

HYPOTHETICAL STRUCTURES OF MAGADIITE AND SODIUM OCTOSILICATE AND STRUCTURAL RELATIONSHIPS BETWEEN THE LAYERED ALKALI METAL SILICATES AND THE MORDENITE- AND PENTASIL-GROUP ZEOLITES¹

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Abstract—Hypothetical model structures for magadiite and sodium octosilicate, based on the structure of the zeolite dachiardite, are proposed that consist of layers of 6-member rings of tetrahedra and blocks containing 5-member rings attached to both sides of the layers. The infrared (IR) and nuclear magnetic resonance spectra of magadiite and sodium octosilicate have features in common with spectra of zeolites in the ZSM-5 and mordenite groups. A peak at 1225 cm^{-1} in the IR spectra of magadiite and sodium octosilicate is characteristic of zeolites containing 5-member rings, such as ZSM-5- and mordenite-type zeolites. The defect structures of pentasil zeolites may therefore be akin to layered alkali metal silicates containing zeolite-like domains, in which part of the silanol groups from adjacent silicate layers are condensed (cross-linked) forming siloxane linkages.

Key Words—Alkali metal silicate, Bikitaite, Crystal structure, Dachiardite, Epistilbite, Infrared spectroscopy, Magadiite, Mordenite, Nuclear magnetic resonance, Sodium octosilicate, Zeolite, ZSM-5.

INTRODUCTION

Meier (1978) noted that the zeolites in the mordenite group are characterized by continuous sheets of 6-member rings of TO_4 tetrahedra. The sheets are linked to each other through 4-, 5-, and 6-member rings and apparently contain mainly, if not only, Si in tetrahedral coordination. Kalt (1968) and Bapts *et al.* (1983) determined the structures of the layer silicates KHSi_2O_5 and kanemite, respectively. These structures contain sheets of 6-member rings of HOSiO_3 or MOSiO_3 tetrahedra (Q_3 type), in which three of the four oxygens are bonded to adjacent silicon atoms and the fourth is bonded to a H atom or to an alkali metal atom, M. The sheets of tetrahedra are similar to those in mordenite-group structures, but they are not linked to each other to form three-dimensional frameworks.

Schwieger *et al.* (1985) and Pinnavaia *et al.* (1986) recently proposed structures for several layered alkali metal silicates that contain both Q_3 and Q_4 tetrahedra. In the Q_4 tetrahedra, the four oxygen atoms bridge adjacent silicon atoms. Beneke and Lagaly (1977) showed that the layered alkali metal silicates related to kanemite, including magadiite, transform readily into one another under hydrothermal conditions. For example, magadiite can be synthesized from sodium

octosilicate by Soxhlet extraction with water. Layered alkali metal silicates have also been reported as co-products in the synthesis of high-silica zeolites, such as ZSM-5 (Gatti *et al.*, 1986). No evidence of transformations showing a direct linkage between the structures of zeolites and the layer silicates, however, is available.

The sheet of 6-member rings of tetrahedra in the layered alkali metal silicates and the mordenite-group zeolites may be a key common feature linking the chemistry of these two families of silicates. Earlier work in this laboratory noted that the 6-member ring sheet in KHSi_2O_5 is of the type I assigned by Meier (1978) to bikitaite, a member of the mordenite group. This observation prompted the present examination of the mordenite-group zeolites as a source of potential models to simulate the structures of the more complex layered alkali metal silicates, such as magadiite and sodium octosilicate.

Infrared and nuclear magnetic resonance spectroscopic methods were used to obtain structural data for magadiite and sodium octosilicate. These data support hypothetical model structures for magadiite and sodium octosilicate and provide insight into the chemistry of these materials and the relations between zeolites and layered alkali metal silicates.

EXPERIMENTAL

Materials

Sodium octosilicate, $8\text{SiO}_2 \cdot \text{Na}_2\text{O} \cdot 9\text{H}_2\text{O}$, was prepared from 10 kg of DuPont colloidal silica (Ludox

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Table 1. Composition of natural and synthetic magadiite.

Sample	Weight percent (mole ratios)			Total
	SiO ₂	Na ₂ O	H ₂ O	
Magadiite, ¹ Trinity Center	82.3 (12.7)	6.71 (1.00)	10.0 (5.14)	99.0
Magadiite, ¹ Synthetic-1	84.8 (13.3)	6.56 (1.00)	7.80 (4.09)	99.2
Magadiite, ¹ Synthetic-2	87.0 (13.7)	6.31 (1.00)	8.10 (4.41)	101.4
Magadiite, Eugster (1967)	77.6 (14.4)	5.56 (1.00)	14.6 (9.05)	97.8
Magadiite, Lagaly <i>et al.</i> (1975)	75.8 (13.4)	5.84 (1.00)	18.36 (10.8)	100
Magadiite, Lagaly <i>et al.</i> (1975)	74.9 (13.9)	5.58 (1.00)	18.19 (11.2)	98.7

¹ This study.

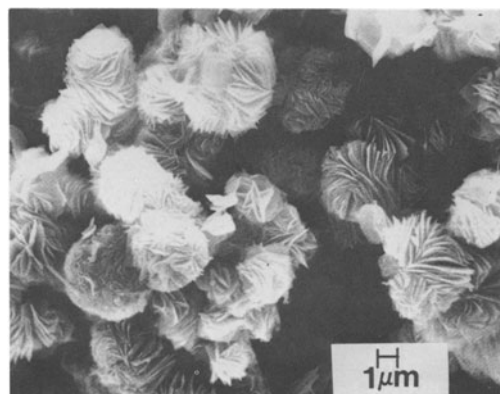
AS-40) and 800 g of reagent grade NaOH pellets (97% NaOH, VWR Scientific) following the procedure outlined by Iler (1964). The natural magadiite came from Trinity Center, California. Synthetic magadiite was prepared from 55.47 g of silicic acid (86.5% SiO₂, Fish-

er Scientific), 24.70 g of sodium carbonate (Baker), and 246.46 g of water. The silicic acid was added to the aqueous carbonate to make a homogeneous mixture, which was placed in a Teflon-lined pressure vessel and heated at 175°C for 19 hr. The product was separated by filtration and air dried at room temperature under flowing air.

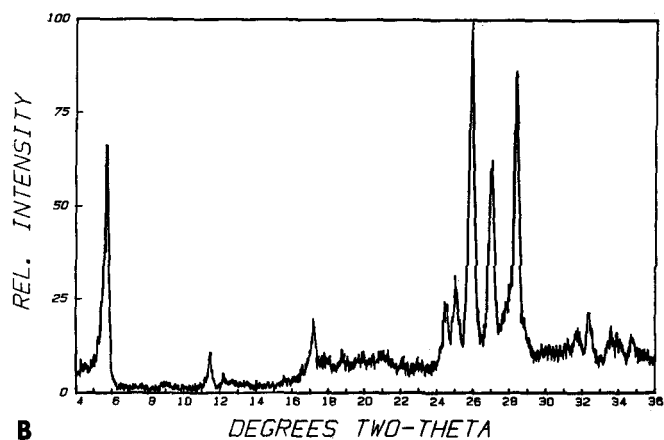
Analytical

The materials were analyzed by X-ray powder diffraction (XRD), scanning electron microscopy (SEM), infrared spectroscopy (IR) and nuclear magnetic resonance (NMR) spectroscopy. A Philips Electronic Instruments XRD unit equipped with a theta-compensating slit, a long-line focus, a wide-angle goniometer, a monochromator, and a scintillation detector was used to record XRD patterns, using CuK α radiation.

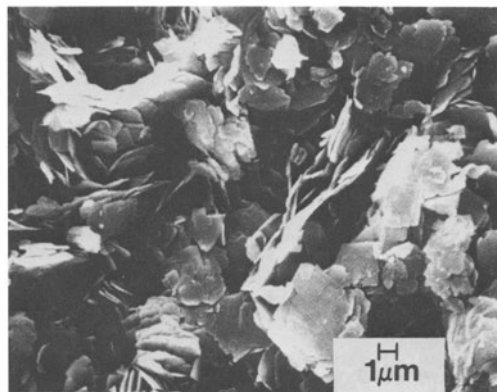
SEM analyses were carried out in a ISI-40 unit to study morphology, crystal size, and homogeneity of the samples. IR analyses were made on FTIR spectrometers, either Nicolet MX-1 or 60-SX, using KBr wafers.



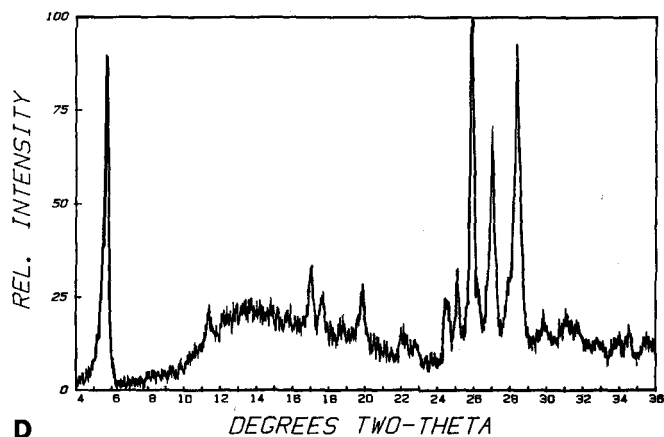
A



B

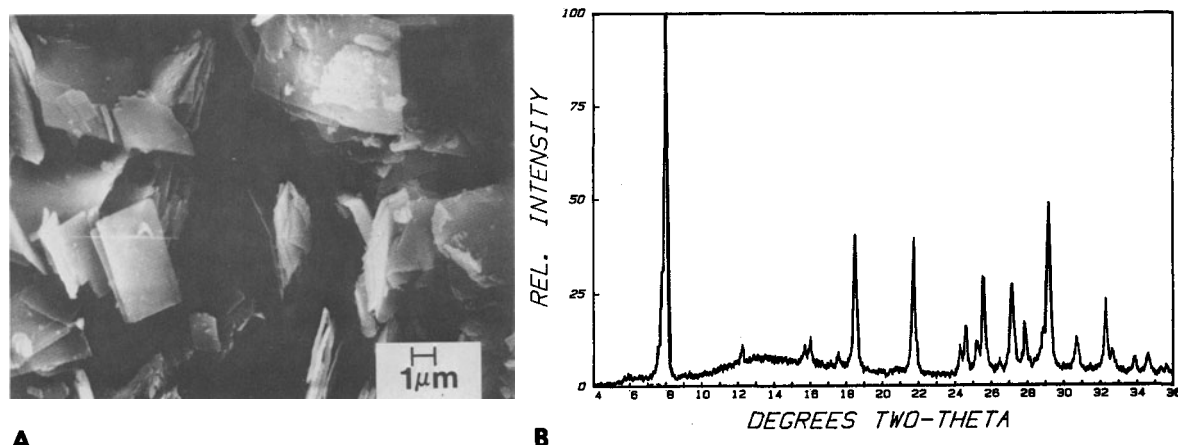


C



D

Figure 1. Scanning electron microscopic and X-ray powder diffraction (CuK α radiation) data for synthetic magadiite (A, B) and Trinity Center natural magadiite (C, D).



A **B**
Figure 2. (A) Scanning electron microscopy and (B) X-ray powder diffraction (CuK α radiation) data for sodium octosilicate.

Solid state ^{29}Si NMR spectra were obtained at 71.45 MHz on a Bruker CXP-200 spectrometer equipped with a 8.45 Tesla magnet. The samples were held at the magic angle and spun at a rate of 4.1 kHz. The magic angle was set by maximizing the ^{127}I sideband manifold of KI. Pulse widths of 4 μs and 10 s pulse repetition times were used. Chemical shifts are reported with respect to liquid tetramethylsilane.

RESULTS AND DISCUSSION

Chemical composition and structure

Neutron activation analyses of the magadiite samples studied here are compared with literature analyses in Table 1. The $\text{SiO}_2/\text{Na}_2\text{O}$ mole ratio ranges from about 12 to about 14; the water content ranges from about 8 to 18 wt. %. The differences in water content are probably due to differences in the drying procedures used by the several authors. The range of $\text{SiO}_2/\text{Na}_2\text{O}$ mole ratios is probably due to the fact that several of the samples contain small amounts of crystalline and noncrystalline impurities, as suggested by X-ray powder analyses (Figure 1), and to the different synthesis conditions employed.

XRD patterns of representative samples of the magadiite and sodium octosilicate used in this study are shown in Figures 1 and 2. Accompanying SEMs show that the synthetic magadiite products consist of plates that form cabbage-like aggregates about 10 μm in diameter. In the natural sample from Trinity Center, the cabbage-like aggregates apparently have been broken apart leaving a mosaic of overlapping plates. The XRD pattern of the octosilicate sample is shown in Figure 2. The crystals (Figure 2) are rectangular plates, 3–4 μm on a side and a few hundred Ångstroms thick.

Infrared spectroscopic analysis

IR data are summarized in Table 2. The IR spectra of magadiite and sodium octosilicate, synthesized as

outlined above and dried at room temperature (Figure 3) have peaks at about 1225 cm^{-1} . A similar peak at about the same frequency is characteristic of zeolites containing 5-member rings, including the mordenite group and the pentasil-type materials (Jacobs *et al.*, 1981). A peak at about the same frequency has also been observed in the IR pattern of sepiolite (J. J. Fripiat, Department of Chemistry, University of Wisconsin, Milwaukee, Wisconsin, personal communication, 1987). Jansen *et al.* (1984) showed that for pentasil zeolites the 1225- cm^{-1} peak is associated with a T–O asymmetric stretch. The presence of this peak in the IR spectra of magadiite and sodium octosilicate suggests that 5-member rings are probably present in their structures. This peak was not observed in the IR spectra of KHSi_2O_5 , reported by Kalt (1968) or in that of kanemite reported by Johan and Maglione (1972). Both KHSi_2O_5 and kanemite are based on sheets of 6-member rings; no blocks containing 5-member rings are present.

The IR spectrum of magadiite (Figure 3) shows a peak at 1237 cm^{-1} and shoulders at 1210 and 1175 cm^{-1} . The IR spectra of dachiardite and epistilbite, members of the mordenite group, also show shoulders at 1210 and 1175 cm^{-1} , respectively (Table 2). The IR spectrum of sodium octosilicate (Figure 3) has a peak at 1233 cm^{-1} . Epistilbite and dachiardite have similar structures, consisting of sheets of 6-member rings connected by 5- and 4-member rings (Meier, 1978). Based on the work of Jacobs *et al.* (1981) and Jansen *et al.* (1984), the peaks at about 1225 cm^{-1} are probably connected to the presence of structural blocks or cages constructed of 5-member rings of TO_4 units. The blocks may include other types of rings as well. Magadiite probably contains structural blocks similar to those found in dachiardite and epistilbite, inasmuch as the bands at 1210 and 1175 cm^{-1} are common to the IR spectra of the layered alkali metal silicate structure and the two zeolites. These blocks consist of four, puckered

Table 2. Infrared data for layered alkali metal silicates and zeolites (1500–400 cm^{-1}).

Material	Asymmetric stretch ¹		Symmetric stretch ¹		Double rings ¹	TO-bend ¹
	Ext. ²	Int. ²	Ext. ²	Int. ²	Ext. ²	Int. ²
Mordenite ³	1223sh	1045s	800w	720w	580, 560w	450s
ZSM-5 ³	1225sh	1093s	790w	—	550m	450s
Dachiardite ³	1210sh	1050s	775w	670w	558w	440s
Epistilbite ³	1175sh	1050s	795w	690w	563w	455s
Octosilicate ⁴	1235m	1057s	824w	690vw	620w	455s
Magadiite ⁴			780ww	705vw		
	1237sh	1082s	824w	690vw	620w	455s
	1210sh	1055sh	788w	705vw	576w	445s
	1175sh				546w	411sh

sh = shoulder, s = strong, w = weak, vw = very weak.

¹ See Jansen *et al.* (1984) for assignments.

² Ext. = external; Int. = internal.

³ Jansen *et al.* (1984).

⁴ This work.

5-member rings (type B blocks, Jansen *et al.*, 1984), as shown in Figure 4B.

Because the peak at 1237 cm^{-1} has no obvious counterpart in the IR patterns of the zeolites examined, this peak and the peak in the IR pattern of sodium octosilicate at 1233 cm^{-1} appear to be peculiar to these layer silicate structures and probably reflect a different type of block, in which some of the TO_4 tetrahedra are Q_3 type (see Figure 4C).

Zeolites having chains and blocks of 5-member rings

also yield IR peaks in the 650–500- cm^{-1} region (Jansen *et al.*, 1984). The IR pattern of magadiite shows peaks at 620, 576, and 546 cm^{-1} and that of sodium octosilicate, at 620 cm^{-1} (Figure 3, Table 2). The peaks at 576 and 546 cm^{-1} in the IR pattern of magadiite are in the same range reported for type-B blocks in high-silica zeolites (Jansen *et al.*, 1984). The IR patterns of dachiardite and epistilbite show peaks at 558 and 563 cm^{-1} , respectively (Jansen *et al.*, 1984). These peaks and the 1237- and 1233- cm^{-1} peaks are probably due

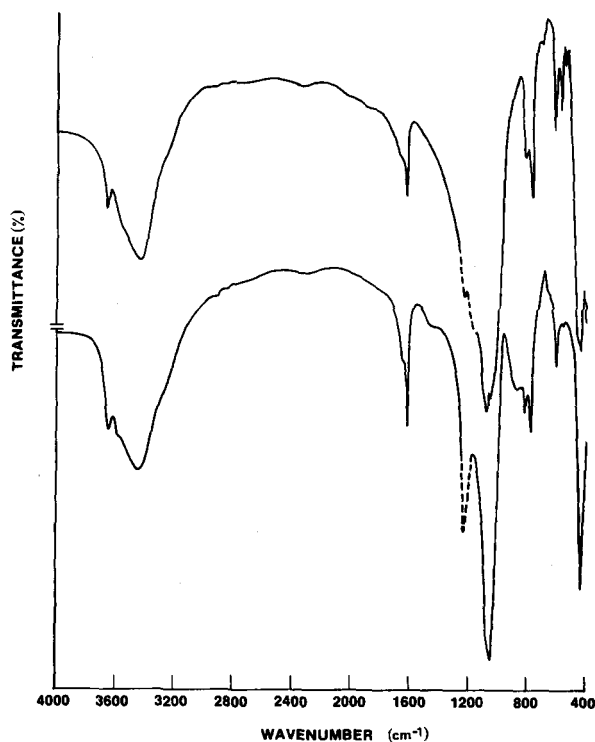


Figure 3. Infrared spectra of synthetic magadiite (top) and sodium octosilicate (bottom). KBr pellets.

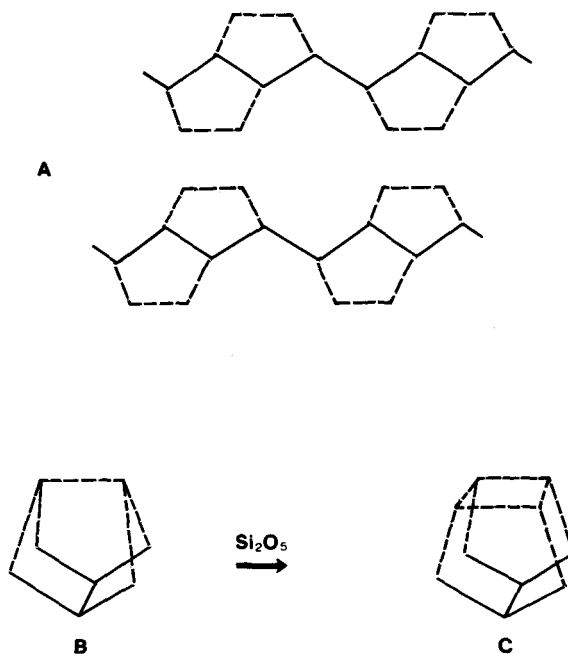


Figure 4. Schematic views of the model structure of magadiite: (A) a-b plane of the dachiardite derived model; (B) type-B block; (C) octosilicate block. Note: $\text{Si}_2\text{O}_5(\text{ONa})_2$ has been reduced to Si_2O_5 to show only atoms in the block.

to 5-member-ring vibrations, following the proposal of Jacobs *et al.* (1981) that vibrations due to blocks containing 5-member rings give rise to bands in the 1225-cm^{-1} region.

The internal symmetric- and asymmetric-stretch regions in the IR patterns of magadiite and sodium octosilicate have peaks at about the same frequencies as those in the IR patterns of dachiardite and epistilbite (Table 2). The IR pattern of mordenite has a peak at 720 cm^{-1} , but no corresponding peak exists in the IR pattern of the zeolite ZSM-5. Thus, the structures of magadiite and the octosilicate appear to be more closely related to those of the zeolites dachiardite and epistilbite than to those of the zeolites mordenite and ZSM-5. The positions of the external symmetric-stretch and the T-O-bend peaks in the IR patterns of magadiite and sodium octosilicate are also close to similar peaks found in the IR patterns of dachiardite and epistilbite (Table 2).

In the OH region (Figure 3), the IR pattern of magadiite has peaks at 3658 and 3439 cm^{-1} ; sodium octosilicate has similar peaks at 3654 and 3444 cm^{-1} (see also Table 2). These peaks are similar to those reported by Rojo *et al.* (1983), who noted two types of O-H groups in H-magadiite by IR and NMR. In the same study, these authors pointed out that the high-frequency peak changed slightly if the sample was heated to 500°C , whereas the peak at about 3440 cm^{-1} lost intensity.

Following Tsuchida (1982), the peak at about 3660 cm^{-1} was tentatively assigned to isolated Si-OH groups, which were probably on the external surface of the crystals. The peak at about 3440 cm^{-1} may be due, at least in part, to internal Si-OH groups between the layers of the solid. The absence of a band at 3720 cm^{-1} in magadiite suggests that Si-OH groups in this solid are isolated from each other, in good agreement with Rojo *et al.* (1983), who reported a 5-\AA distance between hydrogen atoms in residual Si-OH groups in H-magadiite.

²⁹Si NMR spectroscopy

The ²⁹Si NMR spectra of magadiite and octosilicate are shown in Figure 5, and the data are summarized in Table 3. Both Q₃- and Q₄-type Si sites appear to be present. The Q₄ regions of both the natural and synthetic samples of magadiite show at least three components at about -109.5 , -111 , and -113 ppm (Figures 5 and 6 and Table 3), with the -111-ppm signal being the strongest. In the Q₃ region, a peak at about -100 ppm is also present. The Q₄/Q₃ ratios for the two synthetic samples of magadiite (Table 3) are different even though they were prepared by similar procedures. On heating magadiite to 250°C the Q₄/Q₃ ratio increased significantly (Figure 6, Table 3). The Q₄/Q₃ ratio for magadiite heated to 250°C is given as large in Table 3 because the area under the Q₃ peak (Figure 6)

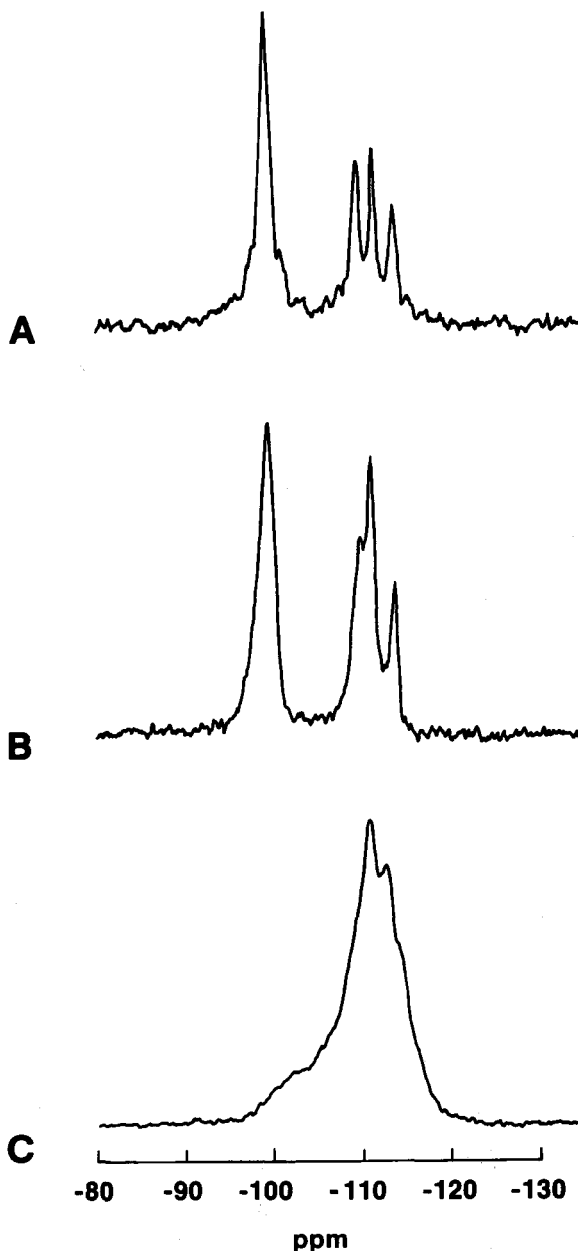


Figure 5. ²⁹Si nuclear magnetic resonance spectra of synthetic magadiite-2 (top) and sodium octosilicate (bottom).

could not be quantified precisely. Thus, the differences between the Q₄/Q₃ ratios in Table 3 and those reported for magadiite by Schwieger *et al.* (1985) and Pinnavaia *et al.* (1986) are probably due to cross-linking of silanol groups from adjacent layers forming siloxane linkages and resulting in more condensed structures having a higher Q₄/Q₃ ratio. The increase in the Q₄/Q₃ ratio of magadiite on heating to 250°C (Figure 6, Table 3), also observed by Pinnavaia *et al.* (1986), suggests that the layer silicate structure condensed on heating to a material which became enriched in Q₄ domains at the

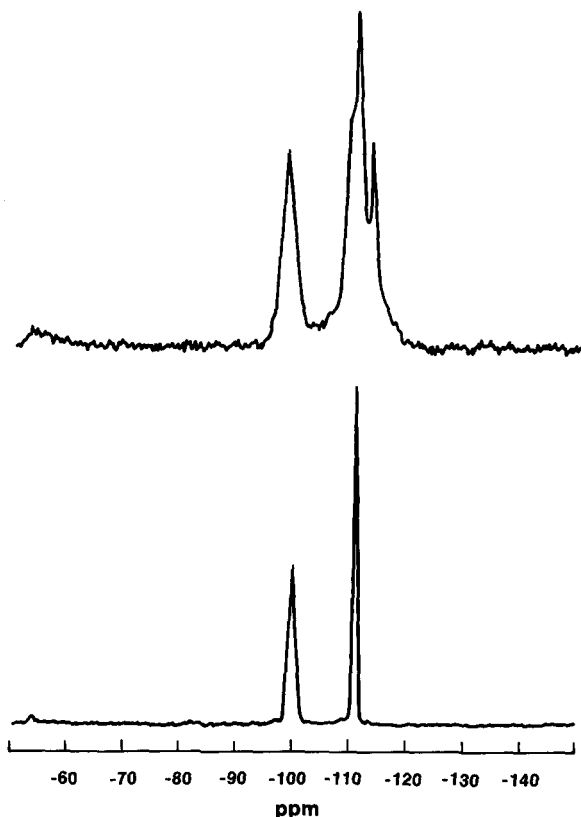


Figure 6. ^{29}Si nuclear magnetic resonance spectra of: (A) natural magadiite; (B) synthetic magadiite-1; (C) synthetic H-magadiite-2 heated to 250°C.

expense of Q_3 sites. Magadiite, therefore, appears to be a family of materials having various degrees of condensation.

The ^{29}Si NMR spectrum of sodium octosilicate contains very narrow resonances (Figure 4). Peaks at about -100 and -111 ppm are present in the Q_3 and Q_4 regions, suggesting a structure having a significant degree of condensation. The linewidths of these two peaks is narrower relative to the corresponding peaks in magadiite (Figure 4). The Q_4/Q_3 ratio is 0.92. The Q_4/Q_3 ratio in magadiite varies from 1.0 to about 2.5 or larger for heated samples (Table 3), suggesting that it is a more condensed structure than the octosilicate.

The positions of the Q_3 peaks in magadiite and octosilicate are similar to that of the Q_3 peak reported by Boxhorn *et al.* (1984) for ZSM-5. As shown above, the intensity of this peak decreased on heating the samples to about 250°C, in excellent agreement with the behavior of ZSM-5 (Boxhorn *et al.*, 1984). Likewise, the location of the Q_4 signal for these layered solids is within the range observed in the NMR spectra of samples of silicalite and 5-member ring zeolites (Klinowski, 1984). The ^{29}Si NMR results suggest that the magadiite-type layered solids and the 5-member ring zeolites of the mordenite and pentasil families may have structural similarities.

PROPOSED STRUCTURE

As pointed out by Meier (1978), the structures of mordenite-group zeolites contain continuous sheets of 6-member rings of tetrahedra. Each Si or Al atom (T atom) in these sheets is bonded via oxygens to three other T atoms. The fourth bond is directed out of the sheets. In the mordenite-group structures, an equal number of these fourth bonds are directed to either side of the sheet. Depending on the orientation of the TO_4 groups in the sheets, four distinct arrangements exist in the mordenite group, defined by Meier (1978) as types I, II, III, and IV. The layer silicates KHSi_2O_5 and kanemite and the zeolite bikitaite contain a type-I sheet in their structure. Type-I sheets contain equal numbers of alternating tetrahedra pointing up and down. The structure of KHSi_2O_5 is obtained by cutting the 4-member rings connecting the 6-member ring sheets in the bikitaite structure and using the open 4-ring sites to locate H and K atoms.

The similarities between the IR and NMR spectra of the layered alkali metal silicates magadiite and sodium octosilicate and those of the zeolites of the mordenite group (*vide supra*) suggest that the unknown structures of the layered alkali metal silicates may be related to the mordenite-group structures in the same manner that bikitaite is related to KHSi_2O_5 and kanemite.

A hypothetical structure for magadiite was derived from the structure of dachiardite (Gottardi and Meier, 1963) following the same procedure used to obtain the structure of KHSi_2O_5 from that of bikitaite. Dachiar-

Table 3. ^{29}Si Nuclear magnetic resonance data of layered alkali metal silicates.

Sample	Si chemical shifts (in ppm vs. TMS)				Q_4/Q_3^1
	Q_3		Q_4		
Magadiite, Trinity Center	-99.7	-109.5	-111.2	-113.6	1.2
Magadiite-1	-99.1	-109.4	-110.6	-113.2	1.0
Magadiite-2	-99.1	-109.4	-110.6	-113.2	2.5
H-Magadiite ² (230°C)	—	-110.9	-113.0	-114.5	large
Octosilicate	-100		-110.9		1.1

¹ Q_4/Q_3 = ratio of areas under Q_4 and Q_3 peaks.

² H-magadiite-2 heated in air.

Table 4. Crystallographic coordinates of atoms in model magadiite structure derived from dachiardite.

Atom	Coordinates		
	X	Y	Z
Si(1)	0.21126	0.84561	0.29551
Si(2)	0.20801	0.35290	0.28739
Si(3)	0.12449	0.73781	0.00000
Si(4)	0.12371	0.37788	0.00000
O(1)	0.16201	0.80020	0.16926
O(2)	0.15677	0.35159	0.17826
O(3)	0.25739	0.75460	0.30479
O(4)	0.11734	0.55363	0.00000
O(5)	0.20147	0.32162	0.50000
O(6)	0.19115	0.85903	0.50000
O(7)	0.25000	1.00000	0.25000
O(8)	0.25000	0.50000	0.25000
O(9)	0.06741	0.77744	0.00000
O(10)	0.06851	0.27024	0.00000

Table 5. Interatomic distances in model magadiite structure based on dachiardite.

Atom	Atom	Distance (Å)
Si(1)	O(1)	1.642
	O(2)	1.649
	O(3)	1.647
	O(4)	1.641
Si(2)	O(2)	1.629
	O(3)	1.629
	O(5)	1.627
	O(8)	1.628
Si(3)	O(1,2)	1.670
	O(4)	1.668
	O(9)	1.678
Si(4)	O(2,2)	1.663
	O(4)	1.659
	O(10)	1.647

dite was used as the starting structure because of the observed close similarity between the IR spectra of magadiite and the zeolites dachiardite and epistilbite. The 4-member rings that connect the sheets of 6-member rings in the structure of dachiardite were cut, and every other sheet was then displaced $\frac{1}{2}$ unit cell along the crystallographic c direction. This displacement was necessary to obtain better agreement between the experimental and the calculated XRD data (Table 6). The monoclinic symmetry of the dachiardite structure was retained, but the cell was expanded along the a direction to allow room for ionic coordination of the layers. The unique angle β was adjusted from $107^{\circ}54'$ to 101° to improve the coordination of the oxygen atoms with the alkali metal cations. This modified structure was optimized using the distance least squares (DLS) refinement of Meier and Villager (1969). The resultant structure had 14 atoms in the asymmetric unit having a total of 29 variable coordinates (not fixed by symmetry). Sixty-five significant interatomic distances involved at least one atom of the asymmetric unit, including the nearest neighbor Si–O distances, the O–O distances along the edges of the tetrahedra, and the nearest Si–Si distances.

Each significant interatomic distance was used to write an equation relating the changes to be made in the atomic positions to the overall change required for the distance itself. The problem then was that of a multiple linear regression in which the derivatives of the interatomic distances with respect to the atom coordinates were the data points, the changes needed in the atomic coordinates were the coefficients to be determined, and the differences between actual and ideal interatomic distances were the constants. Inasmuch as the cell parameters of the hypothetical structure of magadiite were known, the derivatives were readily calculable.

The hypothetical model structure shows good agree-

ment with data obtained for magadiite. The hypothetical unit cell of magadiite is monoclinic and its dimensions are $a = 27.5$, $b = 9.20$, $c = 7.52$, and $\beta = 101^{\circ}$. The atomic coordinates and interatomic distances of the dachiardite-based model structure are listed in Tables 4 and 5. The calculated d -values and relative intensities of the proposed structure are compared with data from Brindley (1969) for magadiite in vacuo in Table 6. The model structure consists of continuous sheets of 6-member rings having blocks containing 5-member rings protruding from the two faces of the sheets, as shown in Figure 4. All TO_4 tetrahedra in the sheets of 6-member rings have Si atoms bonding to other Si atoms via oxygen atoms. In the blocks above and below the sheets of 6-member rings the Si atoms form three siloxane bonds with other Si atoms; a silanol group or an oxygen atom occupies the fourth site, resulting in a Q_3 site. The ratio of Q_4/Q_3 sites required by the model structure is 2, which is in good agreement with experimental NMR values given in Table 3. The interlayer spacing of 13.5 Å is identical with that reported by Brindley (1969) for magadiite in vacuo.

The chemical formula for the derived structure is $NaSi_6O_{12}(OH)$. This formula is in reasonable agreement with the formula reported by Eugster (1967) for acid-treated magadiite and kenyaite, $6SiO_2 \cdot H_2O$, and also with the analytical data reported here (Table 1). The difference between the stoichiometries of the model and the natural or synthetic magadiite samples may be due to the fact that the synthetic and natural samples contain small amounts of impurities, such as noncrystalline silica (see baseline in XRD pattern of natural magadiite in Figure 1), or that the layered structure is partially condensed into a three-dimensional structure as suggested by the ^{29}Si NMR data reported here.

If the blocks shown in Figure 4B are enlarged by addition of $Si_2O_5(ONa)_2$ units to form a block having a 4-member ring at the top as shown in Figure 4C (the ONa groups have been omitted in Figure 4C), the re-

Table 6. Experimental X-ray powder diffraction pattern of magadiite (in vacuum) and calculated pattern of model structure of magadiite based on dachiardite.

Magadiite (Brindley, 1969)		Magadiite model ¹	
d (Å)	I	d (Å)	I
13.50	vs	13.50	vs
—	—	8.74	w
7.4	w	—	—
7.25	w	7.24	m
6.71	m	6.75	vw
5.89	w	5.91, 5.77, 5.72	vw
5.32	vw	—	—
5.0–5.2	vw	—	—
4.76	w	—	—
4.49	m	4.56, 4.41	w
—	—	4.38	m
4.1–4.25	m	4.19	vw
—	—	4.03, 3.94	w–m
3.64	w–m	3.62	m
3.46	w–m	3.48, 3.38, 3.37	w
3.31	s–vs	3.29, 3.28	w, w–m
2.9–3.2	m	—	—
2.82	m	2.75	m

vs = very strong; s = strong; m = medium; w = weak; vw = very weak.

¹ Some calculated peaks having very weak intensity are not listed here.

sulting structure requires a $\text{SiO}_2/\text{Na}_2\text{O}$ ratio of 8, which is identical with the ratio required by the formula unit of sodium octosilicate ($8\text{SiO}_2 \cdot \text{Na}_2\text{O} \cdot 9\text{H}_2\text{O}$). Thus, the layers in the octosilicate structure probably consist of a sheet of 6-member rings having cages made of 4-, 5-, and 6-member rings, as shown in Figure 4C. The transformation of sodium octosilicate into magadiite by water extraction (Beneke and Lagaly, 1977) probably involves the loss of $\text{Si}_2\text{O}_5(\text{ONa})_2$ units, which is equivalent to the reverse of the process shown in Figures 4B and 4C. Lagaly *et al.* (1975) showed that the basal spacing of magadiite at 200–400°C is 11.6–11.5 Å, similar to the basal spacing of the octosilicate (11.04 Å) reported by Iler (1964).

Samples of natural and synthetic magadiite probably have adjacent layers bonding to each other creating condensed three-dimensional dachiardite- or epistilbite-like domains as suggested by the common features in the IR spectra of the layered alkali metal silicates and the mordenite-group zeolites. In addition, the NMR data given above support the postulated formation of condensed zeolite-like domains within the layered structures. The indicated structural similarities suggest that dachiardite and epistilbite minerals may coexist with magadiite in natural deposits of this mineral.

Recent IR and NMR evidence has suggested the presence of internal Si–OH groups in samples of highly siliceous ZSM-5 (Woolery *et al.*, 1986; Boxhorn *et al.*, 1984; Brunner, 1987). If zeolite-like domains exist in magadiite as postulated above, the presence of internal silanol groups in siliceous zeolites may possibly be tak-

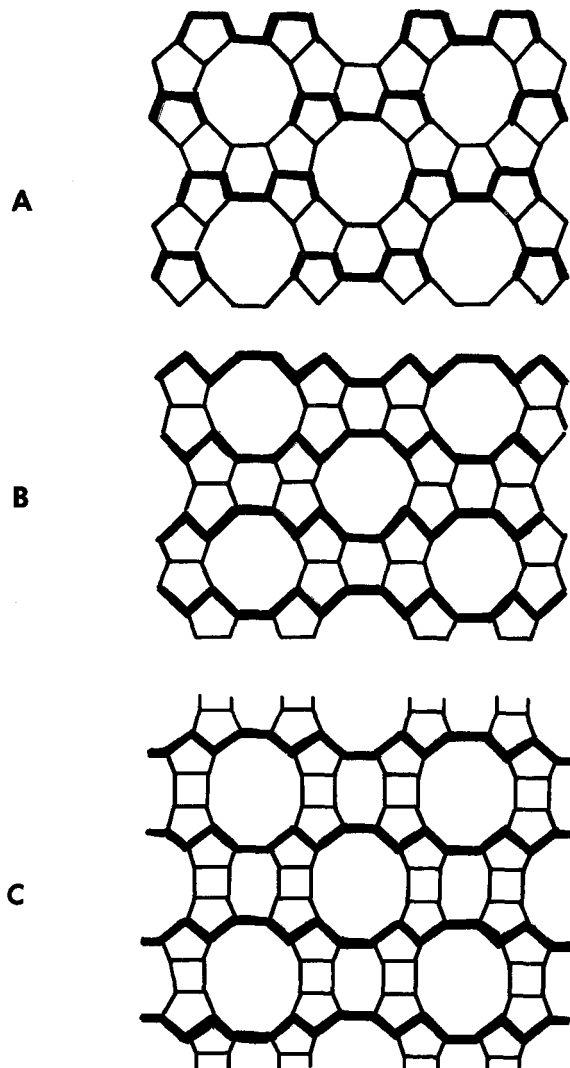


Figure 7. Projections of the skeletal frameworks of ZSM-5 and mordenite zeolites. (A) ZSM-5, *a*-axis projection; (B) ZSM-5, *b*-axis projection; (C) mordenite, *c*-axis projection.

en as evidence of layered silicate domains in the pentasil-type and mordenite-type zeolites.

The *a*- and *b*-axis projections of the idealized structure of ZSM-5 (Kokotailo *et al.*, 1978) and the *c*-axis projection of mordenite (Meier, 1974) are shown in Figure 7. The *c*-axis projection of mordenite and the *b*-axis projection of ZSM-5 are similar. Indeed, if the single 4-member rings which bond the 6-member ring sheets via 5-member rings in the mordenite *c*-axis projection are eliminated, the *b*-axis projection of ZSM-5 is generated. The *a*-axis projection of the ZSM-5 structure has triple bands of 6-member rings, which possess the same puckered structure as the type-IV sheets in mordenite described by Meier (1974).

The formation of defect sites in the mordenite and pentasil structures appears to be related to the presence

of internal silanol sites within the crystals of these materials (Debras *et al.*, 1983; Nagy *et al.*, 1982). The proposed blocks shown in Figure 4C can be generated from the type-B blocks present in the idealized structure of ZSM-5 (Jansen *et al.*, 1984) by the addition of $\text{Si}_2\text{O}_5(\text{ONa})_2$ units, as shown in Figures 4B and 4C. The blocks in Figure 4C are similar to blocks located at the base of the sinusoidal channels in the ZSM-5 structure, above the triple bands of 6-member rings. If some of the TO_4 sites in the 4-member rings in ZSM-5 are converted to Q_3 sites, creating defect sites, domains containing blocks like those shown in Figure 4C are also created in the zeolite structure.

Considering that the number of defect sites in ZSM-5 decreases as the Al content of the solids increases (Woolery *et al.*, 1986), the zeolitic network is probably stabilized if Al is present during the formation of the zeolite. Gatti *et al.* (1986) found that magadiite or ZSM-5-type structures are synthesized together from mixtures having $\text{SiO}_2/\text{Al}_2\text{O}_3 > 100$, and magadiite is the preferred product if Al is almost totally absent. Thus, if Al is present in the synthesis mixture, blocks having defect sites (Q_3) may be transformed into blocks having Q_4 sites, leading to a true tectosilicate structure. Because the 4-member rings in ZSM-5 have been reported to be possible sites of instability domains (Derouane and Fripiat, 1985), the blocks containing these rings in ZSM-5 may be in a condensed state intermediate between that of ideal tectosilicate blocks (all Q_4 sites) and layered alkali metal silicate blocks (some Q_4 sites). Whether Al is actually present in the 4-member rings of ZSM-5 is not certain, but reasonable agreement exists on the presence of Al in the 4-member rings of mordenite (Derouane, 1984; Itabashi *et al.*, 1986). Given the similarity of the ZSM-5 and mordenite structures and the data reported by Gatti *et al.* (1986), the absence of Al may play a key role in the formation of defect sites in the zeolites and defect sites may exist in the 4-member rings in both pentasil zeolites and layered alkali metal silicates. Such defect sites may also exist in the 5-member rings, because the 4- and 5-member rings are adjacent to one another.

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