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Magadiite and H-Magadiite: II. H-Magadiite and its Intercalation Compounds Compounds

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Abstract

Synthetic or natural magadiite, treated by dilute acids, exchanges its interlayer sodium ions for protons to yield H-magadiite, $H_2Si_{14}O_{29} \cdot 5.4H_2O$. H-magadiite forms intercalation compounds with a large number of guest molecules: X-oxides, pyridine derivatives, heterocycles, acid amides, urea derivatives, alkylamines. Heated to 600°C, H-magadiite loses 5 moles H_2O. The resultant compound, stoichiometrically $14SiO_2 \cdot 1.5H_2O$, is stable up to 1100°C and may be considered as a new type of SiO_2 modification with 3 percent H_2O.

Introduction

Magadiite reacts readily with dilute acids (Eugster, 1967; McAtee, House, and Eugster, 1968; Brindley, 1969; Lagaly, Beneke, and Weiss, 1972) quantitatively exchanging its interlayer sodium ions for protons, but retaining its crystallinity to produce "H-magadiite," a compound of stoichiometry $SiO_2 \cdot 0.45H_2O$. We will now show that an appropriate treatment of H-magadiite yields organic intercalation compounds which retain the layer structure of the original Na-magadiite.

Materials and Methods

Formation of H-Magadiite

In our experiments synthetic Na-magadiite in suspensions of 10–20 g/100 ml H_2O was titrated with 0.1N HCl to pH = 2 within 24 hours. The final pH was controlled another 24 hours. Then the product was filtered, washed with water and air-dried. The basal spacing of the air-dried product was 13.2 Å. At pH < 2, especially with acids $\gtrsim$ 2N, dehydrated forms of H-magadiite with basal spacings of about 11.2 Å or mixed-layer intermediates occur.

Formation of Organic Intercalation Complexes

Air-dried H-magadiite (with basal spacing of 13.2 Å) was suspended in pure organic liquids (*e.g.*, dimethylsulfoxide, N-methylformamide, pyridine, methylpyridine) or saturated aqueous solutions (*e.g.*, of urea, imidazole) for at least 100 hours at room temperature and 65°C, respectively.

For X-ray investigations in Debye-Scherrer cameras (radius $r = 18/2\pi$ cm and $36/2\pi$ cm, respectively), these suspensions were sucked in X-ray glass tubes (0.5 mm diameter) with an excess of organic liquid or aqueous solution,

Determination of Specific Surface Area

The specific surface areas of preheated H-magadiite samples were determined by gas adsorption (Ar, N_2, and O_2 at −196°C) by an electronic microbalance (Sartorius, Model 4201). The pressure was measured with a membrane vacuum meter (Type Diavic, Leybold) and a capacitance manometer (Type O3, Granville-Philips). The adsorption isotherms were interpreted by the BET-method. The calculation of BET surface area requires the area A_M of the gas molecule on the surface of adorbens. As surface area of N_2 molecules we used the standard value (A_M = 16.2 Å^2/molecule, Gregg and Sing, 1967). In order to choose reliable values for argon and oxygen we made numerous measurements with argon, oxygen, and nitrogen on non-porous aerosiles and silica, which seem to be most comparable with H-magadiite. The surface areas of argon and oxygen molecules were then adjusted to give the same values for the specific area as nitrogen. We found $A_M(Ar)$ = 16.2 Å^2 and $A_M(O_2)$ = 17.5 Å^2. In the literature, values range from 13.3–18.2 Å^2 for Ar and from

13.5–17.5 Å² for O_2 (McClellan and Harnsberger, 1967).

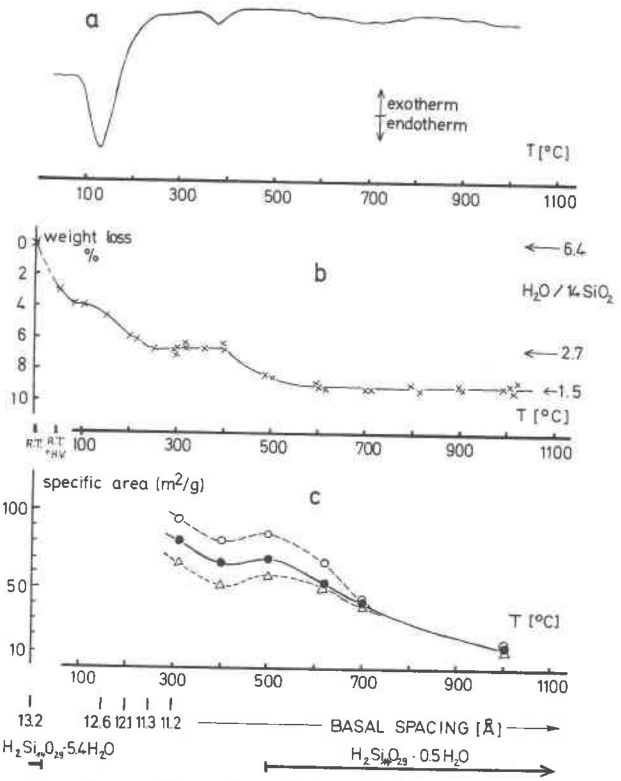


FIG. 1. Thermal behavior of H-magadiite. (a) DTA-curve; (b) weight loss curve; (c) variation of specific area with preheating temperature measured with oxygen (○), nitrogen (●) and argon (Δ) by gas adsorption at −196°C.

Characterization of H-Magadiite

Composition and Thermal Analysis

Synthetic H-magadiite is a pure $SiO_2 \cdot x\,H_2O$ compound. Gravimetric determination for SiO_2 indicated the composition of the air-dried product with a basal spacing of 13.2 Å to be $14SiO_2 \cdot 6.4H_2O$, whereas that with a basal spacing below 13.2 Å was $14SiO_2 \cdot 5H_2O$. By analogy to Na-magadiite, $14SiO_2 \cdot 6.4H_2O$ may be formulated as silicid acid $H_2Si_{14}O_{29} \cdot 5.4H_2O$. This is justified due to titration curves which indicate two moles of NaOH to be necessary to convert the acid into Na-magadiite.

Figure 1 shows the DTA diagram for H-magadiite and the weight loss. Up to 250°C the weight decreases rapidly but remains constant from 250°C to 420°C. After a further decrease a second plateau is reached between 550°C and 1200°C.

The decrease is due to the loss of water. It might appear that above 600°C water is completely desorbed and the heated product is SiO_2. However, careful gravimetric analysis for SiO_2 of the products which have been heated to different temperatures between 25°C and 1200°C, indicates that 1.5 moles H_2O per $14SiO_2$ are retained even at 1000°C. Probably the water is bound in form of isolated $\geqslant$Si–OH groups, which are so much apart from each other that condensation to siloxane groups

$$\geqslant \text{Si–OH} + \text{HO–Si} \leqslant \rightarrow\ \geqslant \text{Si–O–Si} \leqslant + H_2O$$

is prevented. (With uniform distribution of Si–OH throughout the structure, the mean distances between them would be about 7 Å). Formation and stability of isolated $\geqslant$ Si–OH groups at high temperatures at surfaces of high surface silica and aerosiles are discussed particularly by Peri (Peri, 1966; Peri and Hensley, 1968).

Up to 250°C dehydration reduces the basal spacing from 13.2 Å to 11.2 Å. The difference 13.2 Å–11.2 Å corresponds to the loss of a monolayer of water molecules. Values of d_{00l} between 13.2 Å and 11.2 Å are produced by mixed-layer structures with hydrated (13.2 Å) and dehydrated (11.2 Å) interlayer spaces. Up to 1000°C the basal spacing remains constant with 11.2 Å. The positions of the reflections in X-ray diagram do not change above 250°C; their sharpness decreases somewhat. The compound is stable up to 1000°C without marked variation of lattice dimensions. Presumably the layers become attached to each other by $\geqslant$Si–O–Si$\leqslant$ bridges which are formed by condensation of $\geqslant$Si–OH groups of neighboring layers.

The condensation starts at a temperature of about 400°C, at which the capability of forming intercalation compounds as criterion for a layer structure ceases and conversion into Na-magadiite becomes impossible.

The silicid acid rearranges to cristobalite only at temperatures > 1100°C but the transformation temperatures can be decreased significantly by traces of alkali oxides, which are well known to crack Si–O–Si bonds and thus falicitate structural transformations.

Further information may be gained from the specific area S as determined by N_2, O_2, and Ar adsorption at − 196°C. Figure 1 gives the variations of S with preheating temperature. S decreases from about 80 m²/g (for N_2) at 300°C to 67 m²/g at 400°C. In the range of transformation from $14\ SiO_2 \cdot 2.7\ H_2O$ into $14\ SiO_2 \cdot 1.5\ H_2O$ between 400°C and 600°C, S has a slight maximum (about 70 m²/g). At higher temperatures S decreases to 10 m²/g. The specific areas for Ar, N_2, and O_2 are markedly different up to 600°C ($S_{O_2} > S_{N_2} > S_{Ar}$) but become

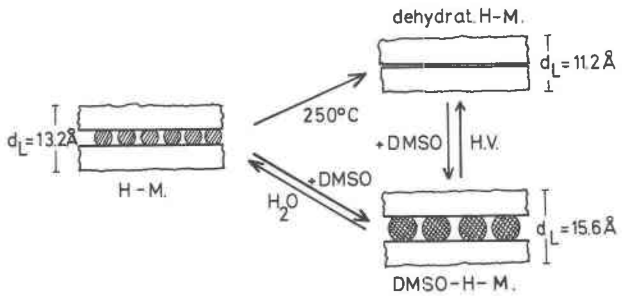


FIG. 2. Schematic representation of intercalation reactions of H-magadiite (H-M) with dimethylsulfoxide (DMSO).

equal for higher temperatures. Thus, special adsorbate-adsorbens interactions play an important role at lower temperatures but disappear for highly heated samples.

The BET-surface is smaller than the calculated internal + external surface (*ca* 714 m²/g). The gas molecules do not fill up the interlayer spaces but are adsorbed mainly onto the external surfaces. At most they can penetrate between the layers only in small regions near the crystal edges. It seems possible that different accessibilities for O_2, N_2, and Ar contribute to the differences in the surface area below 600°. Condensation of the layers between 400–600° close up the interlayer spaces and their accessibilities become very small.

X-ray Analysis of H-Magadiite

If the layer structure of magadiite is retained in its H-form, the *a* and *b* axes of H-magadiite should resemble those of Na-magadiite or be related to them by simple geometrical relations. H-magadiite has an X-ray diagram with only few reflections (Lagaly, Beneke, and Weiss, 1973). Indexing with the same *a* and *b* axes as in Na-magadiite (Brindley, 1968, $a_0 = b_0 = 7.25$ Å) is not possible, but is successful with only slightly changed axes: $a_0 = 7.11$ Å, $b_0 = 7.42$ Å and $\beta = 95°$. Since the X-ray diagram shows only a relatively small number of reflections one cannot exclude other possibilities for indexing the monoclinic powder diagram. For example, a similar agreement between observed and calculated data is reached for $a_0 = 7.39$ Å, $b_0 = 7.42$ Å, and $\beta = 99°$. It seems evident that the exchange of sodium ions for protons somewhat distorts the pseudotetragonal symmetry of the silicate layer. Similar distortion has been observed in magadiite if the interlayer water molecules are removed (Brindley, 1968).

Organic Intercalation Compounds

One might assume that during the exchange of sodium ions for protons ⩾Si–OH groups are formed, and that the silicate layers are linked together by condensation of SiOH-groups of adjacent layers to siloxane groups ⩾Si–O–Si⩽. The capability of formation of organic intercalation compounds, however, proves that such reactions do not occur.

Such organic intercalation compounds were described by Wada (1961) and Weiss (1961) for kaolinite with potassium acetate and urea. Since then more than 100 kaolinite intercalation compounds have been prepared.

H-magadiite forms an intercalation compound with dimethylsulfoxide (DMSO). If air-dried H-magadiite is treated with DMSO, the DMSO molecules penetrate into the interlayer spaces between the silicate sheets and the basal spacing increases from 13.2 Å to 15.6 Å. The reaction is reversible; air-drying or washing with water converts the DMSO intercalation compound into the original H-magadiite with a basal spacing of 13.2 Å. If the DMSO is removed in vacuum, the dehydrated silicic acid with a basal spacing of 11.2 Å is obtained (Fig. 2).

The X-ray diagrams of intercalation compounds differ from that of the pure H-magadiite (Lagaly *et al*, 1973). Only the (040)-reflections remain unaltered or are changed just slightly in their position. The diagram, however, can be easily indexed with nearly the same a_0 and b_0 axes as H-magadiite. Small but significant variations of a_0 and b_0 for different intercalation compounds indicate that the structure of the silicate layer is slightly influenced by the intercalated molecules.

Orientation of the Molecules in the Interlayer Space

The increase in the basal spacing for the DMSO-complex ($\Delta d_L = 2.4$ Å) is markedly smaller than any dimension of the DMSO-molecule, because the intercalation of DMSO-molecules is accompanied by displacement of interlayer water molecules (Fig. 2). The real interlayer distance is therefore $\Delta d_L = 15.6 - 11.2$ Å $= 4.4$ Å. This value is comparable with the molecule dimensions and similar to $\Delta d_L = 4.1$ Å for the kaolinite complex.

The increase of the basal spacing gives some hints as to the orientation of the molecules in the interlayer space, but their exact arrangement cannot be evaluated. In general, the orientation of the molecules varies with their shape and polarity. The X-ray diagram shows too few (001)-reflections for the calculation of one-dimensional Fourier projections, which give detailed information about molecular orientation in the interlayer space. (With kaolinite single crystals the interlayer structure of many intercalation compounds could be determined (Weiss and Orth, 1973)).

TABLE 1. Basal Spacings and Range of Composition of DMSO-Intercalation Compounds

Moles DMSO added to 1 Mole H-Magadiite	Moles DMSO intercalated by 1 Mole H-Magadiite	Basal Spacing (Å)
0.00	0	13.2
0.43	0.4	13.4
0.50	0.5	14.0
0.72	0.7	14.2
1.07	1.0	15.4
1.42	1.3	15.6
1.61	1.5	15.6
2.14	1.8	15.6
4.30	2.0	15.6
6.50	2.0	15.8
∞	2.0	15.8

Composition of the Intercalation Compounds

Direct experimental determination of the composition of the intercalation compounds is difficult. If the excess of the organic compound is removed, molecules diffuse out of the interlayer space. In addition the intercalation compounds are often stable over a large range of composition. An example is given in Table 1 for DMSO. The characteristic X-ray diagram with basal spacings of 15.6 − 15.8 Å is reached for a composition of 1.0 moles DMSO per 14 moles SiO_2.

The area required for a DMSO molecule in a monomolecular layer is not larger than 25 Å^2 ($\approx V_M{}^{2/3}$). Per mole $H_2Si_{14}O_{29}$ (= 859 g) the internal area can be estimated to be

$$2\cdot\frac{859\cdot 10^{24}}{2.5\cdot 11.2} = 61.36\cdot 10^{24}\ \text{Å}^2(\rightarrow 714\ \text{m}^2/\text{g})$$

using a density of about 2.5 g/cm^3 and a layer thickness of 11.2 Å. A monolayer of DMSO molecules between the silicate sheets requires therefore

$$\frac{61\cdot 10^{24}}{2}\cdot\frac{1}{25\cdot 6.02\cdot 10^{23}} = 2.0\ \text{DMSO}/14\ SiO_2$$

It is evident that the characteristic basal spacing is reached if the monolayer of DMSO in the interlayer space is about 50 percent completed.

To get some information about the proportion of organic molecules a limiting composition ξ may be used. ξ is calculated from molecular volume V_M of the organic compound

$$V_M = \frac{M\cdot 10^{24}}{\rho\cdot 6.02\cdot 10^{23}} = \frac{M}{\rho}\cdot 1.66\ (\text{Å}^3)$$

(M, ρ: molecular weight and density of organic compound) and the interlayer volume $a_0b_0\cdot\Delta\ d_L$ to be

$$\xi = \frac{a_0b_0\ \Delta d_L}{V_M}$$

For DMSO: V_M = 118 Å^3, $a_0b_0\Delta d_L = 7.11\cdot 7.42\cdot 4.6 =$ 242.7 Å^3

$$\xi = 2.06\ \text{moles DMSO}/14\ SiO_2$$

in good agreement with above estimation.

The calculation of the limiting composition is based on assumptions that the density of organic molecules in the interlayer space is about the same as in the pure organic compound and that the water molecules are quantitatively displaced from the interlayer space. It is further assumed that the organic molecules do not dip between the oxygen atoms of the silicate layer to any great extent. Even if these assumptions are not strictly correct, the limiting composition is a useful value for characterization of organic intercalation compounds.

Examples of Organic Intercalation Compounds

H-magadiite forms intercalation compounds with different kinds of neutral compounds: X-oxides, acid amides, derivatives of hydrazine or urea, aromatic compounds, alkylamines.

X-Oxides

X-oxides are excellent compounds to be intercalated in H-magadiite, and different types of X-oxides can penetrate between the layers: N-oxides (trimethylamine oxide, pyridine-N-oxide, picoline-N-oxides, quinoline-N-oxides, *etc*); P-oxides (trimethylphosphine oxide, tributylphosphine oxide, trimethylphosphate); S-oxides (dimethylsulfoxide). The basal spacings vary between 14.0 Å and 25 Å; a particularly large increase in the basal spacing is observed for tributylphosphine oxide (d_L = 12 Å). The larger trioctylphosphine oxide and triphenylphosphine oxide do not penetrate directly into the interlayer space.

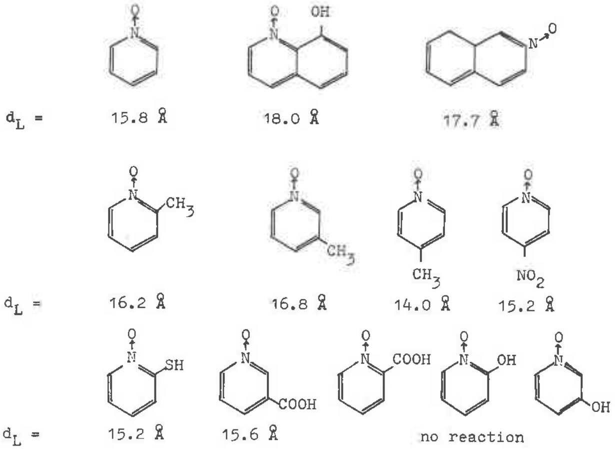


FIG. 3. Basal spacings d_L of H-magadiite intercalation compounds with pyridine-N-oxides.

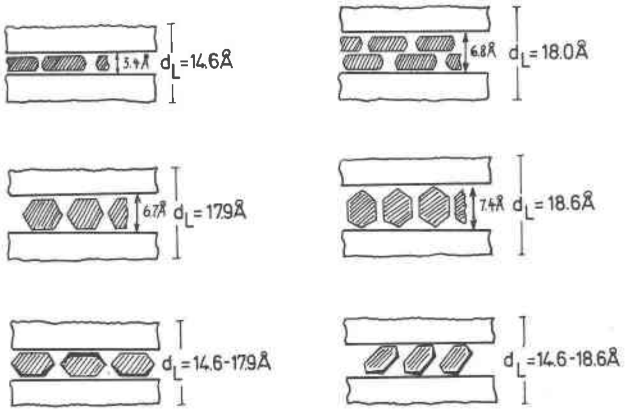


FIG. 4. Arrangements of aromatic rings between the layers of H-magadiite and resulting maximal basal spacings d_L.

In case of aromatic N-oxides the position of the substituents on the aromatic ring largely influences the basal spacings. As examples the basal spacings of pyridine-N-oxide derivatives are compared in Figure 3.

The low basal spacing of 4-methylpyridine-N-oxide indicates that the pyridine ring lies parallel to the silicate layers (Fig. 4). In the other complexes the pyridine ring and the N–O bond must be tilted to the layers. Arrangements in bilayers with the rings parallel to the silicate layers or monolayers with the rings perpendicular to the layers should produce higher basal spacings (Fig. 4). However, they cannot be strictly rejected, since it is unknown in what extent the molecules can dip between the oxygen atoms of the silicate layers.

Pyridine and its Derivatives

Under pyridine the basal spacing of H-magadiite is increased to 16.8 Å. Substitution of $-H$ by $-CH_3$ (methylpyridines = picolines, dimethylpyridines = lutidines and trimethylpyridines) or $-OH$, $-Cl$, $-NO_2$ prevents the intercalation. Only aminopyridines were found to form intercalation compounds. The methylamino-pyridines (picolyle amines) do not react. The basal spacings depend upon the position of the $-NH_2$ and $-CH_3$ groups (Fig. 5). In general no simple arrangements (monolayers or bilayers with the aromatic ring parallel or perpendicular to the silicate layers, Fig. 4) can be postulated.

Comparison of the pK_B values for the pyridine derivatives shows that the reactivity is not directly controlled by the basicity. However, in the case of Cl-, OH-, NO_2-pyridines the basic character might be too low. The capability to displace the interlayer water molecules, steric requirements, and conditions for intensive interactions with the silicate layers seem

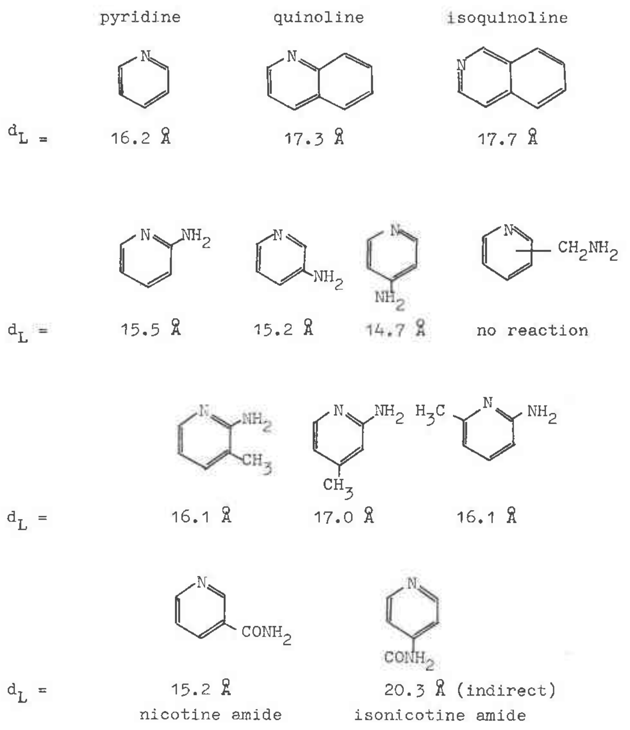


FIG. 5. Basal spacings d_L of H-magadiite intercalation compounds with pyridine derivatives.

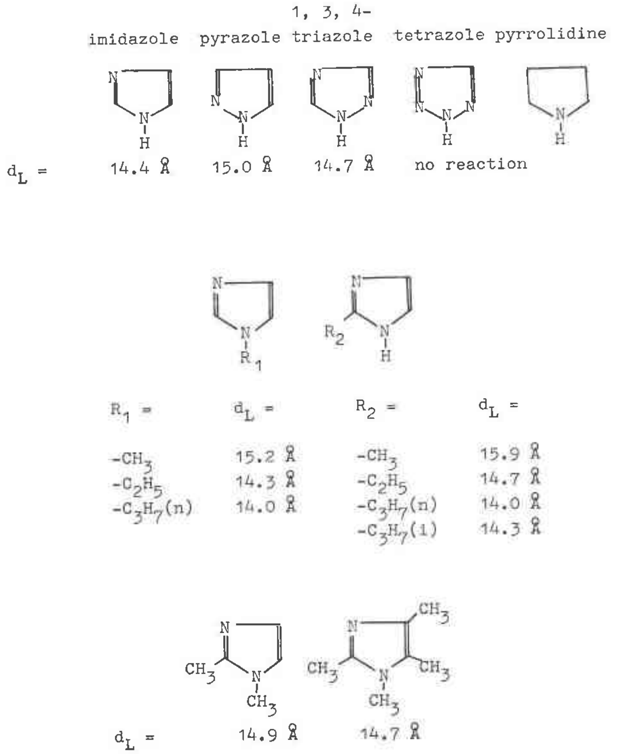


FIG. 6. Basal spacings d_L of H-magadiite intercalation compounds with 5-ring heterocycles.

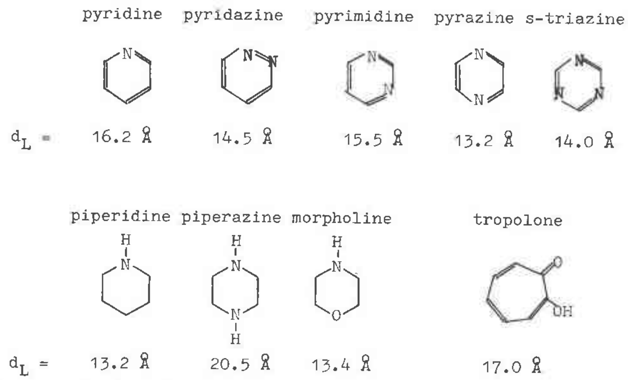


FIG. 7. Basal spacings d_L of H-magadiite intercalation compounds with 6-ring and 7-ring heterocycles.

to be more effective. The quinoline and isoquinoline derivatives can be prepared by heating pyridine-H-magadiite with quinoline or isoquinoline above the boiling point of pyridine. Pyridine in the interlayer space is than displaced by quinoline or isoquinoline.

Other Heterocycles

Besides pyridine, other heterocycles are intercalated: imidazole, pyrazole and triazole (5-ring systems), pyridazine, pyrimidine, s-triazine, piperidine, piperazine (6-ring systems), and tropolone (7-ring system) (Figs. 6 and 7).

As examples for the influence of substituents, the derivatives of imidazole were studied in more detail (Fig. 6). In the case of 1- and 2-alkyl derivatives water is necessary to start the intercalation reaction. The basal spacings somewhat vary with the concentration of the aqueous solution (Table 2).

Acid Amides

Only acid amides with short alkyl chains and their derivatives—for example, formamide, acetamide, and propionamide with its N-methyl and N-ethyl derivatives can be intercalated with H-magadiite. The basal spacings vary between 13.5 and 17.4 Å, but they do not increase linearly with the molecular volume V_M (Fig. 8). Particularly large spacings are observed with the methyl derivatives. Thus, special orientations of the molecules in the interlayer space are more important than pure volume effects. Further interesting compounds, which are intercalated, are caprolactam (d_A = 17 Å) and acrylamide (d_A = 15 Å), which polymerize between the silicate layers. Methacrylamide does not react directly.

TABLE 2. Basal Spacings of Imidazole Intercalation Compounds of H-Magadiite after Reaction at 65°C

Intercalated Compound	m.p. °C	with pure compound	Basal Spacing (Å) with aqueous solutions conc.	1:1 diluted	1:3 diluted
Imidazole	90	14.4	14.4	14.5	14.3
1-Methyl-imidazole	-6	13.2	-	15.2	15.1
1-Ethyl-imidazole	-23	13.2	-	14.3	14.3
2-Methyl-imidazole	140	14.2	15.0	15.4	15.9
2-Ethyl-imidazole	77	13.2	14.7	14.7	14.7

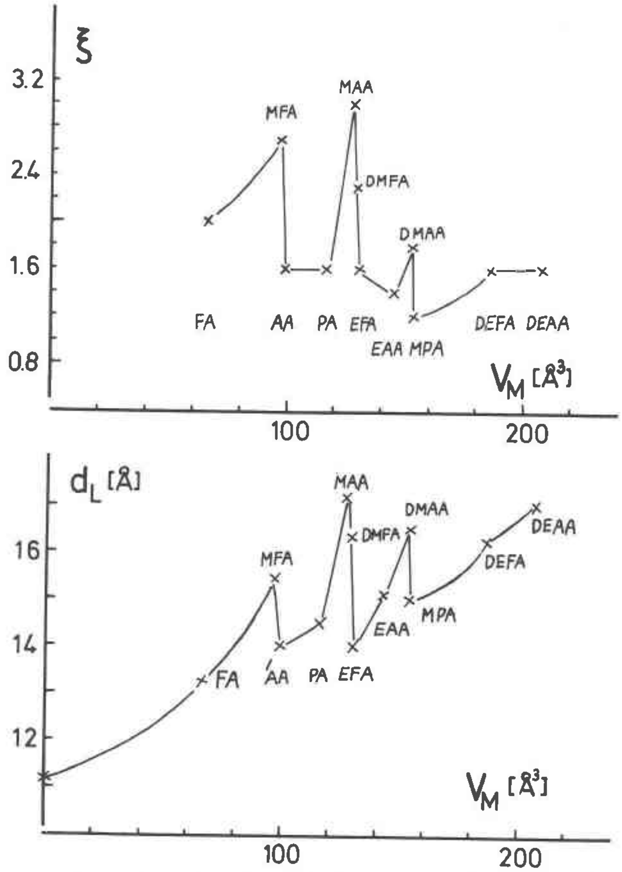


FIG. 8. Basal spacings d_L and limiting composition ξ (moles/14 SiO_2) of acid amide intercalation complexes as function of molecular volume V_M of acid amides. (FA = formamide, AA = acetamide, PA = propionamide, MFA = methylformamide, DEAA = diethylacetamide, *etc*).

Urea and its Derivatives

Urea and its derivatives are intercalated into H-magadiite from their aqueous solution. The basal spacings are more influenced by the positions of methyl and ethyl groups than they are by kaolinite complexes (Fig. 9).

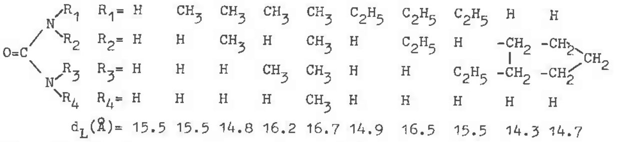
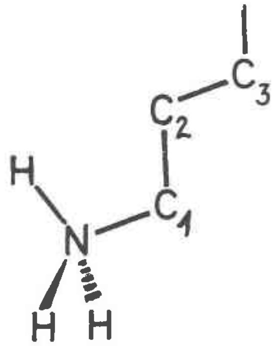


FIG. 9. Basal spacings of H-magadiite-urea intercalation compounds.

With one CH_3-group the basal spacing remains unchanged in comparison with urea; with two methyl groups, it is decreased, if both methyl groups are bound to the same nitrogen atom, but increased if each nitrogen atom has one methyl group. With ethyl groups it is just the opposite.

Alkylamines

The formation of alkylamine complexes represents another type of intercalation reaction. In direct reaction with alkylamines the basal spacing is only slightly enhanced ($d_L \approx 14$ Å). If, however, H-magadiite is first treated with DMSO and then with alkylamines, large basal spacings are observed in case of alkyl chains with more than 3 C atoms (Fig. 10). As n_A, the number of atoms in the chain, increases from 4 to 10, the basal spacings increase in steps. The increase from $n_A = 4$ to $n_A = 5$ (and from $n_A = 6$ to 7 and $n_A = 8$ to 9) is smaller than the increase from $n_A = 5$ to 6 (and from $n_A = 7$ to 8 and from $n_A = 9$ to 10). The basal spacings for n_A = even lie on a line with an increase of $\Delta d_L/\Delta n_A = 2.14$ Å. For $n_A = 0$ a spacing of 19.1 Å is extrapolated. From $n_A = 10$ to $n_A = 11$ the basal spacings increase by 7 Å; with longer chains ($n_A = 11$–18) they lie very near a line with an increase of 2.55 Å, which cuts the d_L axis again at 19.1 Å. From the mean increase in the basal spacings (2.14 Å for $n_A = 4$–10 and 2.55 Å for $n_A = 11$–18) it can be concluded that the alkylamine molecules are arranged in bilayers. Shorter chains ($n_A = 4$–10) are tilted in angles of about 56° ($= \sin^{-1} 2.14/2.56$) to the silicate layers. Longer chains stand upright ($\sin^{-1} 2.55/2.56 = 90°$) on the silicate layers. The alternation in the basal spacing for $n_A = 4$–10 is a consequence of the tilting angle < 90° (Lagaly and Weiss, 1970) and hints to a special orientation of the NH_2 groups on the silicate layer:



With longer chains ($n_A > 10$) which orient perpendicular to the layers, the orientation of the NH_2 groups may be energetically less favorable. The van der Waals energy between the chains, however, is strongly enhanced. As example, $\xi = 5.4$ moles octadecylamine can be intercalated per 14 SiO_2, if the chains stand upright; but only $\xi = 4.4$ moles if they are tilted in an angle of $\alpha = 56°$. The difference corresponds to a van der Waals energy of 18 kcal/14 SiO_2 at least.

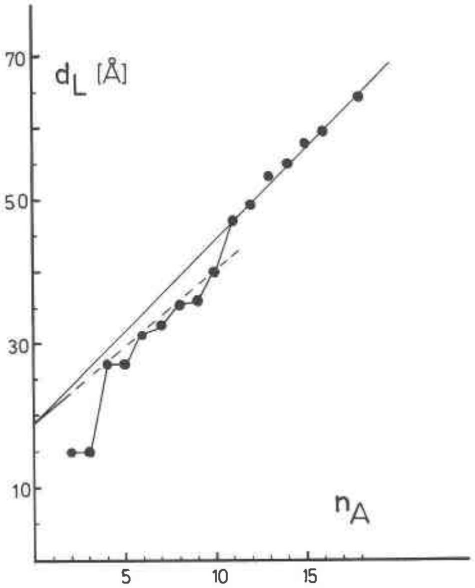


FIG. 10. Basal spacings d_L of the n-alkylamine-DMSO intercalation complexes of H-magadiite. (n_A is the number of carbon atoms in the alkyl chain).

Extrapolation of the basal spacings to $n_A = 0$ gives a strikingly high value (19.1 Å) in comparison to the van der Waals thickness of 11.2 A. Analytical determination of sulfur content in samples which were treated several times with free alkylamine to remove all adhering DMSO made evident that about 2 moles of DMSO/14 SiO_2 remain bound in the interlayer space. This leads to the assumption that monolayers of DMSO are built up between the silicate layer and the polar end groups of the alkylamine molecules.

Comparison with Halloysite and Kaolinite

The intercalation reactivity of H-magadiite may be compared with that of halloysite in the hydrated form with a monolayer of water between the silicate sheets. Table 3 gives the basal spacings d_L and Δd_L values for some intercalation compounds of H-magadiite and halloysite hydrate. Since the monolayer of water requires different apparent spacings (H-magadiite: 13.2-11.2 = 2.0 Å; halloysite: 10.0-7.2 = 2.8 Å), the Δd_L are referred to the basal spacings of the hydrated

TABLE 3. Comparison of Intercalation Compounds of H-Magadiite and Halloysite Hydrate

Guest Molecules	H-Magadiite *			Halloysite Hydrate **		
	Basal Spacing d_L (Å)	d_L-13,2 (Å)	d_L-11,2 (Å)	Basal Spacing d_L (Å)	d_L-10,0 (Å)	d_L-7,2 (Å)
N-Methylformamide	15.9	2.7	4.7	10.9	0.9	3.7
N,N-Dimethyl-formamide	16.7	3.5	5.5	12.1	2.1	4.9
N-Methylacetamide	17.4	4.2	6.2	11.2	1.2	4.0
N,N-Dimethyl-acetamide	16.4	3.2	5.2	12.2	2.2	5.0
N-Methylpropion-amide	15.2	2.0	4.0	11.3	1.3	4.1
N-Ethylurea	14.9	1.7	3.7	10.6	0.6	3.4
N,N-Dimethylurea	14.8	1.6	3.6	11.8	1.8	4.6
N,N'-Dimethylurea	16.2	3.0	5.0	11.2	1.2	4.0
Imidazole	14.4	1.2	3.2	11.3	1.3	4.1
1-Methylimidazole	15.2	2.0	4.0	12.2	2.2	5.0
2-Methylimidazole	15.9	2.7	4.7	11.3	1.3	4.1
Pyridine	15.2	2.0	4.0	12.1	2.1	4.9
Pyridine-N-oxide	15.8	2.6	4.6	12.6	2.6	5.4
2-Picoline-N-oxide	16.2	3.0	5.0	12.6	2.6	5.4
3-Picoline-N-oxide	16.8	3.6	5.6	13.0	3.0	5.8
4-Picoline-N-oxide	14.0	1.8	2.8	13.2	3.2	6.0
Trimethylamine-oxide	15.9	2.7	4.7	11.0	1.0	3.8

* Basal spacing of H-Magadiite 13.2 Å, dehydrated 11.2 Å

** Basal spacing of Halloysite 10.0 Å, dehydrated 7.2 Å (Halloysite from Djebel Debar, Hydrate prepared from Hydrazine Halloysite (Range, Range and Weiss, 1972)).

and dehydrated forms. The apparent spacings $\Delta d_L = d_L - 11.2$ Å and $\Delta d_L = d_L - 10.0$, respectively, which represent the space requirement of the guest molecules, are of the same order of magnitude; differences are caused by different orientations of the guest molecules due to the different silicate layer structures.

Kaolinite hydrates (Range, Range, and Weiss, 1972) react in a similar way. Since kaolinite hydrates are not very stable, intercalation compounds are better prepared from hydrazine- or potassium acetate kaolinite instead of kaolinite hydrate ("indirect reaction"). In most cases the apparent spacings $\Delta d_L = d_L - 7.1$ Å are identical with the corresponding values for halloysite hydrates (Tables 3, 4).

The dehydrated forms of H-magadiite and halloysite are less reactive and comparable with kaolinite. Here, the intercalation requires direct separating of the silicate layers by the penetrating guest molecules; in the case of hydrated forms the reaction succeeds by displacement of the water molecules. The number of directly-reacting compounds is smaller for the dehydrated forms and kaolinite than for the hydrated forms (Table 4).

TABLE 4. Intercalation Reactivity of H-Magadiite (Hydrated Form) and Kaolinite

Guest Molecule	H-Magadiite Direct Reaction	Kaolinite Reaction direct	indirect
	d_L - 11,2 (Å)	d_L - 7,1 (Å)	d_L - 7,1 (Å)
N-Methyl-formamide	4.7	3.6	3.6
N,N-Dimethyl-formamide	5.5	-	4.8
N-Ethyl-formamide	2.8	-	3.8
N,N-Diethyl-formamide	5.2	-	-
N-Methyl-acetamide	6.2	4.2	4.2
N,N-Dimethyl-acetamide	5.2	-	5.3
N-Ethyl-acetamide	3.8	-	4.1
N,N-Diethyl-acetamide	5.9	-	-
N-Methyl-propionamide	4.0	-	4.0
Urea	4.3	3.6	3.6
N-Methylurea	4.3	3.8	3.8
N-Ethylurea	3.7	-	3.8
N,N-Dimethylurea	3.6	-	3.7
N,N-Diethylurea	5.3	-	3.7
N,N'-Dimethylurea	5.0	-	3.9
N,N'-Diethylurea	4.3	-	3.9
Pyridine	4.0	-	4.8
Aminopyridine	3.5-4.3	-	5.0-5.8
Pyridine-N-oxide	4.6	5.4	5.4
2(3,4)Picoline-N-oxide	2.8-5.6	-	5.7-6.4
Imidazole	3.2	4.2	4.2
1-Methylimidazole	4.0	-	5.0
2-Methylimidazole	4.7	-	4.2

Comparison of $H_2Si_{14}O_{29}$•5.4 H_2O with other Crystalline Silicic Acids

There are known several well defined crystalline silicic acids:

$H_2Si_2O_5$-I, II	(Liebau, 1964; Wodtke and Liebau, 1965; Lagaly *et al,* 1974)
$H_2Si_2O_5$-III	(Le Bihan, Kalt, and Wey, 1971)
$H_4Si_4O_{10}\cdot 0.5H_2O$	(Pabst, 1958)

The three forms of $H_2Si_2O_5$ are built up of layers of SiO_4 tetrahedra, which are joined together in form of puckered Si-O-12-rings. In contrast, $H_4Si_4O_{10}\cdot 0.5$ H_2O contains tetragonal layers each built up by two layers of tetrahedra. These silicic acids are capable of forming interlayer compounds, but the reactivity is very different from that of H-magadiite (Lagaly *et al,* 1974).

In 1972 Gude and Sheppard described a crystalline silicic acid, named "silhydrite" which has been found at the Trinity County magadiite deposit. Silhydrite is related to magadiite and may be considered as a natural form of H-magadiite. With the reported water content (2.7 $SiO_2\cdot H_2O$ = 14 $SiO_2\cdot 5.2$ H_2O) silhydrite corresponds to a slightly dehydrated H-magadiite. The basal spacing seems to be markedly higher (= 14.5 Å) than in H-magadiite if the reported (100)-reflection is taken as basal spacing (the X-ray powder diagram has been indexed by the authors with no relation to the indexing of magadiite by Brindley, 1968). The high basal spacing probably is maintained by small amounts of organic material in the interlayer spaces. Such complexes can be prepared from some H-magadiite intercalation complexes, *e.g.*, complexes with urea derivatives by extensive washing with water. The guest molecules are not quantitatively removed from the interlayer spaces due to condensation reactions; the C content of the air-dried products can be $\lesssim$ 1 percent, the H_2O content in the range 4-5 H_2O/14 SiO_2 (~3 $SiO_2\cdot 1$ H_2O) and the basal spacing larger than 13.2 Å (14-15 Å).

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