

Kanemite—innercrystalline reactivity and relations to other sodium silicates

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Abstract

The sodium silicate kanemite (idealized: $\text{NaHSi}_2\text{O}_5 \cdot 3\text{H}_2\text{O}$) is shown to have a layer structure probably built up by "Zweiereinfachschichten." The interlayer water can be reversibly removed, and the sodium ions can be exchanged by organic cations and by protons. The innercrystalline reactivity reveals relations to other sodium silicates. Kanemite can be synthesized from NaOH-SiO_2 mixtures or sodium silicate solutions or obtained by alteration of sodium silicates such as $\text{Na}_2\text{Si}_2\text{O}_5$, makatite ($\text{Na}_2\text{Si}_4\text{O}_9 \cdot 5\text{H}_2\text{O}$), and magadiite ($\text{Na}_2\text{Si}_{14}\text{O}_{29} \cdot 11\text{H}_2\text{O}$).

Introduction

Only five alkali silicate minerals are known as opposed to the large number of other silicate minerals. The anhydrous sodium disilicate $\text{Na}_2\text{Si}_2\text{O}_5$ (natrosilite) was described by Timoshenkov *et al.* (1975). The other sodium silicates are the hydrous silicates magadiite $\text{Na}_2\text{Si}_{14}\text{O}_{29} \cdot 11\text{H}_2\text{O}$ and kenyaite $\text{Na}_2\text{Si}_{22}\text{O}_{45} \cdot 10\text{H}_2\text{O}$ (Eugster, 1967), makatite $\text{Na}_2\text{Si}_4\text{O}_9 \cdot 5\text{H}_2\text{O}$ (Sheppard *et al.*, 1970) and kanemite $\text{NaHSi}_2\text{O}_5 \cdot 3\text{H}_2\text{O}$ (Johan and Maglione, 1972). The peculiarity of these minerals demands the study of their chemical reactivity. Possibly all sodium silicates have layer structures with innercrystalline reactivity. Four types of reactions are particularly pronounced: exchange of the interlayer sodium ions by organic long-chain cations, innercrystalline swelling of these organic derivatives, transformation by H^+/Na^+ exchange into crystalline silicic acids, and intercalation of several classes of organic compounds by the acids. The reactions were first described for magadiite (Brindley, 1969, Lagaly *et al.*, 1972, 1975). Kanemite is of special interest, not only because of its innercrystalline reactivity, but also for its relation to other sodium silicates and the conditions of its synthesis.

Experimental

Synthesis of kanemite

Kanemite with high crystallinity and X-ray dia-

grams identical to those of natural kanemite was prepared from SiO_2 , NaOH , and small amounts of water. To obtain a good mixture between SiO_2 and NaOH , one mole SiO_2 was dispersed in 100 ml methanol, and cold NaOH solution (one mole NaOH in 35 ml H_2O , nearly saturated) was slowly added. The temperature should not rise above room temperature. The gel-like slurry was dried at 100°C , and the opaque material then heated to 700°C for 5.5 hours. In the initial stages of heating the volume of the sample increased, largely owing to escaping water. After cooling to room temperature the product was dispersed in water, and it immediately transformed into kanemite, which was filtered and air-dried. Many synthesis experiments have shown that the formation of well crystallized kanemite requires the ratio NaOH/SiO_2 be 0.8/1 to 1.05/1.

Exchange of organic cations for sodium ions

For cation-exchange experiments with organic cations, aqueous solutions (if necessary with 10% ethanol) of different long-chain alkylammonium chlorides: *n*-alkylammonium chlorides RNH_3^+Cl ; trimethyl alkylammonium chlorides $\text{RN}(\text{CH}_3)_3^+\text{Cl}$; dimethyl dialkylammonium chlorides $\text{R}_2\text{N}(\text{CH}_3)_2^+\text{Cl}$ ($\text{R} = \text{C}_n\text{H}_{2n+1}$) were added to kanemite. One g kanemite was treated two times with 100 ml of 0.1*N* alkylammonium chloride solution for one week. The reaction proceeded best in the pH range 8-9 at 65°C . The organic derivatives were freed of intercalated excess of alkylamine and alkylammonium chloride by

several washings with ethanol/water and dried in vacuo ($P \leq 0.01$ torr) at 65° . X-ray diagrams were recorded after each step of preparation.

Exchange of protons for sodium ions

A suspension of kanemite was brought to pH = 0–1 with dilute HCl or treated with 80 percent H_2SO_4 for 24 hours. The product was filtered, X-rayed, and immediately used for intercalation reactions. Experimental details of intercalation reactions are given by Lagaly *et al.*, 1975. The X-ray investigations were made with Debye-Scherrer powder cameras (diameter $360/2\pi$ mm) and $CuK\alpha$ radiation. A special orifice allowed the detection of large basal spacings.

Results and discussion

Preparation of kanemite

Formation of kanemite does not require such special conditions as one might expect from the rare natural occurrence. The survey in Figure 1 shows that kanemite can be obtained in different ways from SiO_2 -NaOH mixtures, sodium silicate solutions or by alteration of other sodium silicates such as $Na_2Si_2O_5$, makatite, and magadiite.

The simplest method for preparation of kanemite starts from a 1:1 SiO_2 -NaOH mixture heated to $700^\circ C$ as previously described. The preparation of the gel with methanol and only small amounts of water guarantees the formation of pure kanemite. In water the $700^\circ C$ product hydrates immediately to kanemite. Transformation into kanemite can also be achieved by water-vapor adsorption. At 40 percent relative humidity, a 10 Å product is formed, and hydration into pure kanemite requires a humidity of about 80 percent.

Dehydration at 600 – $700^\circ C$ and rehydration offers a general method for kanemite preparation from other sodium silicates. Precipitates from sodium silicate by methanol, when heated to $700^\circ C$, react with water to form kanemite. β - $Na_2Si_2O_5$ can be transformed into kanemite by treatment with water/methanol, drying at $100^\circ C$, heating to $700^\circ C$ for 5–21 hours, and rehydration. Treatment with water/methanol in the first step attacks the structure by hydrolysis, but complete destruction must be avoided in order to obtain well-crystallized kanemite; the dehydration at $700^\circ C$ must be longer than 5 hours but should not exceed 21 hours. Shorter or longer reaction times produce samples which do not react with water to form kanemite. α - $Na_2Si_2O_5$ has to be heated for 24 hours at $700^\circ C$ after treatment with wa-

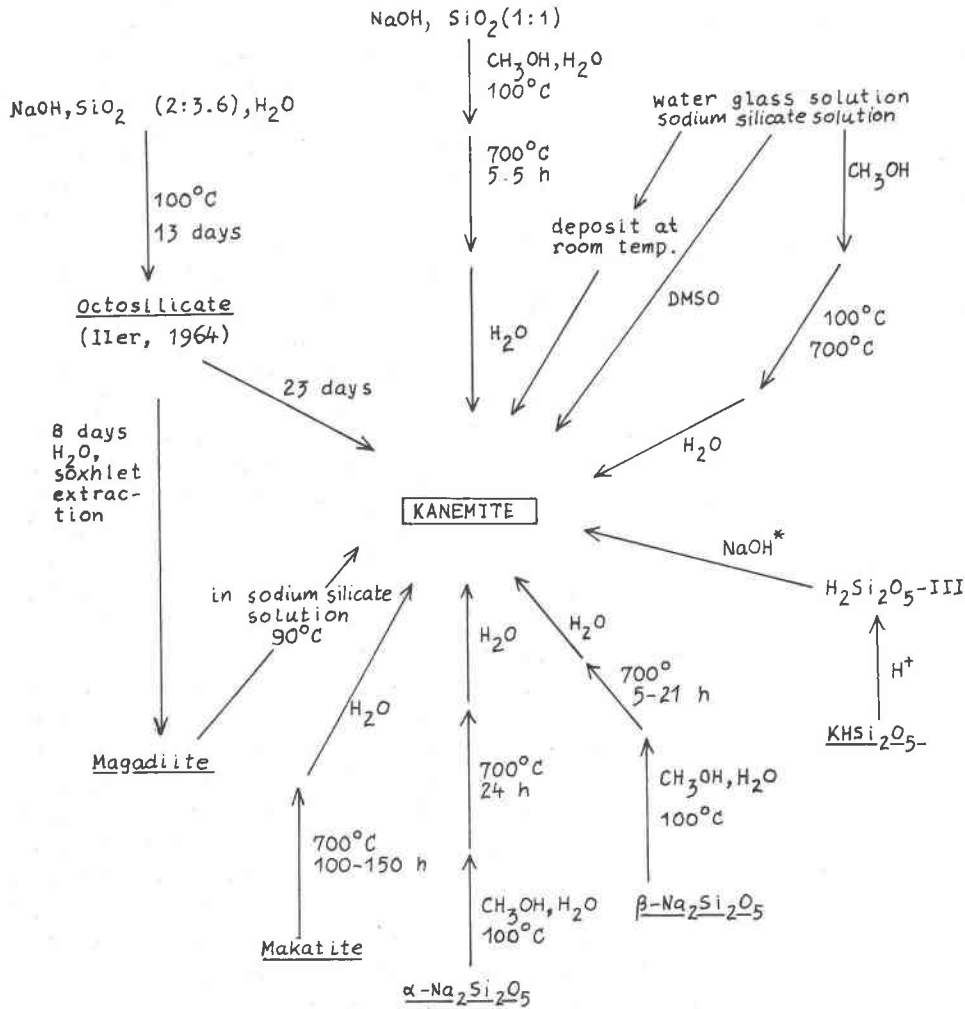
ter/methanol. Other conditions give samples which do not react with water. Makatite is transformed into kanemite without preceding water/methanol treatment. The dehydration requires 100–150 hours at $700^\circ C$ in order to obtain well-ordered kanemite after rehydration. Kanemite itself, heated to $700^\circ C$, rehydrates with water into the original form. Increasing dehydration time at $700^\circ C$ reduces the crystallinity (sharpness of X-ray reflections) of the rehydrated products. Samples heated for more than 24 hours do not rehydrate into kanemite.

For any pretreatment, dehydration time and temperature are decisive factors in kanemite formation. Evidently a reaction time has to be chosen such that layers of SiO_4 -tetrahedra capable of adsorbing H_2O molecules are built up. These thin sheets of SiO_4 -tetrahedra may be deformed at $700^\circ C$ so that the interlayer sodium ions obtain a less favorable coordination and tend to hydrate with water. The products of the various sodium silicates heated to $700^\circ C$ are crystalline with very similar X-ray diagrams, differing mainly in the intensities of the reflections. The powder patterns of some of the samples investigated are listed in Table 1. Johan and Maglione (1972) interpreted the kanemite heated to $700^\circ C$ as a mixture of different phases, but fast rehydration even by water-vapor adsorption (at relative humidities $\geq 70\%$) proves it to be a single phase.

Kanemite also forms at low temperatures. We sometimes found kanemite as deposit in sodium silicate solutions preserved for a long time at room temperature. Magadiite reacts with sodium silicate solutions at $90^\circ C$ and becomes kanemite. A mixture of 2 NaOH, 3.6 SiO_2 and 13 H_2O yields within 13 days at $100^\circ C$ the octosilicate described by Iler (1964) as an intermediate compound, and becomes kanemite within 23 days. Kanemite was first prepared from $H_2Si_2O_5$ (from $KHSi_2O_5$) by reaction with NaOH (Kalt and Wey, 1968).

Analytical composition

Whereas the SiO_2 content of kanemite can be directly determined by gravimetric methods, the determination of the Na₂O content of the synthetic kanemite presents a special problem. Synthesis of kanemite from the SiO_2 /NaOH mixture proceeds by formation of a $Na_2Si_2O_5$ phase at $700^\circ C$, which transforms into kanemite by removal of sodium (as NaOH) by water. Subsequent washings with water continually release sodium from the solid, indicating that kanemite is hydrolyzed even at pH ≈ 9 . It is impossible to leach out the excess alkali without re-



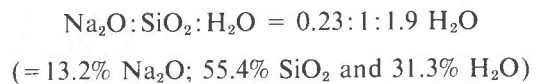
* Kalt and Wey, 1968

Fig. 1. Survey of methods for kanemite syntheses

removal of sodium from the kanemite structure. Extraction of sodium by subsequent washings is shown in Figure 2. The typical X-ray diagram of kanemite (Johan and Maglione, 1972) with only slight variations of intensities is maintained down to $\text{Na}_2\text{O}/\text{SiO}_2 = 0.1$. About 70 percent of the sodium of the idealized formula of kanemite can be removed without destruction of the structure. For $\text{Na}_2\text{O}/\text{SiO}_2 \lesssim 0.05$ several reflections are broadened and finally disappear.

The H_2O content cannot be exactly determined from the weight loss at high temperatures, because kanemite transforms above 700°C into tridymite,

which retains some water in the structure. Since preparation of kanemite involves the hydration of the sodium silicates heated to 700°C , the Na/Si ratio of synthetic kanemites has to be determined for each sample. For the cation-exchange experiments we used a sample of the composition:



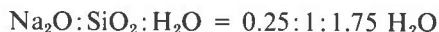
very similar to the mineral (idealized: $\text{NaHSi}_2\text{O}_5 \cdot 3\text{H}_2\text{O}$) analyzed by Johan and Maglione (1972):

Table 1. X-ray powder data of different sodium silicates after dehydration at 700°C (reflections with $I < \sim 10$ not completely listed)

Kanemite		Kanemite		Makatite		α -Na ₂ Si ₂ O ₅		α -Na ₂ Si ₂ O ₅		β -Na ₂ Si ₂ O ₅		β -Na ₂ Si ₂ O ₅		NaOH/SiO ₂ -Gel	
Dehydration time:															
24h		30h, 38h***		95h		5.5h*		24h*		24h		21h*		5.5h*	
$d(\text{\AA})$	I	$d(\text{\AA})$	I	$d(\text{\AA})$	I	$d(\text{\AA})$	I	$d(\text{\AA})$	I	$d(\text{\AA})$	I	$d(\text{\AA})$	I	$d(\text{\AA})$	I
		13.6	10												
		11.6	40												
5.97	30	7.69	20	6.05	25	6.01	30	6.05	10			6.85	10	6.85	20
		5.85	10									6.05	40	5.98	50
		5.44	30												
4.91	50	4.97	30	4.89	35	4.93	80	4.93	70	5.25	10	5.22	10	4.89	70
		4.68	20	4.70	35					4.93	70	4.90	60		
		4.48	30												
4.31	20	4.30	40												
		4.06	100	4.05	100							4.18	30	4.16	40
4.07	100														
3.94	70			3.95	40	3.96	70	3.95	20			3.96	100	3.96	100
		3.88	30							3.86	50				
3.79	70	3.76	40	3.79	60	3.77	100	3.77	100	3.77	100	3.78	90	3.77	80
3.63	30	3.65	60			3.63	20	3.62	10			3.62	10	3.63	30
3.44	30	3.46	50	3.44	50	3.44	10	3.45	10			3.43	20	3.44	30
3.30	40	3.36	20	3.32	50	3.30	90	3.30	90	3.30	90	3.31	60	3.30	50
						3.20	20	3.20	30	3.20	30	3.20	20		
3.01	30	3.12	30	3.15	40									3.09	20
		3.03	40	3.01	30	3.02	20	3.01	10	3.03	30	3.02	60	3.01	40
		2.96	30			2.89	10					2.90	30	2.90	20
2.85	30	2.84	40	2.84	60	2.83	20	2.84	10			2.84	40	2.83	40
2.72	20	2.72	30	2.71	30	2.72	10	2.72	20	2.73	20	2.73	20	2.71	20
2.64	20			2.63	35	2.64	50	2.64	50	2.64	50	2.64	30	2.64	40
2.52	50					2.54	30	2.54	30	2.53	30	2.56	30	2.54	30
				2.49	70									2.49	20
2.41	50	2.45	80	2.42	70	2.43	70	2.45	70	2.45	80	2.43	80	2.42	90
										2.20	10				
								2.14	10	2.14	10				
2.08	40					2.09	30	2.09	10			2.09	50	2.09	70
						2.01	20	2.00	20	2.00	20				
Rehydration to kanemite:															
yes		no		yes		no		yes		no		yes		no	

*Before dehydration at 700°C the samples were wetted with methanol/water and dried at 100°C.

**Similar pattern as Na₆Si₈O₁₉ (ASTM 18/1239)

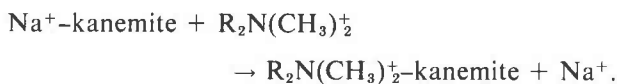


Owing to the high reactivity with protons, the mineral occurs only in alkaline regions (interdune depression of Andjia, Kanem region; northeastern edge of Lake Chad; Maglione, 1971). In regions with $\text{pH} < 10$ the sodium content will be less than the idealized formula $\text{Na}_2\text{O}:\text{SiO}_2 = 0.25:1$. Since the X-ray pattern does not change if moderate amounts of sodium are leached out, the mineral can easily be detected by its powder diagram. The occurrence of the Chad kanemite in trona nodules (Maglione, 1971; Johan and Maglione, 1972) presents a special opportunity for its detection. The solution of trona ($\text{NaHCO}_3 \cdot \text{Na}_2\text{CO}_3 \cdot 2\text{H}_2\text{O}$) is the $\text{HCO}_3^-/\text{CO}_3^{2-}$ buffer system which maintains pH at 10 and prevents

the depletion of sodium, not only in nature but also during isolation of the mineral in the laboratory.

Organic derivatives

The sodium ions of kanemite can be exchanged by large organic cations, and organic derivatives of kanemite are formed as follows:



The X-ray pattern changes with the chain length R of the organic cations; the variation resembles that of other layer silicates (magadiite, $\text{Na}_2\text{Si}_2\text{O}_5$, 2/1 clay minerals). The spacing of only one axis, the b axis of Johan and Maglione (1972), is increased by the in-

corporation of the large organic cations into the kanemite structure. The basal spacing as distance of the layers in *b* direction is then determined from the (0*k*0) reflections. For example, the powder diagram of trimethyl hexylammonium-kanemite with a spacing of 14.9₄ Å can be indexed with the axes:

$$a = 7.28, \quad b = 2 \times 14.9_4 = 29.8_7, \quad c = 4.96 \text{ Å}$$

n-alkylammonium ions

With *n*-alkylammonium ions it is difficult to obtain organic derivatives with well-developed X-ray diagrams. In the stability range of kanemite the hydrolysis equilibrium



is shifted to free amine and the cation exchange is impeded. Decreasing the pH to enhance the equilibrium concentration of R-NH₃⁺ initiates a sodium depletion of kanemite. The cation exchange reaction proceeds well only in a narrow pH-range (about pH = 8–9), which depends upon concentration, chain length of the alkylammonium ions, and stoichiometry of kanemite. The basal spacings of the alkylammonium derivatives (Fig. 3) reveal that, in addition to the exchanged alkylammonium ions, alkylamine molecules are intercalated which ensure a sufficiently high packing density of the chains in the interlayer space.

Dimethyl dialkylammonium ions

The X-ray patterns of the dimethyl dialkylammonium derivatives show sharp and very strong (0*k*0) reflections. From *n_c* = 6 to *n_c* = 14 (*n_c* is the number of carbon atoms in the alkyl chain), the spacings increase linearly. Washing with ethanol-water and drying reduces the spacings (Fig. 3).

The basal spacings exceed the values for a monolayer arrangement of the R₂N(CH₃)₂⁺ ions, but do not reach those of a bilayer structure with perpendicularly-oriented alkyl chains (Fig. 3). The differences between theoretical values for a bilayer structure and observed spacings are similar to those of dimethyl dialkylammonium magadiite (Lagaly *et al.*, 1972, 1975); the mean increase of the spacings for *n_c* = 6–14 is 1.7 Å per carbon atom for kanemite and 1.8 Å for magadiite. Evidently the interlayer structure is of the same kind of a gauche-block structure (Lagaly *et al.*, 1975; Lagaly, 1976).

Considering the analytical composition and unit-cell dimensions, one does not expect the observed basal spacings. The unit cell of kanemite with *Z* = 4

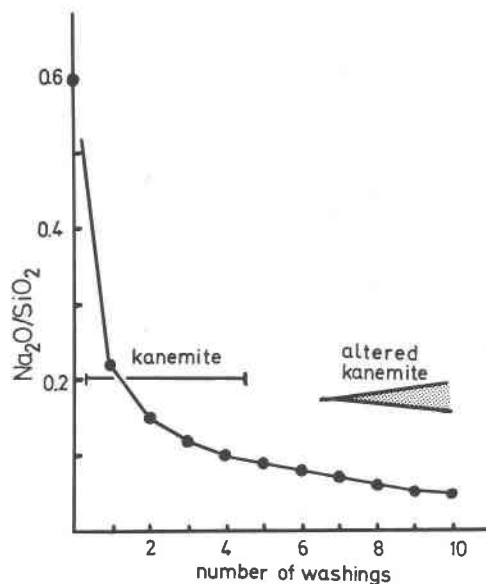
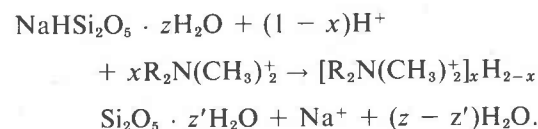


Fig. 2. Extraction of sodium (as NaOH) from kanemite by repeated washings with water (1 g kanemite washed with 25 ml H₂O)

(=4 sodium ions) contains two silicate layers; the area per sodium ions between the layers (equivalent area) is $ac/2 = 18 \text{ Å}^2$. This is somewhat less than the cross-section area of an all-trans alkyl chain. If each dimethyl dialkylammonium ion (two alkyl chains per ammonium ion) replaces a sodium ion, the organic cations should arrange themselves in close-packed bilayers with the chains perpendicular to the silicate layers and with basal spacings of 38 Å for *n_c* = 10 and 48 Å for *n_c* = 14 instead of 30 Å and 36 Å.

Since the sodium ions are quantitatively released, the reaction proceeds as a simultaneous exchange of sodium ions by dimethyl dialkylammonium ions [R₂N(CH₃)₂⁺] and protons:



The extent of Na⁺/H⁺ exchange is controlled by the number of dimethyl dialkylammonium ions allowing formation of a stable gauche-block structure.

Typical gauche-block structures require an area of about 34–38 Å² per alkyl chain (Lagaly, 1976; Lagaly and Beneke, 1976). The unit cell with two sheets of SiO₄ tetrahedra and an area of $ac = 36 \text{ Å}^2$ contains 4 NaHSi₂O₅ formula units and includes two bilayers of organic cations. Therefore a maximum of $(2 \times 2 \times 36)/(4 \times 34) = 1.06$ alkyl chains or $x = 0.5$ dimethyl

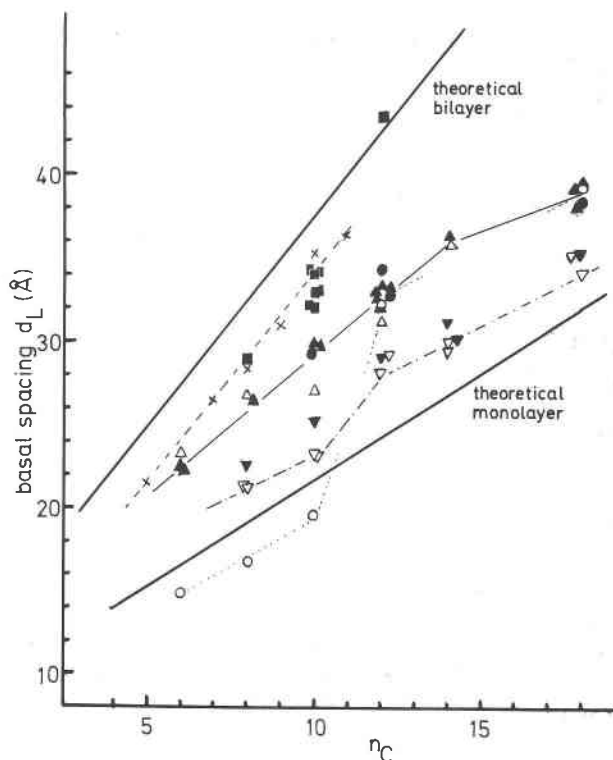
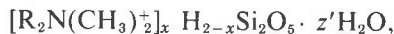


Fig. 3. Organic derivatives of kanemite: basal spacings d_L versus number n_C of carbon atoms in the alkyl chain:

- : alkylammonium ions exchanged for sodium ions (under equilibrium solution)
- , ○: trimethyl alkylammonium ions exchanged for sodium ions (under equilibrium solutions and after air-drying)
- ▲, △: dimethyl dialkylammonium ions exchanged for sodium ions (under equilibrium solution and after air drying)
- ▼, ▽: the same, but samples washed and air dried or dried in vacuo (65°C , $P \leq 0.01$ Torr)
- ×: alkylamine complexes of H-kanemite

dialkylammonium ions are required per formula unit.

In addition to the dimethyl dialkylammonium cations which replace the sodium ions, dimethyl dialkylammonium cations together with their anions (co-ions) are intercalated. These "dimethyl dialkylammonium chloride molecules" are removed by washing the exchanged kanemite with ethanol-water. From the resulting decrease of the basal spacing, one calculates that about 0.15 dimethyl dialkylammonium chloride molecules are removed. The stoichiometry of the dimethyl dialkylammonium kanemites is expected to be



with $x = 0.3 - 0.4$.

The experimental data prove the proposed model of cation exchange. Reaction with dimethyl didodecylammonium ions gives samples with complete exchange of sodium atoms and $x = 0.49$ (air dried), $x = 0.37$ (washed, air-dried) and $x = 0.32$ (extensively washed, dried in high vacuum).

Similar observations were made with $\text{K}_4\text{Nb}_6\text{O}_{17}$ (Lagaly and Beneke, 1976). Owing to the high interlayer cation density (equivalent area: 12.8 \AA^2), the potassium ion exchange proceeds only to the extent that stable gauche-block structures can be formed.

Among all types of long-chain alkylammonium compounds the dimethyl dialkylammonium ions are best suited as organic cations for cation-exchange reactions, because of good reproducibility and the formation of stable and well-ordered structures as shown by sharp and intense X-ray maxima. The presence of two alkyl chains per ammonium ion facilitates the formation of stable gauche-block structures even if the amount of exchanged ammonium ions is only 40 percent of the total cation-exchange capacity.

Other organic cations

Besides n -alkylammonium ions and dimethyl dialkylammonium ions, a variety of other long-chain alkylammonium ions can be introduced between the layers: dimethyl alkylammonium ions, dimethyl alkylbenzylammonium ions, N -alkylpyridinium ions, and others. Data for trimethyl alkylammonium ions are also shown in Figure 3. In the air-dried samples the short-chain trimethyl alkylammonium ions form monolayers, the long-chain ions ($n_C \geq 12$) gauche block-type bilayers.

Swelling of organic kanemites

The dimethyl dialkylammonium derivatives were selected to study the swelling of organic kanemites. Best suited are alkanol and alkylamine as guest molecules, which easily penetrate into the interlayer space and increase the basal spacing. If the alkanol or alkylamine molecules have the same chain length as the alkylammonium ions, the gauche-block structures rearrange into structures with very large basal spacings, suggesting bilayers with perpendicular orientation of chains (Table 2).

The mean increase of the basal spacing d_L with chain length is larger than 2.5 \AA , the maximum value ($= 2 \times 1.27 \text{ \AA}$) for bilayers of chains with their chain axes normal to the layer. With all C-C bonds and N-C bonds in trans-conformation, the two alkyl chains of dimethyl dialkylammonium ions are not parallel to each other; by rearrangements of trans-

bonds into gauche-bonds near the nitrogen atom, the alkyl chains can be directed more or less parallel to each other (see Lagaly *et al.*, 1975). The mean increase $\Delta d_L > 2.5 \text{ \AA}/-\text{CH}_2-$ indicates that shorter chains of the dimethyl dialkylammonium cations are not parallel to each other, but become more and more parallel with increasing chain length. According to the data in Table 2 and Figure 4, parallel orientation is reached for $n_C \geq 12$. Table 2 also gives basal spacings for such combinations of alkanol molecules (n_A carbon atoms in chain) and dimethyl dialkylammonium ions (n_C carbon atoms in chain) that $n_A + n_C = \text{constant}$. Only for $n_A = 14, n_C = 10$ is the basal spacing the same as the symmetric case $n_A = n_C = 12$. If $n_A < 12$ the spacings are near the theoretical line for $n_A = n_C$, indicating that they are mainly determined by bilayers of alkanol molecules normal to the layers. The thickness of the bilayer is only slightly increased by the longer alkyl chains of the organic cations. From volume changes by intercalation of the alkanols, one calculates that 1.33–1.6 alkanol molecules are intercalated per dimethyl dialkylammonium ion; thus 40–45 percent of the chains of the bilayers belong to the alkanol molecules.

With $n_C = 12$ and n_A increasing from 1 to 16 (Fig. 4), different types of interlayer structures are passed: gauche-block structures ($n_A = 2-6$), bilayer structures with spacings mainly determined by the alkanol molecules ($n_A = 8-12$), and bilayer structures with spacings determined by the chain length of the cation ($n_A > 12$).

Transformation of kanemite into crystalline silicic acids

If a suspension of kanemite is titrated with 0.1N HCl, the curve pH *vs.* amount of HCl has two inflection points corresponding to 70 percent (at pH = 8.5) and 100 percent (at pH = 5) exchange of sodium ions by protons. The first inflection point (70 % of total Na content $0.23 \text{ Na}_2\text{O}/\text{SiO}_2$ released = $0.07 \text{ Na}_2\text{O}/\text{SiO}_2$) corresponds to the limit of the stability range of kanemite, which is reached at a ratio $\text{Na}_2\text{O}/\text{SiO}_2$ of about 0.1. At pH = 5 the sodium ions are quantitatively replaced by protons, but typical silicic acid diagrams develop only at pH < 2.

Johan and Maglione (1972) reported the crystalline compounds in acidic milieu to be $\text{H}_2\text{Si}_2\text{O}_5$ -III. In general a mixture of three silicic acids is obtained; their ratio depends upon the experimental conditions. The main component is $\text{H}_2\text{Si}_2\text{O}_5$ -III; $\text{H}_2\text{Si}_2\text{O}_5$ -II and $\text{H}_2\text{Si}_2\text{O}_5$ -IV are formed in smaller proportions. $\text{H}_2\text{Si}_2\text{O}_5$ -III was first prepared by Wey and Kalt

Table 2. Basal spacings of organic derivatives of kanemite, interlayer spaces containing dimethyl dialkylammonium ions (n_C carbon atoms in the alkyl chain) and alkanol (R-OH) or alkylamine (R-NH₂) (n_A carbon atoms in the alkyl chain)

Combinations	n_A	n_C	Basal Spacings (Å)			
			observed		calculated*	
			R-OH	R-NH ₂	a	b
$n_A = n_C$	8	8	29.0	30.2	23	33
	10	10	35.4	34.9	30	38
	12	12	42.5	43.1	34	43
	14	14	48.0	48.0	37	48
$n_A + n_C = 24$	8	16	35.0	38.0		
	10	14	38.8	36.4		
	12	12	42.5	43.1	34	43
	14	10	42.4	40.4		

a: gauche-block structure (type $\frac{n}{2} \perp$)

b: bilayer structure with chains perpendicular to the layers

*see Lagaly *et al.*, 1975

(1967) from KHSi_2O_5 , $\text{H}_2\text{Si}_2\text{O}_5$ -II from $\alpha\text{-Na}_2\text{Si}_2\text{O}_5$ (Schwarz and Menner, 1924; Liebau, 1964; Lagaly *et al.*, 1974) $\text{H}_2\text{Si}_2\text{O}_5$ -IV from $\beta\text{-Na}_2\text{Si}_2\text{O}_5$ (Hubert *et al.*, 1974). Pure $\text{H}_2\text{Si}_2\text{O}_5$ -III can be prepared from kanemite under special conditions, as described in the experimental part.

The innercrystalline reactivity of H-kanemite is very poor. In sharp contrast to the silicic acid obtained from magadiite (Lagaly *et al.*, 1975), which intercalates a large number of small polar organic

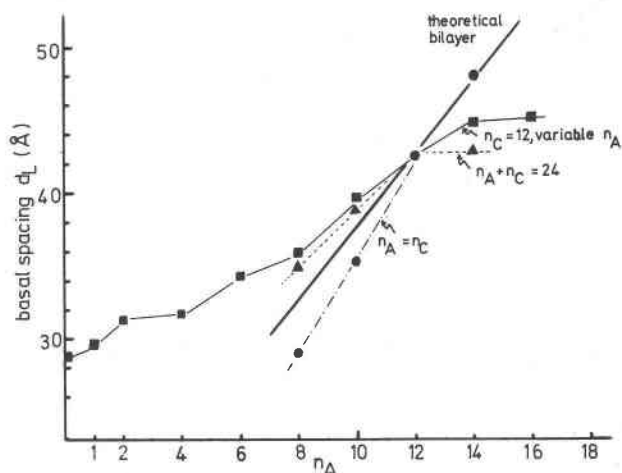


Fig. 4. Clay organic complexes of dimethyl dialkylammonium kanemite (n_C carbon atoms per alkyl chain) with n -alkanols (n_A carbon atoms)

- : $n_A = n_C$
- : $n_C = 12$, variable n_A (1, 2 ... 16)
- ▲: $n_A + n_C = 24$

molecules (dimethylsulfoxide, acid amides, urea, heterocycles, N-oxides, amines), H-kanemite takes up only alkylamines in the interlayer space. The basal spacings of the alkylamine complexes are very similar to those of alkylammonium kanemites (Fig. 3).

Relation of kanemite to other sodium silicates

The investigations reported clearly establish a layer structure for kanemite. The sodium ions between the silicate layers can be reversibly hydrated and dehydrated and exchanged by inorganic and organic cations. The exact structure is still unknown. The reversible transformation of kanemite into disilicic acids $\text{H}_2\text{Si}_2\text{O}_5$ indicates that the SiO_4 -tetrahedra are linked in single sheets in a similar way to the $\text{H}_2\text{Si}_2\text{O}_5$ modifications and the different forms of $\text{Na}_2\text{Si}_2\text{O}_5$. One axis has a length of 4.96 Å, as observed in many other silicates such as α - and β - $\text{Na}_2\text{Si}_2\text{O}_5$, KHSi_2O_5 , $\text{Li}_2\text{Si}_2\text{O}_5$, petalite ($\text{LiAlSi}_4\text{O}_{10}$), sanbornite ($\text{Ba}_2\text{Si}_4\text{O}_{10}$), $\text{K}_4\text{Si}_8\text{O}_{18}$, $\text{Na}_2\text{Si}_3\text{O}_7$, and the micas. This axis is characteristic for tetrahedral layers built up by "Zweiereinfachketten" which are linked to "Zweiereinfachschichten" (nomenclature according to Liebau, 1972). The different types of "Zweiereinfachschichten" mainly result from different ways of folding the layers.

Some problems may arise in interpreting the H_2O content. In relation to the different forms of $\text{H}_2\text{Si}_2\text{O}_5$ and KHSi_2O_5 , kanemite may be formulated as $\text{NaHSi}_2\text{O}_5 \cdot x\text{H}_2\text{O}$ ($= 0.5 \text{Na}_2\text{O} \cdot 0.5\text{H}_2\text{O} \cdot 2\text{SiO}_2 \cdot x\text{H}_2\text{O}$). The investigations which clearly establish the layer structure render a formula $\text{NaHSi}_2\text{O}_4(\text{OH})_2$ (Johan and Maglione, 1972) less probable, since only one OH group can be bound per tetrahedron in layer structures. The water molecules are arranged between the layers. Since the unit cell with $4 \times \text{NaHSi}_2\text{O}_5$ has an area $a c = 36 \text{Å}^2$ and contains two silicate layers, a monolayer of water molecules between the silicate sheets requires about $\frac{1}{4}(2 \times 36)/10 = 1.8$ moles H_2O per $\text{NaHSi}_2\text{O}_5 = 0.9$ moles H_2O per SiO_2 (area occupied by a water molecule about 10Å^2). Additional water molecules (at least 0.5 moles per SiO_2) can be trapped in the holes of the folded SiO_3OH hexagonal rings. The water contents of the sample investigated by Johan and Maglione ($0.25 \text{Na}_2\text{O} \cdot 0.25 \text{H}_2\text{O} \cdot \text{SiO}_2 \cdot 1.5 \text{H}_2\text{O}$) and of our sample ($0.23 \text{Na}_2\text{O} \cdot 0.27 \text{H}_2\text{O} \cdot \text{SiO}_2 \cdot 1.6 \text{H}_2\text{O}$) are in good agreement. The slightly higher water content probably results from physically adsorbed water at the external surfaces and between the crystals.

Drying kanemite over P_4O_{10} or treatment with ethylene glycol reduces the basal spacing by about the diameter of a water molecule (from 10.2 Å to 7.66 Å).

The related weight loss (14.4%) corresponds to desorption of 0.8₅ moles H_2O per SiO_2 . Evidently the interlamellar monolayer of water molecules is desorbed. The remaining water molecules are trapped in the holes of the folded (SiO_3OH) rings of the collapsed structure and are desorbed at higher temperatures up to 300°C. This temperature involves also the expulsion of water from the SiOH groups, so that 92 percent of the total water content is desorbed up to 300°C. Broadening and disappearance of several reflections indicate some accompanying structural changes. Above 500°C the X-ray diagram becomes sharper and the typical diagram of the 700°C phases develops. For comparison, KHSi_2O_5 decomposes with the complete expulsion of the water from the silanol groups up to 400°C and becomes amorphous.

The survey of methods of preparation of kanemite in Figure 1 is instructive in relating kanemite to other sodium silicates. The α and β - $\text{Na}_2\text{Si}_2\text{O}_5$ are transformed into kanemite by special procedures which involve hydrolytic attack, but not a complete destruction of the structure. Evidently the structural remnants act as nuclei for the formation of the new structure.

Makatite is another sodium silicate which seems to be related to kanemite. Makatite heated to 700°C and treated with water rehydrates immediately to kanemite. The silicic acid prepared from makatite exhibits the same poor inner-crystalline reactivity as H-kanemite.

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