

## A hydrated potassium layer silicate and its crystalline silicic acid

K. BENEKE, G. LAGALY

Institut für anorganische Chemie der Universität Kiel, Olshausenstrasse 40, D-2300 Kiel, F.R.G.

### ABSTRACT

A potassium silicate has been prepared from dispersions of  $\text{SiO}_2$  in aqueous solutions of KOH and from potassium water-glass solutions at 60–100 °C. This silicate is related to magadiite, but differs from the potassium form of magadiite by reversible interlamellar hydration between a state with a water monolayer (basal spacing 15.1 Å) and a bilayer arrangement (basal spacing 17.3 Å). Removal of the interlayer water decreases the spacing to 12.8 Å. In contrast to magadiite and its potassium analogue, the silicate intercalates a variety of organic guest molecules.

Cation exchange with protons (leaching in acids) transforms the silicate into a crystalline silicic acid (basal spacing: about 15 Å in water, 13.4 Å dried at room temperature, 11.6 Å heated above 300 °C). This acid is characterized by very pronounced intracrystalline reactivity. It intercalates a large number of organic compounds including alkanols, nitriles, ketones, and amino acids.

### INTRODUCTION

Synthesis of hydrated alkali silicates is governed by the nature of the alkali ion. In dispersions of silica in sodium hydroxide solutions or from sodium water-glass solutions at or above 100 °C, magadiite ( $\text{Na}_2\text{Si}_{14}\text{O}_{29} \cdot x\text{H}_2\text{O}$ ) forms preferentially (Lagaly et al., 1975; Schwieger et al., 1987) whereas  $\text{K}_2\text{Si}_{20}\text{O}_{41} \cdot x\text{H}_2\text{O}$  is easily precipitated from dispersions in potassium hydroxide solutions (Beneke et al., 1984). This potassium silicate is closely related to kenyaite ( $\text{Na}_2\text{Si}_{20}\text{O}_{41} \cdot x\text{H}_2\text{O}$ , Eugster, 1967; McAtee et al., 1968; Fletcher and Bibby, 1987), except for an increased intracrystalline reactivity (Beneke and Lagaly, 1983). Evidently, potassium ions exert an opposite influence on the reactivity of hydrated layer silicates and three-layer clay minerals. Potassium ions reduce or even block the intracrystalline reactions (cation exchange, swelling) of more highly charged clay minerals, but increase the reactivity of hydrated layer silicates. This observation is confirmed by a new layered potassium silicate that, below 100 °C, forms from silica dispersed in potassium hydroxide solution or from potassium water-glass solutions.

### PROCEDURES

Aqueous dispersions of  $\text{SiO}_2$  and KOH were allowed to stand at 60–120 °C (Table 1). A gel-like, but crystalline material (here defined as K-SH) with a basal spacing of 17.3 Å was formed after some time. Longer periods of reaction transformed K-SH into the potassium silicate  $\text{K}_2\text{Si}_{20}\text{O}_{41} \cdot x\text{H}_2\text{O}$ .

In reproducing identical runs, traces of potassium silicate first appeared after different time periods ranging between 1 and 3 months at 70 °C. Formation of the silicate is probably delayed by nucleation problems. At 60 °C, the reaction required about 6 months. K-SH was formed most rapidly at 90 °C from dispersions containing 3 mol  $\text{SiO}_2$ , 1 mol KOH and 30 mol water (Table 1). The potassium silicate also formed rapidly (in 20 d at

70 °C) from a solution of potassium water glass. The water glass used here was type 28/30 from Henkel Comp. (Germany) with 21 wt%  $\text{SiO}_2$ , 8.1 wt%  $\text{K}_2\text{O}$ , and was partially neutralized by adding 3 mL conc.  $\text{H}_2\text{SO}_4$  to 100 mL, which adjusted the molar ratio  $\text{SiO}_2/\text{KOH}$  to about 4/1.

The presence of carbonate ions retards or even impedes formation of the potassium silicate K-SH.

The precipitated products were separated from the mother liquid by filtration. Extensive washing with water was avoided, because this transformed the silicate into the silicic acid. The samples were air- or freeze-dried. The chemical composition of the air-dried samples was obtained from weight loss at 1200 °C before and after extraction of potassium by 1M hydrochloric acid. The extracted potassium was determined by a DC plasma emission spectrometer (Spectra Span IV, Beckman Instruments).

The crystalline silicic acid H-SH was prepared by leaching the silicate in an excess of 1M hydrochloric acid. The samples were washed with distilled water and air-dried.

Weight-loss curves were obtained by stepwise heating of a sample for one or more days at the desired temperatures (Fig. 1). Recording in a usual TG/DTA device led to less reliable values, because the release of water proceeds very slowly (for instance, weight loss of the acid at 300 °C: 8.9% after 24 h, 9.3% after 3 d, 9.5% after 7 d). Smaller weight losses were observed when samples were heated directly to higher temperatures, presumably because some amounts of water remain trapped between collapsing layers. Isothermal dehydration and rehydration were studied by equilibrating 100-mg samples over standard solutions for humidity control.

The new potassium silicate hydrate K-SH and the potassium silicate hydrate  $\text{K}_2\text{Si}_{20}\text{O}_{41} \cdot x\text{H}_2\text{O}$  were identified by their X-ray powder diagrams, which were obtained in Debye-Scherrer cameras (diameter 11.46 cm,  $\text{CuK}\alpha$  radiation, Ni filter, intensities from visual inspection).

To study intracrystalline reactions, the air-dried potassium silicates or silicic acids were mixed with a small excess of the liquid guest compound. After standing some days at room temperature or at 65 °C, the mixture was transferred into Lindemann glass

TABLE 1. Preparation of the new potassium silicate hydrate K-SH

Starting materials (mol)			Time of reaction (days) and type of products*	
SiO <sub>2</sub>	KOH	H <sub>2</sub> O		
Temperature of reaction: 60 °C				
3	1	40	160 d: a;	200 d: K-SH
Temperature of reaction: 70 °C				
4	1	40	35 d: a;	48 d: K-SH
3	1	40	100 d: a;	120 d: K-SH
3	1	35		62 d: K-SH
3	1	25		17 d: K-SH
2	1	40	95 d: a;	125 d: K-SH
Temperature of reaction: 90 °C				
3	1	35		13 d: K-SH
3	1	30		13 d: K-SH
3	1	25	13 d: a;	20 d: K-SH
3	1	20	9 d: a;	27 d: K-SH

\* a = product amorphous. K-SH identified by the X-ray powder pattern. Some amorphous material may also be present.

tubes and X-rayed. Several solid guest compounds (urea and derivatives, amino acids, etc.) were applied in saturated aqueous solutions.

## RESULTS

### Potassium silicate

The potassium silicate K-SH forms predominantly from dispersions containing 2–4 mol SiO<sub>2</sub> and 20–50 mol water per mol KOH. Evidently, it is an intermediate phase during formation of K<sub>2</sub>Si<sub>20</sub>O<sub>41</sub>·xH<sub>2</sub>O. At temperatures ≥ 100 °C, formation of K<sub>2</sub>Si<sub>20</sub>O<sub>41</sub>·xH<sub>2</sub>O is relatively fast, and the intermediate product is difficult to detect. This product was observed at early states of reaction in some runs at 95 °C. The presence of sodium ions impedes formation of potassium silicates and promotes formation of magadiite.

The irregularly shaped thin plates of K-SH, as observed by scanning electron microscopy (Fig. 2), are quite different from the spherical aggregates of magadiite and K<sub>2</sub>Si<sub>20</sub>O<sub>41</sub>·xH<sub>2</sub>O (Lagaly, 1979; Beneke and Lagaly, 1983, 1984; Schwioger et al. 1985). The chemical composition of the air-dried precipitates is about K<sub>2</sub>O·14SiO<sub>2</sub>·8H<sub>2</sub>O. The products were washed with a small amount of water to avoid removal of lattice potassium. Repeated washing with ethanol removed only small amounts of KOH, and the amount of adherent mother liquid was probably small.

When an aqueous dispersion of the potassium silicate was titrated with hydrochloric acid (Fig. 3), the changes below pH = 7.5 were similar to those for other alkali silicates (cf. Fig. 3, in Lagaly, 1979). The upward deviation of the titration curve above pH = 7.5 is related to dissolution and hydrolysis of some amounts of silicate. For the same reason, pH of the aqueous dispersion increases slowly from about 8.7 to 9.5 within 2 h under conditions as in Figure 3.

In contact with the mother liquid, the basal spacing of K-SH is 17.3 Å. The powder pattern of the air-dried sample displays only a few reflections (Table 2a) besides the typical basal reflection at *d* = 15.1 Å (air-dried samples)

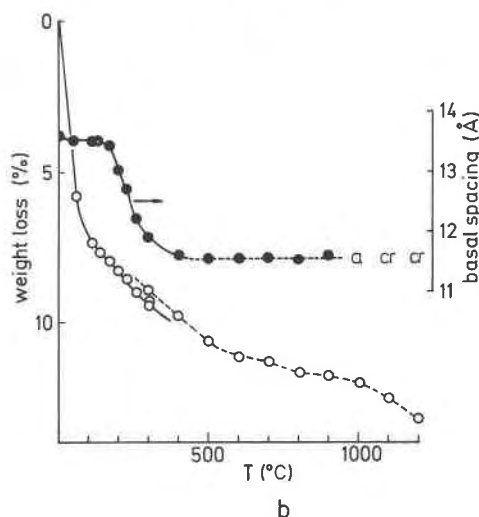
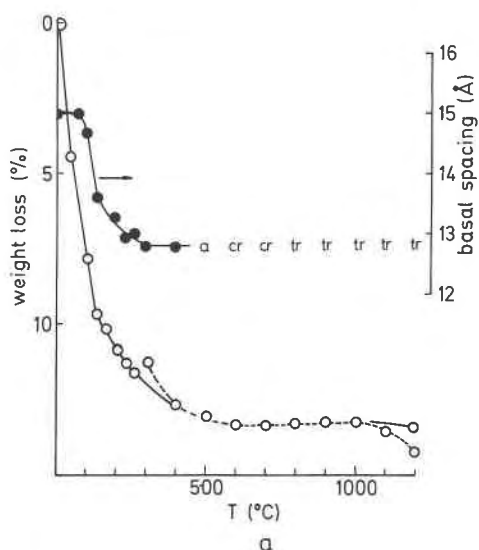


Fig. 1. Thermal changes of (a) the potassium silicate K-SH and (b) the derived crystalline silicic acid H-SH between room temperature and 1200 °C, ● basal spacing, ○ weight loss. Solid lines = samples heated several days at temperatures below 400 °C; dashed lines = samples heated for 24 h; a = amorphous; cr = cristobalite; tr = tridymite.

and a reflection at *d* = 3.43 Å. Rehydration in water increases the spacing again to 17.3 Å. Drying above 200 °C decreases the spacing to 12.8 Å (Fig. 2a). These samples do not rehydrate to 17.3 Å when dispersed in water. Samples dried at 300 °C and rehydrated give a spacing of 13.3 Å. After heating to 400 °C, rehydration ceases, and the spacing remains unchanged at 12.8 Å. At about 500 °C, the material becomes amorphous, but recrystallizes at 600 °C. The crystalline products are low cristobalite and, in distinctly smaller amounts, α-quartz. Well-crystallized tridymite is formed at 800 °C and is stable at least up to 1200 °C. Above 1000 °C, considerable amounts of K<sub>2</sub>O are desorbed.

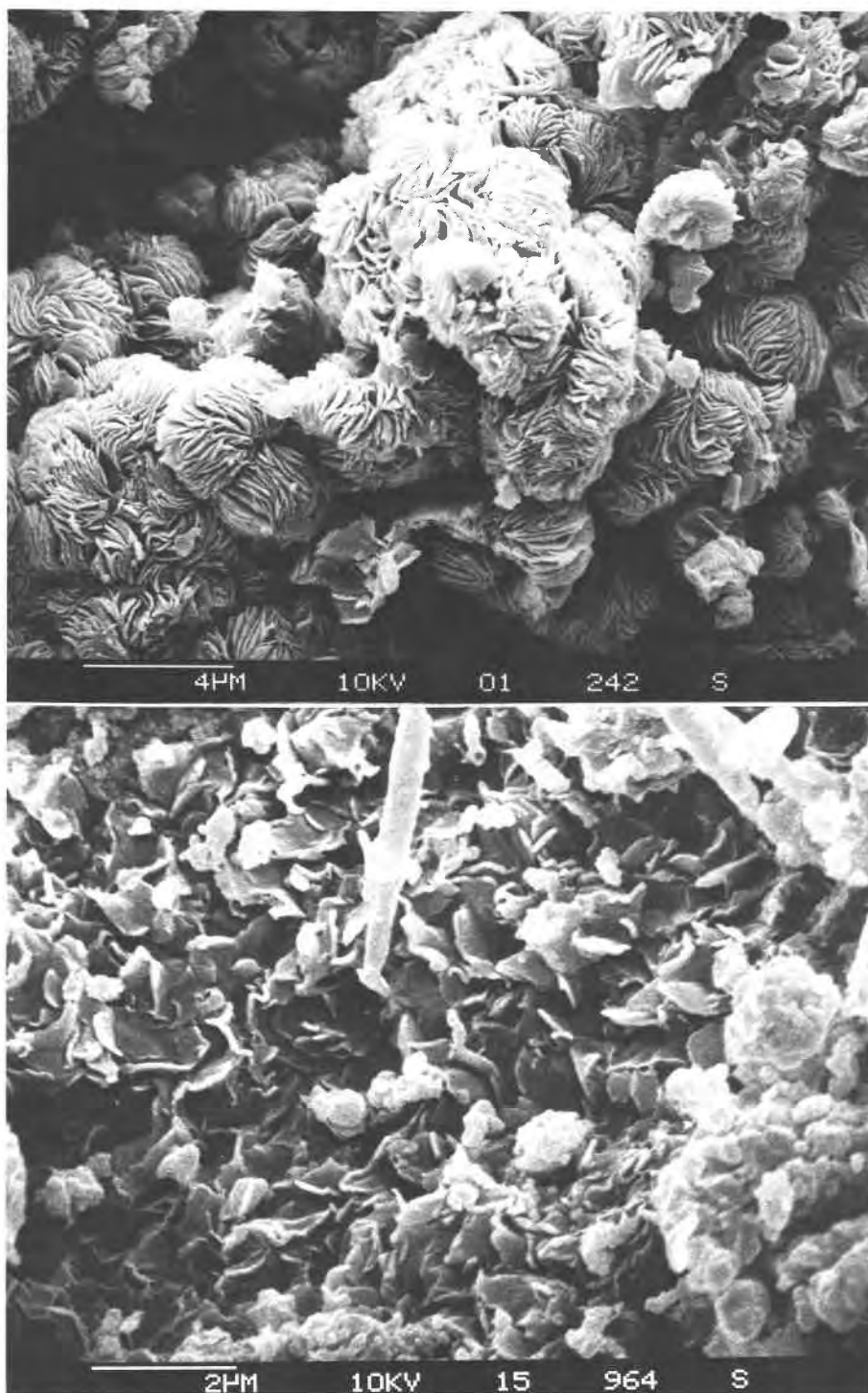


Fig. 2. Scanning electron micrographs of (a) the potassium silicate hydrates  $K_2Si_{20}O_{41} \cdot xH_2O$  and (b) K-SH, prepared from 3 mol  $SiO_2$  and 1 mol KOH in 40 mol  $H_2O$  at 70 °C, after 120 d.

In contrast to magadiite, the potassium silicate K-SH intercalates a variety of organic compounds (Table 3). A pronounced ability to intercalate guest molecules is very typical of this silicate and also of the derived silicic acid H-SH (see below).

#### The crystalline silicic acid

The potassium silicate K-SH is easily transformed into the silicic acid H-SH by leaching in diluted acids. Type and concentration of the acids are not decisive. For in-

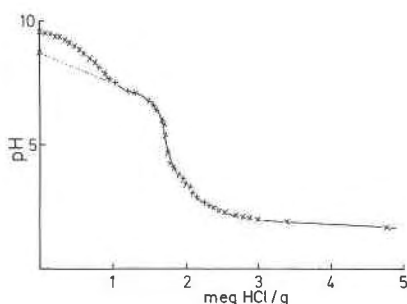


Fig. 3. Titration of the potassium silicate K-SH with 0.1M hydrochloric acid (145.34-mg potassium silicate dispersed in 50 mL water; water content of the potassium silicate 13.4%).

stance, 0.1N and 2N HCl, HNO<sub>3</sub>, and H<sub>2</sub>SO<sub>4</sub> led to identical products. The shape of the platelike particles remains nearly unchanged. A spacing of 13.0 Å is typical of the air-dried acid (Table 2b). It increases to about 15 Å when the acid is dispersed in water. The broadened basal reflection indicates that the degree of order of the rehydrated form is lower than in the 13.4-Å phase. Leaching in acids at 100 °C produces samples that, after air-drying, reveal the same basal spacing but only expand to 14.2–14.4 Å in water.

The water content of the silicic acid H-SH is insensitive to the relative humidity between 40 and 60%, but changes strongly at lower or higher humidity (Fig. 4). The ratio H<sub>2</sub>O/SiO<sub>2</sub> increases from about 0.2 at 0% to about 0.8 at 87% relative humidity and is accompanied by basal-spacing changes from 13.0 to 14.0 Å. Capillar condensation increases water adsorption continuously above 70% relative humidity, so that the stepwise increase of the basal spacing from 13.6 to 14 Å is not reflected.

The spacing of the air-dried acid remains nearly unchanged up to about 170 °C, then decreases to 11.6 Å and remains constant up to 900 °C (Fig. 2). At 1000 °C, the material becomes amorphous. Formation of cristobalite starts at about 1100 °C. In spite of the constant basal spacing, water is still desorbed between 400 °C and 1200 °C. The weight loss increases continuously from 10% to 13.3%. After heating to 1200 °C, the H<sub>2</sub>O/SiO<sub>2</sub> ratio is <0.01. The composition of the 11.6-Å phase varies between 0.12 and 0.06 H<sub>2</sub>O/SiO<sub>2</sub>, and the air-dried acid has the composition SiO<sub>2</sub>·0.5H<sub>2</sub>O.

TABLE 2A. Powder-diffraction pattern of potassium silicate K-SH

Air dried		Under water	
<i>d</i> (Å)	<i>I</i>	<i>d</i> (Å)	<i>I</i>
15.1	100	17.2	100
5.00*	20	7.08	10
3.43	50	5.00	10
3.14*	30	3.58	20
2.96	10	3.43	40
2.85	10	3.32	30
1.82	20	3.14	30
		1.83	30

\* Reflection broadened.

TABLE 2B. Powder-diffraction pattern of the crystalline silicic acid H-SH

Dried over P <sub>2</sub> O <sub>5</sub>		Air-dried	
<i>d</i> (Å)	<i>I</i>	<i>d</i> (Å)	<i>I</i>
13.0	100	13.4	100
7.22	50	7.20	40
6.50	50	6.63	50
3.61	50	5.31	20
3.36	80	4.44*	10
1.83	10	3.98*	10
		3.5–3.4†	
		1.83	20

\* Reflection broadened.

† Broadened band at 3.4–3.5 Å.

Samples heated to 170 °C rehydrate into the 15-Å form. Dehydration at higher temperatures decreases the proportion of expandable interlayer spaces. After rehydration, the spacing remains below 15 Å. The interlayer space of samples heated to an excess of 300 °C is no longer expanded by rehydration. Very likely, siloxane bridges between adjacent silicate layers prevent separation of the layers.

The surface acidity of H-SH (between Hammett surface acidity H<sub>0</sub> = -3.0 and H<sub>0</sub> = +1.5) corresponds to the acidity of the acid from K<sub>2</sub>Si<sub>20</sub>O<sub>41</sub>·xH<sub>2</sub>O (Werner et al., 1980). Titration of the acid with KOH in the presence of KCl indicates a K<sup>+</sup>/SiO<sub>2</sub> ratio of about 2/14, very close to the Na<sup>+</sup>/SiO<sub>2</sub> ratio in magadiite. Generally, exact values are difficult to obtain from such titration curves (cf. Beneke et al., 1984) so that this value may be considered as a first approximation.

#### Intercalation capabilities

Most striking is the ability of the acid to intercalate a very large number of guest molecules. The basal spacing of the acid after intercalation of a few selected guest compounds is reported in Table 4. In contrast to other crystalline silicic acids that intercalate only a few types of compounds, the acid H-SH reacts with alcohols; glycols;

TABLE 3. Basal spacing of K-SH and H-SH in the presence of guest molecules

Guest compound	Basal spacing (Å)	
	K-SH	H-SH
air-dried sample	15.1	13.4
under water	17.3	15.0
acetamide	17.7	15.4
<i>N</i> -ethyl urea	15.8	17.0
piperazine	19.6	19.8
2,5-dimethyl piperazine	20.3	19.8
ephedrine	24.2	24.2
imidazole	21.4	16.4
trimethylamine- <i>N</i> -oxide	21.3	15.8
ethylene glycol	17.6	17.1
glycerol	17.2	16.5
methanol	16.0	16.5
butanol	14.8	15.9

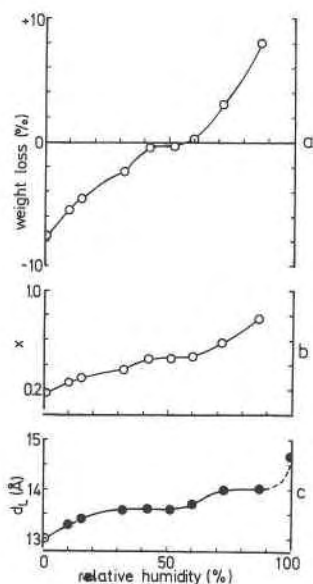


Fig. 4. Water content of the crystalline silicic acid H-SH at different relative humidities: (a) weight changes of an air-dried sample, (b)  $\text{H}_2\text{O}/\text{SiO}_2$  ratio  $x$ , (c) basal spacing  $d_L$ .

nitrils; acid amides and derivatives; urea and derivatives; amine oxides, sulfoxides, and phosphine oxides; several amino acids; aliphatic and aromatic amines; aromatic heterocycles; and ketones. The reactivity with alcohols, nitriles, ketones, and several amino acids distinguishes this acid from other intracrystalline reactive layered materials.

Noteworthy is the lattice expansion to about 19.6 Å

TABLE 4. Basal spacings of the silicic acid H-SH after intercalation of guest molecules (basal spacing of air-dried acid: 13.4 Å)

Group of compounds	Guest molecules	Basal spacing (Å)
alcohols	methanol	16.5
	butanol	15.9
	octanol	15.6
	ethylene glycol	17.1
	glycerol	16.5
	hexanediol-1,6	15.3
ketones	acetone	15.7
nitriles	acetonitrile	15.9
	butyronitrile	16.2
amines	ethylene diamine	15.6
	hexamethylene diamine	17.9
	triethylene diamine	21.4
	piperazine	19.8
	ephedrine	24.2
	decylamine	40.4
	aniline	15.9
	trimethylamine- <i>N</i> -oxide	15.8
	pyridine- <i>N</i> -oxide	16.5
	dimethyl sulfoxide	16.6
acid amides		see Table 5
urea derivatives		see Table 5

TABLE 5. Basal spacings of H-SH and the acid form of magadiite

Guest compound	Basal spacing $d_L$ (Å)			$D^\dagger$ (Å)
	Acid form of magadiite	H-SH	$\Delta d_L + 2.8^*$ (Å)	
<i>N</i> -methylformamide	15.9	17.0	6.4	5.7
propionamide	14.5	17.7	7.1	6.1
<i>N</i> -ethyl formamide	14.0	17.1	6.5	6.3
<i>N,N</i> -dimethyl formamide	16.7	16.8	6.2	6.3
<i>N</i> -methyl acetamide	17.4	19.4	8.8	6.2
<i>N,N</i> -dimethyl acetamide	16.5	17.2	6.6	6.7
<i>N,N</i> -diethyl formamide	16.5	17.5	6.9	7.0
<i>N</i> -methyl urea	15.5	15.7	5.1	5.3
<i>N</i> -ethyl urea	14.9	17.7	7.1	5.5
<i>N,N</i> -dimethyl urea	16.2	16.7	6.1	6.2
dimethyl sulfoxide	15.8	16.6	6.0	6.1
ethylene glycol	15.4	17.1	6.5	5.6

\*  $\Delta d_L = d_L - 13.4$  (Å), for S-SH.

†  $D$  = diameter of the guest molecule.

(broadened reflections) by potassium acetate. Potassium acetate is a highly effective intercalation agent for kaolinite, but does not react with almost all other types of layered materials.

The intracrystalline reactivity toward many guest compounds is lost above 200 or 230 °C. Several guest molecules, for instance, hydrazine hydrate and piperazine, can penetrate between the layers and increase the basal spacing, even if the acid has been heated at 260 °C for a period of 7 d. One may conclude that condensation of adjacent layers starts above this temperature.

## DISCUSSION

The variation of the basal spacing of the potassium silicate K-SH and the derived crystalline silicic acid suggests that these compounds are intracrystalline reactive layered silicates. The alkali/SiO<sub>2</sub> ratio is close to that of magadiite. However, K-SH is not simply the potassium analogue of magadiite Na<sub>2</sub>Si<sub>14</sub>O<sub>29</sub>·*x*H<sub>2</sub>O. The potassium analogue of magadiite prepared from the acid form of magadiite and KOH reacts quite differently. The most striking difference is the reversible hydration and dehydration of K-SH that is accompanied by basal spacing changes between 15.1 and 17.3 Å. The 15.1-Å form corresponds to an intercalation of a water monolayer between the silicate layers. The spacing of 17.3 Å indicates an intercalation of a bilayer of water molecules. Magadiite and the potassium analogue do not expand beyond 15.6 Å in contact with water. If potassium silicate K-SH and magadiite had an identical layer structure, the crystalline acids would be identical. This is not observed. The striking property of the acid H-SH is the interlamellar hydration in water, which increases the basal spacing from 13.4 Å to about 15 Å. The acid form of magadiite does not intercalate a second layer of water molecules when dispersed in water. Samples of H-SH heated to an excess of 400 °C reveal higher basal spacings (11.6 Å) than the acid form of magadiite (11.2 Å). A further difference is the intracrystalline reactivity toward several classes of

guest compounds. For instance, the acid form of magadiite does not intercalate alcohols, nitriles, and ketones. The different basal spacings after intercalation of guest molecules (i.e., Table 5) also reveal a structural difference between both the crystalline silicic acids.

In most cases the guest molecules displace interlayer water molecules. In a first approximation, the sum  $\Delta d_L + 2.8$  ( $\Delta d_L$  represents the increase of the basal spacing in angstroms; 2.8 Å is the diameter of a water molecule) should be close to the diameter  $D$  of the guest molecule. This condition is often fulfilled, but deviations of some tenths of angstroms occur, as the guest molecules seldom adopt spherical conformation. On the other hand, the deviations are not very large because the mean diameter of *small* molecules (calculated from the molecular volume) is often not very different from the largest dimension of the extended molecules. This condition is certainly not fulfilled for longer chain molecules. The interlayer separation by propionamide is distinctly larger than the diameter of the hypothetical sphere. Dimethyl urea molecules are compact molecules, and the interlayer separation approximately corresponds to the spherical diameter. In contrast, *N*-ethyl urea adopts a more extended conformation, which produces a higher basal spacing. The large interlayer separation after intercalation of *N*-methyl acetamide is also observed for the acid form of magadiite.

In most cases, the interlayer separation of H-SH by small guest molecules is distinctly higher than for the acid form of magadiite and suggests a closer packing of the guest molecules in the interlamellar monolayer. The basal spacings of the alkanol complexes give values of  $\Delta d_L + 2.8$  between 4.7 and 5.3 Å, which corresponds to the thickness of an alkyl chain. The alkanol molecules seem therefore to be intercalated with their long axes parallel to the silicate layers.

### CONCLUSION

The hydrated potassium silicates K-SH and  $K_2Si_{20}O_{41} \cdot xH_2O$  only form in alkali solutions with high potassium content, whereas the presence of sodium ions promotes formation of magadiite. Thus, hydrated potassium silicates should be formed in nature under very particular conditions only. A further cause, which should restrict these materials, is the low stability of the hydrated alkali silicates. Leaching in water, for instance, transforms them into crystalline silicic acids. Silicic acids can also be formed from several other minerals (such as gillespite, apophyllite, carletonite, sanbornite, litidionite: Pabst, 1958; Guth et al., 1978; Frondel, 1979; Lagaly and Matouschek, 1980).

The silicic acids may be overlooked in nature because of identification difficulties. These difficulties might arise from the variable interlayer spacing and the ability of the acids to intercalate guest molecules. Silhydrite (Gude and Sheppard, 1972) is the only natural silicic acid that has been described. It represents the acid form of magadiite, but its properties are affected by intercalated organic material (Beneke and Lagaly, 1977).

### REFERENCES CITED

- Beneke, K., and Lagaly, G. (1977) Peculiarities of intercalation reactions of the natural silicic acid silhydrite. *Clay Minerals*, 12, 363-365.
- (1983) Kenyaite—Synthesis and properties. *American Mineralogist*, 68, 818-826.
- (1984) Kristalline Kieselsäuren. *GIT—Fachzeitschrift für das Laboratorium*, 516-527.
- Beneke, K., Kruse, H.-H., and Lagaly, G. (1984) Eine kristalline Kieselsäure mit hoher Einlagerungsfähigkeit. *Zeitschrift für anorganische und allgemeine Chemie*, 518, 65-76.
- Eugster, H.P. (1967) Hydrous sodium silicates from Lake Magadi, Kenya: Precursors of bedded chert. *Science*, 157, 1177-1180.
- Fletcher, R.A., and Bibby, D.M. (1987) Synthesis of kenyaite and magadiite in the presence of various anions. *Clays and Clay Minerals*, 35, 318-320.
- Frondel, C. (1979) Crystalline silica hydrates from leached silicates. *American Mineralogist*, 64, 799-804.
- Gude, A.I., and Sheppard, R.A. (1972) Silhydrite,  $3SiO_2 \cdot H_2O$ , a new mineral from Trinity County, California. *American Mineralogist*, 57, 1053-1065.
- Guth, J.-L., Hubert, Y., Kalt, A., Perati, B., and Wey, M.R. (1978) Un nouveau type de silice hydratée cristallisée. *Académie des Sciences, Comptes Rendus Hebdomadaires des Sciences, Série D, Sciences Naturelles Paris*, 286, 5-8 (in French).
- Lagaly, G. (1979) Crystalline silicic acids and their interface reactions. *Advances in Colloid Interface Science*, 70, 46-55.
- Lagaly, G., and Matouschek, R. (1980) Die kristallinen Kieselsäuren aus Apophyllit, Carletonit und Gillespit. *Neues Jahrbuch für Mineralogische Abhandlungen*, 138, 81-93.
- Lagaly, G., Beneke, K., and Weiss, A. (1975) Magadiite and H-magadiite: I. Sodium magadiite and some of its derivatives. *American Mineralogist*, 60, 642-649.
- McAtee, J.L., House, R., and Eugster, H.P. (1968) Magadiite from Trinity County, California. *American Mineralogist*, 53, 2061-2069.
- Pabst, A. (1958) The crystal structure of leached gillespite, a sheet silicate. *American Mineralogist*, 43, 970-980.
- Schwieger, W., Heidemann, D., and Bergk, K.-H. (1985) High resolution solid-state silicon-29 nuclear magnetic resonance spectroscopic studies of synthetic sodium silicate hydrates. *Revue de Chimie Minerale*, 22, 639-650.
- Schwieger, W., Heyer, W., Wolf, F., and Bergk, K.-H. (1987) Zur Synthese von kristallinen Metallsilicathydraten mit Schichtstruktur. *Zeitschrift für anorganische und allgemeine Chemie*, 548, 204-216.
- Werner, H.-J., Beneke, K., and Lagaly, G. (1980) Die Acidität kristalliner Kieselsäuren. *Zeitschrift für anorganische und allgemeine Chemie*, 470, 118-130.

MANUSCRIPT RECEIVED FEBRUARY 24, 1988

MANUSCRIPT ACCEPTED SEPTEMBER 13, 1988