reaction with Co(sep)<sup>3+</sup> at 100°C. Moreover, the particle morphology for the  $Co(sep)^{3+}$  intercalated derivative was the same as the starting Na<sup>+</sup>-magadiite suggesting a topotactic intercalation. However, concomitant with intercalation at 100°C, was the partial demetalation of  $Co(sep)^{3+}$  which resulted in a mixed ion intercalate containing both  $Co^{2+}$  and  $Co(sep)^{3+}$  between the layers. N<sub>2</sub> surface area analysis indicated that only a small amount of microporous surface existed in the  $Co(sep)^{3+}$  intercalated derivative, indicating that most of the interlayer space was stuffed with little or no available microporosity between pillars. Thus, Co(sep)<sup>3+</sup> is not suitable for the pillaring of magadiite, even though this cation has been successfully used previously as a pillaring agent for related ionic structures such as smectite clays [16]. In the case of the layered sodium silicates it seems that pillaring is difficult to achieve by direct ionic exchange. Future work will focus in part on the use of robust organic cation intercalated derivatives of magadiite for



II.9. Proposed positions of  $Co(sep)^{3+}$  ions in the pleated folds of magadiite.  $Co^{2+}$  cations are placed at the ridges which form between folds. Vertices of the magadiite layer represent silicon positions; oxygen positions are between adjacent silicon pairs. The fourth coordination position of silicon is not shown.

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accessing the intracrystalline space of magadiite by organic molecules from aqueous solution.

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### **CHAPTER III**

# Silica Pillared Layered Silicates Derived From the Polymerization of Tetraethylorthosilicate in the Galleries of Alkylammonium Exchange Magadiite

## A. Introduction

Pillared layered materials have attracted widespread interest due in part to their catalytic and molecular sieving properties (1,2). In an effort to broaden the diversity of pillared materials, we have been investigating the pillaring reactions of the lamellar hydrous sodium silicate Na<sup>+</sup>-magadiite (Na<sub>2</sub>Si<sub>14</sub>O<sub>29</sub>·9H<sub>2</sub>O). Other examples of this unique family of silicates include, kenyaite (Na<sub>2</sub>Si<sub>20</sub>O<sub>41</sub>·10H<sub>2</sub>O), and kanemite (NaHSi<sub>2</sub>O<sub>5</sub>·3H<sub>2</sub>O). All are naturally occurring minerals first found in lake beds at Lake Magadi, Kenya (3). These compounds also can be conveniently prepared in the laboratory by hydrothermal synthesis (4-6).

Intercalative ion exchange reactions of Na<sup>+</sup>-magadiite with robust cations as pillaring agents is restrictive due to the relatively high layer charge and non-swellable nature of the layered silicate. Recent attempts to pillar Na<sup>+</sup>-magadiite by ion exchange of cobalt sepulchrate,  $[Co(sep)]^{3+}$ , a metal cage complex noted for its stability in solution (7), afforded instead a non-microporous intercalated derivative in which one half of the metal centers were no longer complexed by the sepulchrate ligand (8).

It has been shown that the hydrated interlayer sodium ions of Na<sup>+</sup>-magadiite and related layered silicates can be exchanged by large alkylammonium cations to form organic derivatives (5,6,9). Analogous onium ion derivatives have been formed by the reaction of the proton exchange from of the layered silicate with alkylamines (10). Alkylammonium derivatives of magadiite and kenyaite have been used as precursors for the reaction of interlayer silanols by organo silanes. For example, dodecyltrimethylammonium intercalates of magadiite and kenyaite react with trimethylchlorosilane to form silane grafted derivatives (11).

In a related strategy to form pillared derivatives, the interlayer SiOH groups of H<sup>+</sup>-magadiite have been investigated for reaction with silane grafting reagents. Ruiz-Hitzky et al. (12) have found that if H<sup>+</sup>-magadiite is preintercalated with polar organic molecules such as dimethylsulfoxide, trimethylsilyl groups can be grafted to the silanol groups of the gallery surfaces. More recently, Sprung and Davis (13) have used polyhedral silicate species derived from phenyltrichlorosilane as pillaring reagents for H<sup>+</sup>-magadiite. The direct reaction of H<sup>+</sup>-magadiite with this pillaring reagent resulted in partially pillared derivatives of H<sup>+</sup>-magadiite. The resultant calcined products exhibited surface areas in the range 100-200 m<sup>2</sup>/g and basal spacings near 15.6 Å.

The goal of this work was to utilize the intercalation chemistry of magadiite to generate pillared microporous materials. The used to form pillared derivatives involves strategy the preintercalation of H<sup>+</sup>-magadiite by long-chain alkylamine molecules, followed by the intercalation of a siloxane pillaring reagent, such as tetraethylrothosilicate, which can graft with the interlayer SiOH groups and also self polymerize to form SiO<sub>2</sub> aggregates. Recently Landis et al. (14) reported that n-alkylammonium-magadiite samples produced from aqueous solution react with tetraethylorthosilicate to produce high surface area pillared materials (BET surface area = 530  $m^2/g$ ). Although their strategy is similar to ours differences exist in the preparation of the n-alkylammonium derivatives which affect the basal spacings and surface areas of the final materials. Up to this point no in depth characterization of these synthetic products has been reported. Also, a systematic evaluation of the dependence of the physical properties of the resultant materials on different synthetic proceedures have not been investigated.

# **B.** Experimental

# 1. Synthesis of H<sup>+</sup>-magadiite.

H+-magadiite was prepared by titration of Na<sup>+</sup>-magadiite with 0.1 N HCl by adaptation of the method of Lagaly et. al. (10). A suspension composed of of Na<sup>+</sup>-magadiite (18.5 g) and 460 mL of deionized H<sub>2</sub>O was titrated slowly with 0.1 N HCl. The solution pH was lowered to 1.9 over a period of 12 hours and maintained at a value of 1.9 for an additional 12 hours. The pH of the solution was measured continuously by using a Fisher Accumet Digital pH meter. Solid H<sup>+</sup>-magadiite was separated by centrifugation and washed with deionized H<sub>2</sub>O until Cl<sup>-</sup> free. The resultant product was dried in air at 40°C.

#### 2. Synthsis of Octylammonium-magadiite.

A reactive gel of octylammonium magadiite was formed by allowing H<sup>+</sup>-magadiite (0.5 g, 0.57 mmol) to react at room temperature with excess octylamine (2.0 g, 15 mmol). During octylamine addition, the H<sup>+</sup>-magadiite solid absorbs the liquid amine immediately forming a gray gelatinous mixture that will not flow. The resultant gel was used without further treatment for all reactions. And the second second

## 3. Synthsis of Silica Intercalated Magadiites.

Silica intercalated derivatives of magadiite were prepared by the reaction of neat tetraethylorthosilicate, TEOS, with a gel composed of octylammonium-magadiite solvated in excess octylamine. To three 150 ml Erlenmeyer flasks each containing the previously described octylamine H<sup>+</sup>-magadiite gel (2.5 g, 0.57 mmol H<sup>+</sup>-magadiite) were added three different aliquats of TEOS (6.3 g, 31 mmol), (10.3 g, 51 mmol), and (17.7 g, 87 mmol). The reaction flasks were covered and the mixtures were stirred vigorously for 24 hours. The siloxane intercalated reaction products were separated by centrifugation, and dried from ethanol in air at 40°C. Calcined derivatives were prepared by heating the air-dried solids in air at 360°C for four hours.

## 4. Physical Measurements

Basal spacings were determined from the OOI x-ray reflections of oriented film samples using a Rigaku Rotaflex diffractometer equipped with Cu K $\alpha$  radiation. Samples of Na<sup>+</sup>-magadiite, H<sup>+</sup>magadiite and the uncalcined TEOS/magadiite reaction products were prepared by depositing on a glass slide a suspension of the solids and allowing the suspension to air dry at 40°C. Samples of the calcined silica intercalated magadiite were prepared for X-ray diffraction analysis by heating the uncalcined TEOS/magadiite reaction products on glass microscope slides to 360°C in air for four hours. The basal spacing of octylammonium-magadiite solvated by excess octylamine was obtained by smearing a thin film of the gel across a glass microscope slide and then recording the diffraction pattern of the wet sample.

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<sup>29</sup>Si MAS NMR experiments were performed on a Varian 400 VXR solid state NMR spectrometer operated at 79.5 MHz. A Bruker multinuclear MAS probe equipped with zirconia rotors was used for all measurements. The <sup>29</sup>Si relaxation times for Na<sup>+</sup>-magadiite, H<sup>+</sup>magadiite, and the uncalcined and calcined TEOS/magadiite reaction products were determined by the inversion recovery method. <sup>29</sup>Si MAS spectra were obtained by using 4.6 us 90° pulse widths. A total of 12 scans were accumulated for each sample. The spinning rate was 5 kHz. Delay times approximately five times as large as T<sub>1</sub> were used in order to obtain quantitative integral intensities. Cross polarization experiments were carried out with delay times of 10 s and contact times of 1000  $\mu$ s.

Nitrogen adsorption/desorption isotherms were determined on a Quantachrome Autosorb Sorptometer at liquid  $N_2$  temperature using ultrahigh purity  $N_2$  and He as adsorbate and carrier gases, respectively. All samples were outgassed at 150°C under vacuum for 12 hours. Surface areas were determined using the BET equation and the t-plot method (15).

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Fourier transform infrared spectra were obtained on an IBM IR44 spectrometer using the KBr pressed-pellet technique. All pellets contained 0.5% sample by weight.

Thermogravimetric analyses were performed using a Cahn TG System 121 thermogravimetric analyzer. All samples were heated to 1000°C at a heating rate of 5°C/min.

- C. Results and Discussion
- 1. Na<sup>+</sup>- and H<sup>+</sup>-magadiite.

The basic hydrolysis of silica gel at 150°C under autogenus pressure produced a well-crystallized Na<sup>+</sup>-magadiite product. The Xray diffraction pattern of an air dried film sample, shown in Figure III.1A., exhibited several 001 reflections corresponding to a basal spacing of 15.6 Å. Despite the planar structure of Na<sup>+</sup>-magadiite and efforts to produce well oriented films, several hkl reflections with



III.1. X-ray diffraction patterns for film samples of (A) Na<sup>+</sup>-magadiite, and (B) H<sup>+</sup>-magadiite. 22

 $h \neq k \neq 0$  were observed due to the rosette-like morphology of the aggregated platelets. The peak positions for this synthetic product agree closely with values reported previously (16,17) for synthetic and natural magadiite.

The slow titration of Na<sup>+</sup>-magadiite with 0.1 N HCl resulted in the exchange of sodium ions for protons in the layer structure (18). The x-ray diffraction pattern of an air dried H<sup>+</sup>-magadiite film, shown in Figure III.1B., exhibits 001 reflections corresponding to a basal spacing of 11.2 Å, in agreement with earlier work (18). This decrease in basal spacing relative to the sodium form indicates a loss of interlayer H<sub>2</sub>O upon replacement of Na<sup>+</sup> by H<sup>+</sup>. Also, the general broadening of the diffraction peaks indicates that greater stacking disorder occurs upon proton exchange.

The sodium content of synthetic  $Na^+$ -magadiite depends in part on the extent of hydrolysis that occurs upon washing the product. Washing with water initially removes excess NaOH associated with the material. However, repeated washing leaches  $Na^+$  cations from the interlayer and causes hydrolysis.

The chemical composition of the Na<sup>+</sup>-magadiite used in this work was obtained by combining the results of thermogravimetric analyses and chemical analyses. As shown by the thermogravimetric curve in Figure III.2., air dried Na<sup>+</sup>-magadiite that has been well washed to remove excess NaOH, loses 13% of its total weight as water below 200°C. An additional 1.6% is lost between 200°C- 1000°C. The weight loss above 200°C is assigned to the dehydroxylation of SiOH



III.2. Thermogravimetric analysis curves obtained under flowing argon for (A) Na<sup>+</sup>-magadiite, and (B) H<sup>+</sup>-magadiite.

groups. By combining the Na<sub>2</sub>O content (4.98%) and weight loss, we obtained an empirical composition for synthetic Na<sup>+</sup>-magadiite of Na<sub>1.7</sub>Si<sub>14</sub>O<sub>27.9</sub>(OH)<sub>1.9</sub>  $\cdot$  7.6 H<sub>2</sub>O. This result is in general agreement with the ideal formula of Na<sub>2</sub>Si<sub>14</sub>O<sub>29</sub>  $\cdot$ 9H<sub>2</sub>O put forth by Lagaly et al. (9), Garces et al. (17) and McAtee et al. (19). The samples synthesized in this work (cf.,Table II.I.) straddle these compositions, depending on post hydrothermal treatment of the product, especially the number of washings. The water content can also vary dramatically depending on drying conditions. The low sodium content of our washed product, 1.7 Na<sup>+</sup> per 14 Si, was a direct result of hydrolysis caused by the extensive washing with water.

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Thermal analysis of H<sup>+</sup>-magadiite, as shown by the curve in Figure III.2B., indicated an initial weight loss below 300°C of 2.1% due to the desorption of H<sub>2</sub>O. The 4.0% weight loss above 300°C was attributed to the elimination of OH groups from the structure. The water loss together with the virtual absence of sodium, is in agreement with an approximate unit cell composition of H<sub>4</sub>Si<sub>14</sub>O<sub>30</sub>. H<sub>2</sub>O. This formula agrees well with the compositions reported by other workers (10,13).

### 2. Octylamine/Octylammonium Magadiite.

Lagaly and co-workers (10) have previously reported that H<sup>+</sup>magadiite intercalated by dimethylsulfoxide reacts with alkylamines to form ordered bilayers of alkylamine molecules between the silicate layers. Analogous gallery ordering is known to occur for nalkylammonium montmorillonites swollen by n-alkylalcohols or n-

alkylamines (20). The air-dried product resulting from the direct reaction of octylamine with H<sup>+</sup>-magadiite exhibits a basal reflection indicative of a 2.9 Å gallery height or a 14.1 Å basal spacing as shown by the diffraction pattern in Figure III.3A. Thus, octylammonium cations were intercalated with the chains oriented parallel to the silicate layer. The X-ray diffraction pattern of air dried octylammonium-magadiite changes dramatically upon solvation by excess octylamine, as shown in Figure III.3B. The gallery height for the amine-solvated gel was 22.8 Å, which indicated the formation of bilayers of octylamine between the layers.

#### 3. TEOS/magadiite Reaction Products.

The products obtained by the reaction of the octylamine/octylammonium-magadiite gel with TEOS was dependent on reaction stoichiometry. Depending on the molar ratio of TEOS to magadiite, products with different basal spacings were obtained. Figure III.4. illustrates the X-ray diffraction patterns for the uncalcined siloxane intercalates isolated from reaction mixtures containing 54, 90, and 153 moles TEOS/moles of magadiite. These patterns indicate basal reflections corresponding to basal spacings of 23.3 Å, 25.2 Å and 28.1 Å respectively. Thus there was an apparent increase in basal spacing with increasing amount of TEOS used in the reaction. Since the layer thickness of magadiite is  $\approx 11.2$  Å, the basal spacings correspond to gallery heights of 12.1 Å, 14.0 Å and 16.9 Å, respectively. These gallery heights decrease from the initial gallery height of 22 Å observed for the octylamine/octylammonium-



III.3. X-ray diffraction patterns for film samples of octylammonium-magadiite (A) sample air-dried at 25°C and (B) solvated by excess octylamine.



III.4. X-ray diffraction patterns for film samples of the uncalcined TEOS/magadiite reaction products that resulted from treatment of octylamine solvated octylammonium-magadiite with tetraethylorthosilicate. The TEOS/magadiite mole ratios were (54:1), (90:1) and (153:1).

magadiite precursor gel, so that the gallery shrinks by  $\approx$  5-10 Å when octylamine is replaced by TEOS.

The X-ray diffraction patterns shown in Figure III.5. for the products calcined in air at 360°C, indicate a further decrease of 2-3 Å in gallery height for each derivative. Also, there is a decrease in the degree of order along the c-axis, as evidenced by a broadening of the basal reflection of each derivative. Table III.I. summerizes the d spacings and gallery heights for the starting materials along with those for the calcined and uncalcined TEOS/magadiite reaction products.

The chemical compositions of the products derived from reaction of octylamine/octylammonium-magadiite with TEOS were obtained by combining TGA and C, H, N, chemical analyses. All nitrogen was assumed to be due to the presence of octylammonium cation and all excess carbon was attributed to the presence of residual alkoxide ( $C_2H_5O_2$ ), associated with polymerized siloxane. Table III.II. provides the elemental compositions of H+-magadiite, octylammonium-magadiite and the uncalcined TEOS/magadiite reaction products as a function reaction stoichiometry. It is noteworthy that the percentage of octylamine present in the uncalcined reaction products decreases as the amount of TEOS used in the reaction increases. This may indicate that neutral amine is replaced to a larger extent as the amount of TEOS present in the reaction mixture increases. The three reaction products also contain residual alkoxide. It is noteworthy that the amine content of the samples is similar to the amount present in the octylammonium-


III.5. X-ray diffraction patterns for film samples of TEOS/magadiite reaction products after calcination. Calcined in air at 360° C for four hours.

Sample	Basal Spacing, Å	Gallery Height, Å
Na+-magadiite	15.6	4.4
H+-magadiite	12.4	1.2
(air dried)	14.1	2.9
$C_8H_{17}NH_3^+$ -magadilite (amine solvated)	34.0	22.8
TEOS/magadiite (56:1)	23.3	12.1
TEOS/magadiite (92:1)	25.2	14.0
TEOS/magadiite (156:1)	28.1	16.9
TEOS/magadiite (56:1, calcined 360°C)	20.7	9.5
TEOS/magadiite (92:1, calcined 360°C)	22.4	11.2
TEOS/magadiite (156:1, calcined	25.9	14.7
360°C)		

Table III.I.Basal Spacing and Gallery Heights of Magadiite ReactionPrecursors and TEOS Reaction Products

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magadiite derivative, indicating that only strongly bound octylammonium cations remain after treatment with TEOS.

The nitrogen adsorption/desorption isotherms shown in Figure III.6. were obtained for calcined TEOS/magadiite reaction products. The data were plotted according to the BET equation (15) in order to obtain surface area values. The equivalent surface areas for H<sup>+</sup>-magadiite and the calcined derivatives determined from the

Table III.II. Analytical Data

Sample	%SiO2 <sup>a</sup>	%C8H17NH2 <sup>b</sup>	%C2H5-O <sup>b</sup>	%H2O <sup>c</sup>	%Total
H-magadiite	93.9%			6.1%	100%
C <sub>8</sub> H <sub>17</sub> NH <sub>3</sub> +-magadiite (air dried)	84.4%	11.1%		5.0%	100%
TEOS/magadiite (56:1)	79.0%	13.5%	2.4%	2.9%	97.8%
TEOS/magadiite (92:1)	77.7%	12.4%	3.8%	4.8%	98.7 <i>%</i>
TEOS/magadiite (156:1)	80.4%	10.4%	3.3%	4.5%	98.6%

<sup>a</sup>Based on weight retained after heating to 1000°C <sup>b</sup>Values obtained by carbon, hydrogen, nitrogen analyses. <sup>c</sup>Obtained by weight loss below 200°C <sup>d</sup>Reaction mixture stoichiometry in moles TEOS/moles magadiite

monolayer volume  $V_m$  (BET) are listed in Table III.III. Microporous volumes for the samples were determined by using the t-plot method (15). The data listed in Table III.III indicate H<sup>+</sup>-magadiite



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III.6. Nitrogen adsorption/desorption isotherms for the calcined TEOS/magadiite reaction products produced with a ratio of (54:1), (90:1) and (153:1) moles TEOS/mole magadiite.

has a total surface area of 45 m<sup>2</sup>/g due exclusively to adsorption at non-porous external surfaces. The calcined products obtained from the TEOS/magadiite reaction exhibited dramatically larger surface areas between 520-680 m<sup>2</sup>/g, depending on the concentration of TEOS used in the reaction mixture. The interlayer space or microporous surface accounts for the majority of porosity introduced into these materials. The amount of external and mesoporous surface, determined by using the parallel pore method (21) vary little between samples. This increase in surface area can be attributed to the pillaring of magadiite by intercalated aggregates of

Table	III.III.	Surface	Area	Anal	ysis	$(m^2/g)$	of	Pillared	Derivatives
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Sample	S <sub>BET</sub>	S <sub>total</sub>	Smic	S
H <sup>+</sup> -magadiite	45	45	0	45
TEOS/magadiite (56:1)	620	635	590	45
TEOS/magadiite (92:1)	680	705	670	35
TEOS/magadiite (156:1)	520	525	480	45

<sup>a</sup> Definitions of abbreviations:  $S_{BET}$  is the N<sub>2</sub> BET surface area. S<sub>total</sub>, S<sub>mic</sub>, and S are the total, microporous, and nonmicroporous surface areas obtained from t-plots of the adsorption data

silica. The relationship between the microporous surface area, Table III.III., and the basal spacing, Table III.I., indicate there is a change in porosity of the calcined TEOS/magadiite reaction products as the TEOS stoichiometry changes. For example, an optimum surface area is obtained at an intermediate  $d_{001}$  value. This effect can be explained by assuming an increase in pillar size as the gallery height increases. Thus, as the pillars increase in size the lateral spacing between pillars will decrease, Figure III.7. An intermediate value of the basal spacing would yield an optimum porosity only if there exists the best compromise between pillar height and lateral pillar spacing. The infrared spectra of calcined and uncalcined TEOS/magadiite (90:1) reaction products are compared in Figure III.8., with the spectra for octylammonium-magadiite and H<sup>+</sup>magadiite. Both the calcined TEOS/magadiite (90:1) product and H+magadiite exhibit the same stretching bands between 4000-400 cm<sup>-</sup> <sup>1</sup>. H<sup>+</sup>-magadiite exhibits infrared bands similar to the sodium form The broad overlaping bands centered at 3445 cm<sup>-1</sup> were (18). assigned to the stretching frequencies of the OH group of either silanol groups or water associated with the silicate (18). The band centered at 1632  $\text{cm}^{-1}$  was attributed to the bending frequencies of H<sub>2</sub>O (18). The bands from 1500 cm<sup>-1</sup>-400 cm<sup>-1</sup> were attributed to the stretching and bending frequencies of the  $SiO_4$  units that make up the layer (17). For Na<sup>+</sup>-magadiite, Garces et al. (17) have attributed the bands at 1237  $cm^{-1}$  to five membered ring blocks of SiO<sub>4</sub> tetrahedra. In addition, the bands at 1210 cm-1 and 1175 cm-1 were attributed to five, six and four membered ring block structures



III.7. Schematic representation for the variation of pillar size with the change in reaction stoichiometry.



III.8. Infrared spectra for KBr pellets (0.25 wt %) of (A) H<sup>+</sup>magadiite, (B) air-dried octylammonium-magadiite, (C) TEOS/magadiite reaction product (90:1) air dried, and (D) TEOS/magadiite (90:1) reaction product after calcining at 360°C.

similar to those found in the zeolites epistilbite and dachiardite (17). Comparison of the infrared spectrum of Na<sup>+</sup>-magadiite with the spectra obtained for the calcined TEOS/magadiite (90:1) product and H+-magadiite indicate an almost identical match of stretching frequencies for the region between 1500 cm<sup>-1</sup> and 400 cm<sup>-1</sup>. It is possible to attribute by analogy the stretching frequencies near 1225  $cm^{-1}$  to the presence of block structures composed of a combination of five, six and four membered rings of  $SiO_4$  tetrahedra in both the calcined TEOS/magadiite (90:1) product and H+-magadiite. In turn, the layer structure of H+-magadiite and the calcined TEOS/magadiite (90:1) product are composed of the same building blocks as Na<sup>+</sup>magadiite. In addition, the presence of absorptions at  $\approx 1225$  cm<sup>-1</sup> indicates there is retention of the layer structure upon pillaring by The infrared spectrum of the uncalcined TEOS/magadiite silica. (90:1) reaction product exhibits IR bands which match the octylammonium-magadiite spectrum closely Figure III.8B-C. In addition to the bands characteristic of the magadiite layers, weak infrared bands at 2962 cm<sup>-1</sup>, 2929 cm<sup>-1</sup>, 2873 cm<sup>-1</sup> and 2859 cm<sup>-1</sup> were observed for the uncalcined TEOS/magadiite (90:1) product. These bands are attributed to the C-H asymmetric and C-H symmetric stretching frequencies of the intercalated octylammonium cation. Weak broad bands centered at 1537 cm<sup>-1</sup> are assigned to the  $NH_3^+$  deformation (bending) frequencies of the ammonium cation. A weak absorption at 1469 cm<sup>-1</sup> results from the C-H asymmetric bending of the alkyl chain. A weak intensity band at 923 cm<sup>-1</sup>, here assigned to the Si-O stretching of SiOH groups in octylammoniummagadiite were also found to be present in freshly precipitated silica

gels near 950 cm<sup>-1</sup> (22) and in hydrolyzed polysiloxane polymers near 890 cm<sup>-1</sup> (23). This indicates first that octylammonium cation remains even after intercalative reaction with TEOS and secondly, that the bands associated with layer structural blocks remain intact after intercalation of the siloxane species. Also, there is a shift in the absorption associated with the Si-O stretching of the SiOH groups from 923 cm<sup>-1</sup> to 958 cm<sup>-1</sup>. This most likely is due to the the overlaping Si-O stretching frequencies of the intercalated siloxane which exhibit higher frequency peaks in polysiloxane polymer 1104  $cm^{-1}$ , (24). After calcination, the bands which were present in the infrared spectrum of the uncalcined TEOS/magadiite (90:1) product near 2900 cm<sup>-1</sup>, 1460 cm<sup>-1</sup> and 1539 cm<sup>-1</sup> dissapear. The loss of these bands results from the oxidation and desorption of octylammonium cation and ethoxide groups present in the material. In addition, the absorption near 958  $cm^{-1}$  in the uncalcined material shifts to 965 cm<sup>-1</sup> after calcination indicating the formation of Si-O-Si linkages (22).

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The <sup>29</sup>Si MAS NMR spectra of the calcined TEOS/magadiite reaction products, shown in Figure III.9., all indicate two general silicon environments, namely a Q<sup>3</sup> type HOSi(OSi)<sub>3</sub> environment near -101.5 ppm and Q<sup>4</sup> type Si(OSi)<sub>4</sub> environments near -111 ppm and -114.5 ppm. The relaxation times for the calcined TEOS/magadiite reaction products were found to be 44 s  $\pm$  5 s for the Q<sup>3</sup> environments and 141 s  $\pm$  11 s for the Q<sup>4</sup> environments. The <sup>29</sup>Si MAS NMR spectra of the uncalcined TEOS/magadiite reaction products, shown in Figure III.10., exhibit Q<sup>3</sup> and Q<sup>4</sup> resonances at



III.9. <sup>29</sup>Si MAS NMR spectra of H<sup>+</sup>-magadiite and calcined TEOS/magadiite reaction products produced with a ratio of (54:1), (90:1), and (153:1) moles TEOS/mole magadiite.



III.10. <sup>29</sup>Si MAS NMR spectra of Na<sup>+</sup>-magadiite, H<sup>+</sup>-magadiite and uncalcined TEOS/magadiite reaction products produced with a ratio of (54:1), (90:1), and (153:1) moles of TEOS/mole magadiite.

approximately the same chemical shift values as the calcined products, Table III.VI., with only slight differences. Calcination results in a slight upfield shift of all chemical shift values probably due to increases in Si-O-Si bond angles. Also,  $O^3/O^4$  ratios for the calcined TEOS/magadiite products are lower than the  $Q^3/Q^4$  ratios for the uncalcined derivatives due to the condensation of  $O^3$  silanol During calcination  $Q^3$  silanol groups which are in close groups. proximity condense to form siloxane bonds. Even after calcination a large amount of  $Q^3$  silanol groups still remain. The absence of  $Q^0$ ,  $Q^1$ , and  $Q^2$  silicon resonances in the <sup>29</sup>Si MAS NMR spectra of both the calcined and uncalcined TEOS/magadiite reaction products indicate TEOS has polymerized to form silicate species which are composed of  $Q^3$  and  $Q^4$  silicon environments. Also, because the  $Q^3/Q^4$  ratios for the products are the same as for H<sup>+</sup>-magadiite it follows that the  $Q^{3}/Q^{4}$  ratio for the intercalated silicate species is close to that of H<sup>+</sup>magadiite.

The <sup>29</sup>Si MAS NMR spectra of the calcined and uncalcined TEOS/magadiite reaction products all exhibit chemical shifts and relative intensities which closely match H<sup>+</sup>-magadiite and Na<sup>+</sup>-magadiite. For instance, Na<sup>+</sup>-magadiite exhibits two general Si environments, namely Q<sup>3</sup> type (HOSi(OSi)<sub>3</sub>) or Na<sup>+</sup>[OSi(OSi)<sub>3</sub>]) and Q<sup>4</sup> type Si(OSi)<sub>4</sub> environments (18,25). The <sup>29</sup>Si MAS NMR spectrum of Na<sup>+</sup>-magadiite, Figure III.10., exhibits a single Q<sup>3</sup> peak centered at -99.8 ppm and three Q<sup>4</sup> resonances occur at -110.7 ppm, -111.7 ppm and -114.2 ppm respectively. Previous workers have published Q<sup>3</sup>/Q<sup>4</sup> ratios for Na<sup>+</sup>-magadiite (17,25). However a careful

Treatment	Sample	Chemical	Q <sup>3</sup> /Q <sup>4</sup>	
		Q <sup>2</sup> *,Q <sup>3</sup>	Q <sup>4</sup>	
	H-Magadiite	-100.4	-110.8, -113.7	0.28
	TEOS/magadiite (56:1)	-99.9	-110.7, -113.9	0.30
	TEOS/magadiite (92:1)	-99.9	-110.8, -113.9	0.29
	TEOS/magadiite (156:1)	-99.9	-110.8, -113.7	0.26
	TEOS/magadiite (56:1, calcined 360°C)	-101.5	-111.1, -114.4	0.21
	TEOS/magadiite (92:1, calcined	-92.2*,-101.4	-111.1, -114.7	0.18
	TEOS/magadiite (156:1, calcined 360°C)	-101.3	-110.6, -114.4	0.17
<b>CP-MAS</b>	_			
	TEOS/magadiite (56:1)	-101.6	-113.7	
	TEOS/magadiite (92:1)	-101.6	-113.2	
	TEOS/magadiite (156:1)	-90.5*, -101.2	-112.7	
	TEOS/magadiite (56:1, calcined	-90.8*, -101.4	-111.9	
	TEOS/magadiite (92:1, calcined	-91.0*, -101.2	-111.7	
	TEOS/magadiite (156:1, calcined	-91.3*, -101.6	-112.9	

Table III.IV. <sup>29</sup>Si MAS NMR Chemical Shift Values and  $Q^3/Q^4$  ratios for H<sup>+</sup>-magadiite and the TEOS/magadiite reaction products.

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<sup>a</sup> Reaction Stoichiometry ratio in moles TEOS/mole H-magadiite

evaluation of the relaxation times of the various <sup>29</sup>Si environments has not been undertaken until now. The differences in  $Q^3$  and  $Q^4$ relaxation times for Na<sup>+</sup>-magadiite, 160 s and 280 s respectively are attributed to the presence of  $H_2O$  in the interlayer. The importance

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of <sup>29</sup>Si-<sup>1</sup>H dipolar relaxation via water molecules has been shown for other layered materials (26). The close proximity of interlayer water to the  $Q^{3}$  <sup>29</sup>Si sites of Na<sup>+</sup>-magadiite allows for there relaxation via  $^{29}$ Si-<sup>1</sup>H dipolar relaxation and in turn reduces the relaxation time of the  $Q^3$  site greatly as compared to the  $Q^4$  site. H<sup>+</sup>-magadiite like Na<sup>+</sup>magadiite, and the calcined and uncalcined TEOS/magadiite reaction products exhibits two general silicon environments, namely Q<sup>3</sup> type HOSi(OSi)<sub>3</sub> and Q<sup>4</sup> type Si(OSi)<sub>4</sub> environments (25). The <sup>29</sup>Si MAS NMR spectrum of H<sup>+</sup>-magadiite, Figure III.10., exhibits a single Q<sup>3</sup> resonance at -100.4 ppm and Q<sup>4</sup> resonances at -110.8 ppm and -113.7 ppm. In general the chemical shift values for H<sup>+</sup>-magadiite closely match those for Na<sup>+</sup>-magadiite and the reaction products. The only noticeable difference between Na<sup>+</sup>-magadiite and H<sup>+</sup>magadiite was the linewidth. This increase in linewidth after exchange of protons for sodium ions may be a result of unaveraged dipolar interactions of the <sup>29</sup>Si nucleus with <sup>1</sup>H. A careful evaluation of the relaxation times,  $T_1$ , for the  $Q^3$  and  $Q^4$  silicon environments in H+-magadiite indicate a marked decrease as compared to Na+magadiite. Relaxation times for H<sup>+</sup>-magadiite are 95 s for both the Q<sup>3</sup> The relative integral intensities and O<sup>4</sup> environments. of H+magadiite indicate a  $Q^3/Q^4$  ratio of 0.28 which agrees closely with the  $Q^3/Q^4$  ratio of the uncalcined TEOS/magadiite reaction products.

Based on a Si<sub>14</sub> unit cell, the  $Q^3/Q^4$  ratio of H<sup>+</sup>-magadiite converts to 3.08 silanol groups/ unit cell. The combination of this information and thermal analysis results in a more accurate unit cell formula for H<sup>+</sup>-magadiite of Na.<sub>0.02</sub>Si<sub>14</sub>O<sub>26.5</sub>(OH)<sub>3.08</sub>•1.5H<sub>2</sub>O.

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The <sup>29</sup>Si CP-MAS spectra of the calcined TEOS/magadiite reaction products, Figure III.11, indicate a new resonance at ~-91 ppm in addition to the enhanced  $O^3$  resonance near 101.5 ppm. These resonances are assigned to  $Q^2$  (HO)<sub>2</sub>Si(OSi)<sub>2</sub> <sup>29</sup>Si environments. The cross polarization <sup>29</sup>Si spectra of the uncalcined TEOS/magadiite reaction products are shown in Figure III.12. These products all exhibit a  $Q^3$  peak near -101.6 ppm and  $Q^4$  resonances at approximately -113 ppm. In each case the  $O^3$  resonance has been enhanced indicating the presence of silanol groups. These  $O^3$ HOSi(OSi)<sub>3</sub> groups may be associated with either the layer or the The uncalcined TEOS/magadiite (153:1) reaction siloxane pillar. product exhibits a weak intensity peak near -90.5 ppm. This indicated the presence of  $Q^2$  (HO)<sub>2</sub>Si(OSi)<sub>2</sub><sup>29</sup>Si environments. The general absence of  $Q^2$  environments in the uncalcined derivatives indicate the O<sup>2</sup> <sup>29</sup>Si environments are present as ethoxide rather than hydroxyl groups which accounts for the lack of enhancement. Calcination results in combustion of the ethoxide groups. Water, produced in the combustion or present in the atmosphere may rehydrate these silicon environments resulting in  $Q^2$  silanol environments which would be enhanced by cross polarization. Proton cross polarization of <sup>29</sup>Si nuclei in H<sup>+</sup>-magadiite, Figure III.12., results in the enhancement of the Q<sup>3</sup>, HOSi(OSi)<sub>3</sub>, resonance centered



III.11. <sup>29</sup>Si CP-MAS NMR spectra of calcined TEOS/magadiite reaction products produced with a ratio of (54:1), (90:1), and (153:1) moles TEOS/mole magadiite. Products calcined at 360°C in air for four hours.



III.12. <sup>29</sup>Si CP-MAS NMR spectra of  $H^+$ -magadiite, and uncalcined TEOS/magadiite reaction products produced with a ratio of (54:1), (90:1), and (153:1) moles of TEOS/mole magadiite.

at -101.6 ppm. The  $Q^4$  Si(OSi)<sub>4</sub> resonances at -111.7 ppm and -114.4 ppm are not enhanced due to the absence of hydroxyl groups at these sites.

Na<sup>+</sup>-magadiite is known to adopt a particle morphology composed of silicate layers intergrown to form spherical nodules resembling rosettes (17). The proton exchange form also has this characteristic particle morphology Figure III.13A. (27). Scanning electron micrographs of octylammonium-magadiite indicate a loss of the initial particle morphology Figure III.14A. It appears that the treatment of H<sup>+</sup>-magadiite with octylamine followed by air drying results in a break up of the spherical nodules with a concomittant random arrangement of the platelets. Scanning electron micrographs of the uncalcined and calcined TEOS/magadiite products, shown in Figure III.14B., and III.14C., respectively, exhibit the same morphology as ocytylammonium-magadiite. The calcined and uncalcined TEOS/magadiite derivatives exhibit particle sizes between  $5\mu$ -1400 $\mu$ , much larger than the particle size of H<sup>+</sup>-magadiite, as shown in Figure III.13B. The similarity between the morphology of octylammonium-magadiite and the calcined and uncalcined TEOS/magadiite reaction products indicated that intercalation of TEOS occured in a topotactic fashion.

## 4. Mechanism of Intercalation.

Reaction of H<sup>+</sup>-magadiite and octylamine forms a derivative with a bilayer structure between the layers of H<sup>+</sup>-magadiite. The bilayer structure was composed of both octylammonium cations and III.13. Scanning electron micrographs of H<sup>+</sup>-magadiite at A) X6000 and B) X600 magnification.

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e at A)

III.14. Scanning electron micrographs at X6000 magnification for A) air-dried octylammonium-magadiite (top left), B) TEOS/magadiite reaction product (54:1) air-dried (top right), C) calcined TEOS/magadiite (54:1) (bottom).





III.15. Schematic representation for the intercalation and pillaring of octylamine solvated octylammonium-magadiite.

neutral octylamine Figure III.15. Reaction of this intercalated derivative with tetraethylorthosilicate results in the replacement of the neutral octylamine with TEOS by a diffusion process. As TEOS replaces octylamine the layer SiOH groups react with the siloxane groups to form siloxane bonds and EtOH. Further hydrolysis of the intercalated siloxane results during air drying and storage of the siloxane intercalated derivative. Calcination results in combustion of octylammonium cations and ethoxide groups which still remain in the material. The loss of organic matter during calcination creates voids within the material and accounts for the microporous surface areas Figure III.15.

The high surface area and crystalline nature of the silica pillared derivatives indicate a high degree of cooperativity in pillar formation. There are four possible driving forces for the formation of descrete pillar domains. For example; i) charge localization within the layer may result in the formation of descrete domains of alkylammonium cations which separate TEOS domains, ii) domains of surface SiOH groups could function as reaction sites for the siloxane reagent resulting in pillar domains, iii) a highly corrugated layer may result in layer structure control over pillar formation, iv) solvation effects between the alkylammonium cations, the layer and TEOS may result in segregation of domains. In addition, the possibility exists that two or more of the above phenomena may work in combination

## D. Conclusions

The reaction of H<sup>+</sup>-magadiite with octylamine results in an octvlammonium intercalated derivative swollen by neutral This derivative has a basal spacing of 34 Å when octylamine. solvated by excess octylamine, but the basal spacing collapses to 14 A after drying. We have demonstrated the utility of this material as a precursor, in the solvated state, for the intercalation of hydrolyzable reagents such as TEOS. Reaction of this precursor with TEOS results in the intercalation and polymerization of TEOS at specific sites on the H<sup>+</sup>-magadiite surface. The mechanism for polymerization appears to occur by a topochemical process with the H-magadiite surface acting as a template. The final reaction product, after calcination, is composed of layers of magadiite separated by regularly spaced silica pillars. By adjustment of the TEOS stoichiometry final products were obtained that possess gallery heights from 9.5 Å to 14.9 Å and microporous surface areas from  $480 - 670 \text{ m}^2/\text{g}$ . In general the surface areas of our materials are higher than those reported by Landis et al. (14). The gallery heights increase with increasing TEOS concentration. However, the microporous surface areas attained a maximum and then decreased which may indicate a change in the pillar size. Interior surface silanol groups of the type  $Q^3$  HOSi(OSi)<sub>3</sub> and  $Q^2$  (HO)<sub>2</sub>Si(OSi)<sub>2</sub> are present in the final pillared products. These silanol groups should prove useful as grafting sites for catalytic metal centers.

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