American Mineralogist, Volume 68, pages 818–826, 1983

Kenyaite—synthesis and properties

KLAUS BENEKE AND GERHARD LAGALY

Institut für anorganische Chemie der Universität
Kiel, Olshausenstraße 40/60, 23 Kiel, Germany

Abstract

The hydrous sodium silicate kenyaite can be synthesized from aqueous suspensions containing SiO_2 and NaOH with SiO_2/NaOH ratios ranging from 5 to 20 and H_2O/NaOH ratios from 50 to 500 at 100–150°C. This phase can also be prepared from concentrated or diluted water glass solutions above 120°C. At 100°C magadiite generally precipitates as the first reaction product and then alters to kenyaite. The stable end product is quartz. This leads to the suggestion of the transformation: magadiite → kenyaite → quartz in agreement with field observations of Eugster (1969).

Formation of kenyaite at 100°C requires several months. The reaction times are much decreased at higher temperatures but under these conditions quartz forms rapidly. Synthetic kenyaites form spherical aggregates of well-developed plates.

Kenyaite gives intracrystalline reactions like other layer silicates. The intracrystalline reactivity reveals some differences between the different samples which are not detected by other methods. The reactivity mainly depends on the time of synthesis and is less influenced by the composition of the starting mixture. Through exchange of protons for the interlayer sodium ions, kenyaite is transformed into a crystalline silicic acid.

Introduction

The four naturally-occurring hydrous alkali silicates presently known were discovered during the last fifteen years at the alkali lakes in Africa: magadiite, kenyaite (Eugster, 1967, Eugster *et al.* 1967) and makatite (Sheppard *et al.* 1970) at Lake Magadi, Kenya, and kanemite at Kanem, Lake Chad (Johan and Maglione, 1972). The chemical compositions of the natural samples were reported as $NaHSi_2O_5 \cdot 3H_2O$ (kanemite), $Na_2Si_4O_9 \cdot 5H_2O$ (makatite), $Na_2Si_{14}O_{29} \cdot 9H_2O$ (magadiite) and $Na_2Si_{22}O_{45} \cdot 10H_2O$ (kenyaite).

Synthetic magadiite forms at 100–120°C from suspensions typically containing 1 mole NaOH, 2 to 6 moles SiO_2 and 10 to 60 moles H_2O (Lagaly *et al.*, 1973). Kanemite and makatite can also be easily prepared (Beneke and Lagaly, 1977a), but synthesis of kenyaite from alkaline suspensions of SiO_2 at 100°C seemed to be difficult, supporting Eugster's suggestion that kenyaite is an alteration product of magadiite (Eugster, 1969). However, when the runs were held at 100°C for longer than 90 days (up to two years) kenyaite was formed.

The X-ray diffraction powder pattern and the $Na_2O/SiO_2/H_2O$ ratios of natural and synthetic kenyaites can vary considerably. It will be shown that the variability results from intracrystalline changes brought about by cation exchange reactions and one-dimensional intracrystalline swelling.

Materials and methods

The synthetic kenyaites were prepared from suspensions of silica (silica gel: "Kieselsäure, gefällt", Merck, Germany, or "Aerosil 200", Degussa AG., Germany) in aqueous NaOH or Na_2CO_3 solutions. In a typical run (sample 27Y, Table 1) 50 g silica gel (= 42 g SiO_2) were dispersed in 250 ml water containing 1.6 g NaOH (= 17.5 moles SiO_2 and 354 moles H_2O per mole NaOH). The suspension was allowed to stand at 100°C with occasional shaking. After 3 months a small amount of kenyaite was formed. Two months later a large amount of precipitate formed which was separated by filtration and then air-dried. Washing with water was usually avoided to prevent the alkali ions from being leached out of the structure.

Most of the runs were performed at 100°C in 100, 250 or 500-ml Teflon vessels with nearly gas-tight screw-on-type caps. Reactions at 125°C were made in 500-ml steel vessels with Teflon packing rings. For the 150°C experiments we used a 750-ml agitated autoclave (Forschungsinstitut Berghof) with complete Teflon lining.

A natural kenyaite from the Magadi area (alluvial channel, Lake Magadi) provided by the Magadi Soda Comp., Kenya, was studied for comparison.

The kenyaites were stored under different conditions (under mother liquid, washed, wet, air-dried, freeze-dried, *in vacuo* and over P_4O_{10}, heated to 60–1200°C). The X-ray powder patterns were recorded in Debye–

0003–004X/83/0708–0818$02.00

Scherrer-cameras (114.59 mm diameter, Cu$K\alpha$-radiation). The amount of impurities in the samples (magadiite or quartz) was roughly estimated from the intensities of the X-ray reflections in the range $4\theta = 51$–57°. Calibration was accomplished by comparing the powder patterns to those made from artificial mixtures of synthetic kenyaite, synthetic magadiite and quartz.

The composition of the precipitates of the different runs was obtained in the usual way (SiO_2 by gravimetric or colorimetric analysis, sodium by atomic absorption, water from weight loss at 1100°C). It was, however, very difficult to obtain the exact composition of the kenyaite itself. The precipitates absorbed mother liquid which could not be removed without leaching sodium ions out of the kenyaite structure. The procedure successfully used for kanemite (Beneke and Lagaly, 1977a) only led to an approximate composition SiO_2/Na_2O = 19–22. Many precipitates apparently contained amorphous silica or quartz as impurities (*cf.* Fig. 2b,f,g) and could not be used for the evaluation of the chemical composition of kenyaite. More reliable values were obtained for the potassium form of kenyaite (see below). This material can easily be prepared from suspensions of SiO_2 in aqueous KOH at 100–125°C (Lagaly, 1980). The precipitate shows no amorphous materials or quartz in scanning electron micrographs. For analysis it was transformed into the corresponding crystalline silicic acid (see below and footnote 1, p. 823). The acid was equilibrated with potassium hydroxide solutions of different concentrations. On the basis of the dissolved amounts of acid the SiO_2/K_2O ratio was determined to be 19.8–20.4.

Intracrystalline reactions of the kenyaites (cation exchange and intercalation) with different types of organic molecules were studied using X-ray powder techniques (Lagaly *et al.* 1975 a,b, Beneke and Lagaly, 1977a). Prior to these experiments the synthetic kenyaites were carefully washed with small amounts of water to remove most of the adhering mother liquid and air-dried or freeze-dried.

The H-form of kenyaite was prepared by addition of large excess of 0.1 m hydrochloric acid. The samples were allowed to stand some days (typically one week) in a refrigerator, then were filtered off and air-dried.

Results

Synthesis

Kenyaite forms from suspensions containing high SiO_2/NaOH ratios (≥8, Table 1). Kenyaite can be detected in the X-ray powder patterns of the precipitates from solutions held at 100°C for 3 to 5 months.

The amount and crystallinity reach optimal values between 8 and 24 months. Longer run times transform kenyaite into quartz, the stable end product. Above 100°C the rate of kenyaite formation is much increased but also increased is the rate of quartz formation. Preparation of kenyaite free of quartz requires special conditions. For example, run 37L (Table 1) yielded a relatively well-crystallized kenyaite without quartz.

The first crystalline product formed in the 100°C-experiments is usually magadiite (Table 1). This phase

Table 1. Synthesis of kenyaite from SiO_2, NaOH, H_2O-suspensions or water glass solutions at 100–150°C

Run No.	T(°C)	Bulk concentration (moles)			Duration required (months)		Conversion to "pure"[****] kenyaite (months)	Total run duration (months)	Products[*]
		SiO_2	H_2O	NaOH	formation of intermediate magadiite	nucleation of kenyaite			
27 Z	100°C	9	222	1	2.3	3	17	24	K+Q (20%)
37 I	100°C	10	93	1	1	9	13	13	K
25 M	100°C	11	100	1	3.5	5	8	13	K
37 S	100°C	16	75	1	1	3	-	10	K+Mg (15%)
39 N	100°C	16	117	1	2	3	8	10	K+Q (<5%)
37 L	125°C	16	138	1	-- ***)	0.3	3	3	K
28 D	100°C	16	444	1	--	<3	4	24	K
27 Y	100°C	18	354	1	--	3	4	4	K
28 E	100°C	22	222	1	--	4	10	24	K+Q (<5%)
41 U	150°C	8	250	1	--	0.1	-	0.25	K+Q (<5%)
41 T	150°C	10	250	1	--	0.1	-	0.25	K+Q (<5%)
41 O	150°C	16	250	1	--	--	-	24 h	amorphous
41 R	150°C	16	250	1	--	about 72 h	-	72 h	K (traces)
41 S	150°C	16	250	1	--		-	96 h	K,Q (traces)
41 K	150°C	16	250	1	--		-	0.2	K+Q (<5%)
41 P	150°C	16	250	1	--		-	0.5	K+Q (<5%)
40 Y	125°C	WGS[**]	(18wt%SiO_2)		--	1.5	-	4	K+Q (5-10%)
40 X	125°C	WGS	(24wt%SiO_2)		0.5	1.5	-	4	K+Q (5-10%)
40 W	125°C	WGS	(30wt%SiO_2)		0.5	1.5	-	4	K+Q (5%)

[*] K = kenyaite, Mg = magadiite, Q = quartz, weight percents of Q or Mg

[**] water glass solution

[***] no intermediate magadiite observed

[****] X-ray diagram showing reflections of kenyaite only. Presence of amorphous silica not excluded

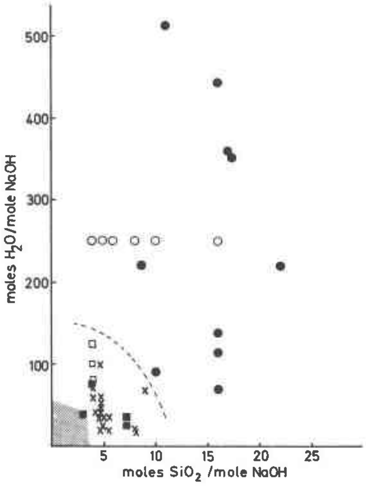

Fig. 1. Syntheses from SiO_2–NaOH–H_2O suspensions at 100°C or 150°C. ● kenyaite (100°C), ○ kenyaite (150°C), × magadiite (100°C), ■ "octosilicate"; (100°C), □ unidentified phase (150°C), stippled area: makatite and "octosilicate" field (100°C), dashed line is the speculated stability field boundary between magadiite and kenyaite.

appears in 1 to 5 months depending on the SiO_2, NaOH and H_2O content and slowly transforms into kenyaite.

In the 100°C runs with high SiO_2/NaOH ratios ($\geq$16) kenyaite can be directly formed and magadiite was not observed as an intermediate. The corresponding composition lie on the "outside" of the speculated stability field of kenyaite in Figure 1 (above the dashed curve).

In the 100°C runs with lower SiO_2/NaOH ratios ($\leq$10) and compositions lying in the speculated stability field of magadiite, magadiite was formed first and then transformed into quartz without going through kenyaite as an intermediate (run $32F_2$, Table 2).

When both SiO_2/NaOH and H_2O/NaOH ratios are low (stippled area in Fig. 1) makatite and "octosilicate" are formed. "Octosilicate" is a hydrated sodium silicate synthesized and described by Iler (1964). As yet, this phase has not been found to occur naturally.

Surprisingly, kenyaite was also formed by heating sodium water glass solutions to $\leq$125°C, even though the composition of these solutions (concentrated solution: $SiO_2/H_2O/NaOH \approx 2:2:1$) lies in the makatite-"octosilicate" field and far away from the kenyaite field (Fig. 1). An amorphous precipitate appears after some days (for instance, 10 days in runs 40X, Y, W) and slowly transforms into poorly crystallized kenyaite which can only be detected by the intense 19.8Å reflection. The crystallinity increases within 3 months but quartz is simultaneously formed. It is likely, that the mechanisms for the formation of kenyaite from water glass and from alkaline SiO_2-suspensions are different.

The alkali ion appears to influence the type of the silicate formed. Sodium ions favor the formation of magadiite which is slowly altered to kenyaite at higher SiO_2/NaOH ratios ($\geq$8). In runs utilizing KOH instead of NaOH the potassium form of kenyaite was first precipitated rather than the potassium form of magadiite. In run 36A NaOH was replaced by a 1:1 mixture of NaOH and KOH, and a mixture of sodium magadiite and potassium kenyaite was obtained. In this respect Li^+, Cs^+, Sr^{2+} and Ba^{2+} ions behave like potassium ions.

In Table 3 the X-ray powder patterns of some synthetic kenyaites from different runs are listed. The variations in the position and intensity of the reflections are evident. These changes are caused by the intracrystalline changes, in particular by changes of the layer distances. The reflection at 3.34Å is from quartz (3.34Å, I = 100), and the intensity of the reflection at 1.82–1.83Å may be slightly increased by the superimposition of a quartz reflection (1.818Å, I = 17).

The SiO_2/Na_2O ratio of the air-dried precipitates ranged from 16 to 28. The water content varied between 10 to 30 moles H_2O/mole Na_2O (the SiO_2/Na_2O ratio for natural kenyaite is 21.7 (Eugster, 1967)). Due to the difficulties in analyzing the precipitates this ratio could not be determined with high reliability.

Table 2. Reaction sequences of some kenyaite synthesis experiments

Run 32 F_2		Run 27 Z		Run 37 I		Run 25 M		Run 41 O/S	
5/38/1* (100°C)		9/222/1 (100°C)		10/93/1 (100°C)		11/100/1 (100°C)		16/100/1 (150°C)	
time (days)	products**	time (days)	products	time (days)	products	time (days)	products	time (days)	products
35	Mg			24	Mg	15	amorph.	1	amorph.
		69	amorph.			54	amorph.	3	some K
		104	K+Mg(40%)	116	Mg	106	amorph.	4	K, < 5%Q
		136	K+Mg(40%)					6	K, < 5%Q
		167	K+Mg(30%)	173	amorph.	153	K+Mg(75%)	14	K, < 5%Q
200	Mg	216	K+Mg(30%)			226	K+Mg(20%)		
240	Mg			255	traces of K	261	K+Mg(10%)		
300	Mg	307	K+Mg(20%)			293	K+Mg(<5%)		
		349	K+Mg(20%)			324	K		
390	Q			384	K	372	K		
510	Q	510	K+Mg(10%)						
		700	K, Q(20%)						

* molar ratios $SiO_2/H_2O/NaOH$

** Mg: magadiite, K: kenyaite, Q: quartz, weight percent of Mg or Q

Table 3a. X-ray diffraction powder data from synthetic kenyaites and the derived crystalline silicic acids

Natural kenyaite$^{2)3)}$		Synthetic kenyaites$^{3)}$						Crystalline silicic acid			
		run 25 M		run 27 Z		run 40 Y		from run 25 M$^{4)}$		from run 40 Y$^{3)}$	
I	d(Å)	I	d(Å)	I	d(Å)	I	d(Å)	I	d(Å)	I	d(Å)
100	19.68	100	19.80	100	19.82	100	19.86	100	19.70	100	18.03
50	9.93	30	9.88	30	9.88	30	9.94	40	9.83	40	9.02
12	5.14			<10	5.04	<10	5.04	20	7.22	20	7.22
35	4.97	10$^{5)}$	4.89	<10	4.94	10	4.98	10	5.37		
28	4.69			20	4.67	20	4.68	20	4.50	20	4.25
		10$^{5)}$	4.24	40	4.26	30	4.26				
10	3.95	10$^{5)}$	3.79	10	3.93	20$^{5)}$	3.93	30$^{5)}$	4.01	30	3.66
20	3.64			20	3.64	20	3.65	40	3.62	30	3.51
22	3.53			10	3.51	10	3.51				
85	3.43	80	3.43	80	3.43	80	3.43	80	3.44	100	3.35
45	3.32			100	3.34$^{6)}$	70	3.34$^{6)}$				
55	3.20	50	3.19	80	3.19	70	3.19	60	3.21	20	3.20
14	2.93	20	2.93	10	2.93	30	2.93	10	2.93	10$^{5)}$	2.93
12	2.83			10	2.83	10	2.83	10	2.77		
3	1.88	20	1.83	50	1.82	50	1.83	40	1.83	50	1.83

[1] Debye-Scherrer camera, dia. = 114.59 mm, CuK_α-notation
[2] from Eugster (1967) and McAtee et al., 1968 (not a complete list)
[3] air-dried, [4] wet, [5] very broad, [6] quartz?

Magadiite–kenyaite transformation

In most experiments with $SiO_2/NaOH \leq 16$ magadiite appears as precursor of kenyaite; the final end product is quartz. A transformation magadiite → kenyaite → quartz is evident. This same sequence was postulated by Eugster (1967) and documented by his subsequent field work at the magadi area (Eugster, 1969). However, the transformations as expressed by the equations (2) and (4) (Eugster, 1969) cannot proceed simply by leaching the sodium ions out of the magadiite structure. Exchange of the sodium ions leads to H-magadiite ("crystalline silica hydrate", see footnote 1, p. 823, Eugster, 1967; Brindley, 1969; Lagaly *et al.*, 1975b). Silhydrite found in Trinity county, California (Gude and Sheppard, 1972) is in fact the natural form of H-magadiite (Beneke and Lagaly, 1977b).

The silicate layers of magadiite are about 11Å thick and those of kenyaite about 17.7Å. A solid-state transformation requires a thickening of the magadiite layers by condensation of silicic acid which has to penetrate through the interlayer spaces to the reacting sites. From our present knowledge about the intracrystalline reactivity of magadiite this process is not very likely. An alternative explanation would be that sodium ions are lost in every second interlayer space followed by condensation of the two adjoining silicate layers into pairs. Brindley and Chang (1974) suggested a similar mechanism for the dehydration of a chlorite. The silicate layers can easily condense with each other (Lagaly *et al.*, 1979), but the loss of sodium ions in every second interlayer space cannot be easily achieved or requires a high degree of cooperativity.

The natural process in the field as an open system cannot be specified at present. The 100–150°C experiments gave no evidence for the occurrence of these proposed mechanisms.

During the synthesis runs small amounts of the suspensions were X-rayed in Debye–Scherrer cameras. In the first stages of the runs only reflections of magadiite were

Table 3b. X-ray diffraction powder data from synthetic potassium silicate ($K_2Si_{20}O_{41} \cdot H_2O$), its sodium exchanged form ($Na_2Si_{20}O_{41} \cdot H_2O$), and the derived crystalline silicic acids

$K_2Si_{20}O_{41} \cdot xH_2O^{1)}$				$Na_2Si_{20}O_{41} \cdot xH_2O^{1)}$		Crystalline silicic acids			
						from $K_2Si_{20}O_{41} \cdot xH_2O$		from $Na_2Si_{20}O_{41} \cdot xH_2O$	
run 25H		run 34S		from run 34S		run 25H$^{2)}$		from run 34S$^{1)}$	
I	d(Å)	I	d(Å)	I	d(Å)	I	d(Å)	I	d(Å)
100	19.86	100	20.1	100	19.86	100	17.85	100	18.03
40	9.72	30	9.88	30	9.83	50	8.89	30	8.93
10	7.22	<10	7.22			30	7.28		4)
30	4.86	30	4.91	20	4.89	10$^{3)}$	6.73		
				10$^{3)}$	4.26	20	5.91		
10	3.87	<10$^{3)}$	3.83	10$^{3)}$	3.83	30	4.44	40	4.50
20	3.66	10	3.63			10	3.67		
90	3.43	90	3.43	80	3.43	50$^{3)}$	3.39	30	3.28
40	3.20	60	3.20	50	3.20		4)		4)
20	2.93	20	2.93	20	2.93				
50	1.84	50	1.83	20	1.83	40	1.84	20	1.83

[1] air-dried, [2] freeze-dried, [3] very broad, [4] several broad reflections with I < 10

observed. The intensity of the reflections, in particular the basal reflection at d = 15.6Å, then decreased while reflections of kenyaite, in particular the 19.8Å-reflection, appeared and increased in intensity. During the runs the reflections of magadiite and kenyaite changed in intensity but the position and half-width did not change. If line broadening was observed it did not exceed that expected for the decreasing particle size. Thus, a phase intermediate between magadiite and kenyaite or an interstratified structure was not detected. The transformation, therefore, does not proceed as a topochemical reaction. Most likely, it proceeds through an amorphous phase. In run 37I (Table 2), for example, the first precipitate was magadiite which then became X-ray amorphous after 116 days and then transformed into kenyaite.

Morphology and particle size

Synthetic kenyaites are often obtained in more or less spherical nodules of plate-like crystals (Fig. 2) which resemble synthetic magadiite aggregates (*cf.* Fig. 10, Lagaly, 1979). Sometimes the nodules are embedded in matrix of amorphous silica (Figs. 2a, b). The samples from water glass solutions at 125°C consist of open aggregates of well-developed plates (Fig. 2d) and resemble the natural samples (Fig. 2e). These different types of sample aggregation suggest that the formation of kenyaite in water glass solutions and in SiO_2-suspensions follows different reaction mechanisms.

Quartz formed by decomposition of kenyaite appears as small spheres (Figs. 2f–h) which are often much smaller than 1 μm in diameter and often possess a pockmarked surface (Fig. 2h).

Intracrystalline reactions

The unit cell dimensions of kenyaite often change when the crystals are subjected to changing physical conditions, are placed in various liquids, or are treated with acids or solutions of organic cations. Most pronounced is

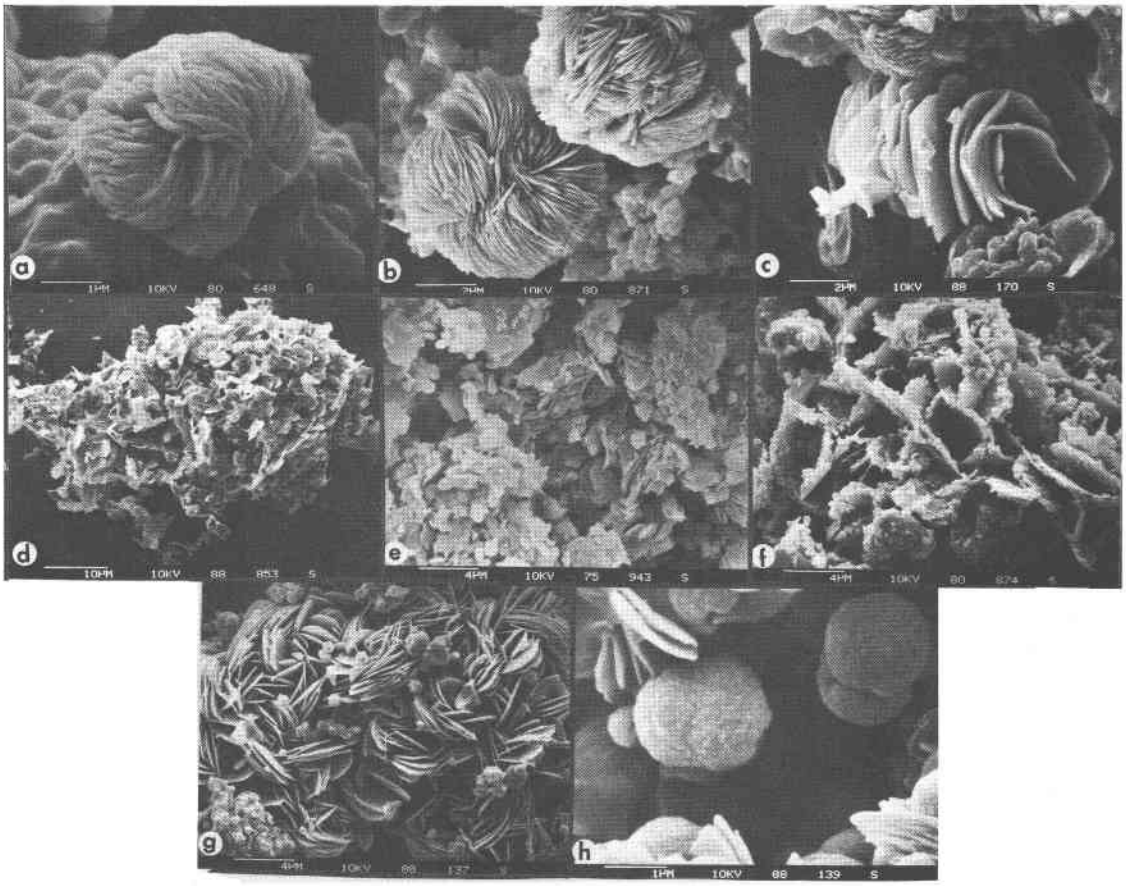

Fig. 2. Scanning electron micrographs of kenyaites (parentheses: run, temperature, reaction time and $SiO_2/H_2O/NaOH$ in moles): (a) run 28 D (100°C, 2 years, 16:444:1), closely packed nodules of kenyaite plates; (b) run 37 L (125°C, 3 months, 16:138:1), spherical aggregates of the plates and amorphous material; (c) run 37 S (100°C, 10 months, 16:75:1), loosely packed plates; (d) run 37 U (125°C, 3.5 months, water-glass) less regular developed plates; (e) natural kenyaite (Lake Magadi, Kenya); (f) run 27 Z (100°C, 2 years, 9:222:1), alteration of kenyaite into small quartz particles; (g) run 28 E (100°C, 2 years, 22:222:1), well developed kenyaite plates and spherical quartz particles; (h) run 28 E, surface morphology of the quartz particles.

the shift of the intense X-ray reflections at 19.8Å and 9.9Å to higher *d*-values (Table 4). The changes resemble those observed when magadiite is similarly treated and are typical for reactive hydrated layer structures (Eugster 1967, Brindley 1969, Lagaly *et al.* 1973, 1975 a,b). Thus, the reflections at 19.8Å and 9.9Å are considered to be basal reflections; probably the first and second order reflections.

Some of the basal spacing changes listed in Table 4 should be explained. The decrease by 2Å from 19.7Å to 17.7Å suggests a loss of a monolayer of water. The stability of the 17.7Å-spacing up to the transformation into quartz (700°C) suggests that this spacing corresponds to the van-der-Waals-thickness of the single kenyaite layer. Thus, the silicate layers in air dried kenyaite appear to be separated by a monolayer of water molecules.

Long-chain organic cations (cationic surfactants) replace interlayer sodium ions by ion exchange. The large *d*-spacings (24–44Å, Table 4) indicate that the cations are aggregated in bimolecular layers as previously described for magadiite (Lagaly *et al.* 1973, 1975 a,b) and kanemite (Beneke and Lagaly, 1977a). In general, the reaction of primary alkylammonium ions with alkali layer silicates requires special experimental conditions (Lagaly *et al.*, 1973; Kalt *et al.*, 1979). This is also true for kenyaite, but unlike other alkali silicates kenyaite easily reacts with phenyl- and benzylammonium cations.

In the presence of glycol, glycerol, N-methyl formamide, urea, *etc.*, the spacings are increased (Fig. 3) because the organic molecules displace interlayer water molecules and occupy more interlayer space. The basal spacings often depend on the method of preparation of the parent compound (kenyaite) and particularly on the reaction times. The lattice spacings tend to decrease with increasing reaction times and reflect the presence of unexpanded interlayer spaces.

Table 4. Basal spacings of synthetic kenyaites under different conditions

Treatment	basal spacings (Å)
kenyaite, air dried (different samples)	19.7 - 19.9
under o.1 m acid (HCl, H_2SO_4, $HClO_4$, HNO_3 etc.)	19.6 - 19.8*
then air-dried	17.6 - 18.0
kenyaite, 120°C (vacuum $< 10^{-2}$ torr)	17.8
kenyaite, 200°C	17.7
kenyaite, 400°C	17.7
kenyaite, 600°C	17.7
kenyaite, 700°C	quartz
kenyaite + 0.1 m aqueous solution of	
decylammonium chloride	40.6
dodecylammonium chloride	44.4
trimethyl decylammonium chloride	39.2
trimethyl dodecylammonium bromide	42.5
dimethyl didecylammonium chloride	39.2
dimethyl didodecylammonium chloride	43.6
trimethyl phenylammonium chloride	24.6
trimethyl benzylammonium chloride	27.2
triethyl benzylammonium chloride	29.5

* exceptions see Figure 5

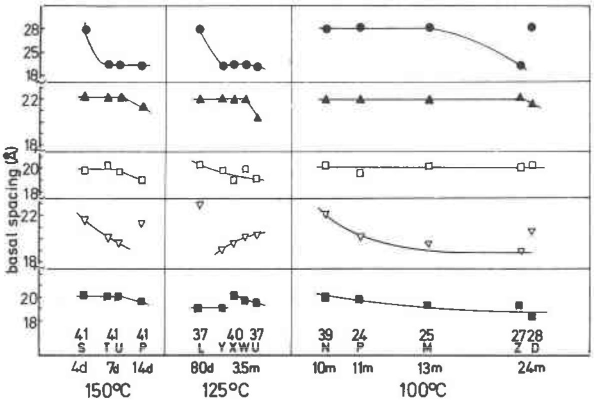

Fig. 3. Intracrystalline reactivity of kenyaites (prepared at 100, 125 and 150°C and at different reaction times) with respect to various liquids (● ephedrine, ▲ ethylene glycol, □ glycerol, ▽ = N-methyl formamide, ■ = dimethyl formamide).

H-kenyaite

If kenyaite is stored in an excess of diluted acids (for instance 0.1 m hydrochloric acid) all interlayer sodium ions are exchanged by protons. The product is a crystalline silicic acid.[1] Titrating kenyaite suspensions with 0.1 m HCl shows that the exchange starts at pH 9–10 but mainly proceeds at pH about 7 (Fig. 4). However, the exchange is not quantitative at the "equivalent points" even though the hydrochloric acid was added in rates not faster than 1.3 ml/h. At the "equivalent points" 40 to 70 percent of the sodium ions were exchanged. Some of the sodium ions are evidently fixed in the interlayer sites. Usually, the basal spacing of the kenyaites in suspension remains nearly unchanged (19.6–19.8Å) (Table 4) during the H^+/Na^+ exchange. The spacing then collapses after air drying to 17.6–18.0Å. One monolayer of water is

---

[1] Crystalline silicic acids are obtained by exchanging the interlayer cations of alkali layer silicates and some other layer silicates with protons (Schwarz and Menner, 1924; Pabst, 1958; Wey and Kalt, 1967; Lagaly and Matouschek, 1980; Frondel, 1979; review: Lagaly, 1979). Since these compounds are rather acidic (Werner *et al.*, 1980) "crystalline silicic acid" or "crystalline phyllosilicic acid" (Liebau, 1964) is a useful nomenclature. Nevertheless, some authors use the notation "crystalline silica hydrate" ("SH-phase, Eugster, 1967) or, more simply, "leached gillespite" (Pabst, 1958) or "leached magadiite." At present more than 15 different silicic acids are known. Since a systematic nomenclature is lacking, the acids, at least those derived from minerals, are called "H-magadiite, H-apophyllite, H-kenyaite, *etc.*".

Eugster (1967) reported $6SiO_2 \cdot H_2O$ for his "SH-phase" which is the crystalline acid from magadiite. The crystalline silicic acid reported here and prepared from synthetic kenyaite has the approximate composition $SiO_2 \cdot H_2O$ in air-dried state and $SiO_2 \cdot 0.2H_2O$ after freeze-drying. Note that the water content changes with the relative humidity.

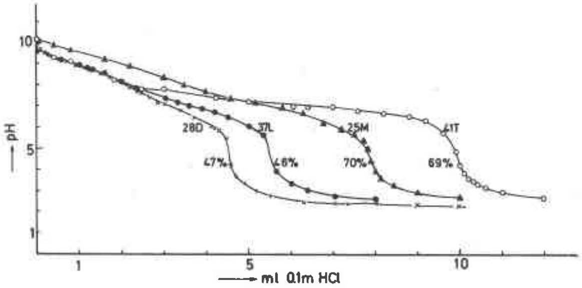

Fig. 4. Titration data of kenyaite suspension (1g/100 ml water) with 0.1 m HCl; rate of addition of HCl ≤ 1.3 ml/h. Percent sodium ions exchanged by protons at the "equivalent points" are indicated. $Na_2O/SiO_2/H_2O$ in 28D: 1:28:17.4; in 37L 1:17.7:29.5; in 25M: 1:25.5:10.9; in 41T 1:15.8:23.

apparently desorbed from each interlayer space. Rehydration of this H-kenyaite in water does not increase the spacings above 18.6Å. Evidently, only some of the collapsed interlayers are rehydrated. Dehydration at higher temperatures (24 hours at 200°C) decreases the proportion of the expandable interlayers and the maximum spacing after rehydration is 18.0Å. In repeated dehydration/rehydration cycles the maximum spacing is further decreased and finally the lattice expansion is completely blocked. A single dehydration step at 300°C (24 hours) has the same effect.

Some synthetic kenyaites, in particular from runs at 125 and 150°C (for example, runs 40Y, 41P, 41T) give crystalline silicic acids with basal spacings less than 19.6Å, even in the wet state (Fig. 5). During the H^+/Na^+ exchange some interlayer spaces apparently lose the water monolayers leading to an interstratification of hydrated (d = 19.8Å) and dehydrated interlayers (d = 17.6Å). Treatment of H-kenyaite with sodium hydroxide solutions reconstitutes the kenyaite.

The surface acidity of H-kenyaite in aqueous dispersion ($-3 < pK_s < +1.5$) resembles that of other highly condensed crystalline silicic acids (Werner *et al.*, 1980). It is independent of the kind of the acid (HCl, H_2SO_4, HNO_3, acetic acid, *etc.*) used for the H^+/Na^+-exchange.

H-kenyaite like the other crystalline silicic acids (Lagaly, 1979) intercalates several organic compounds (Fig. 5). Most reactive are aliphatic amines. Some H-kenyaites do not expand to the maximum value and reflect the lowered reactivity of the parent kenyaites.

Comparison with other layer silicates

Kenyaite appears to be related to a potassium silicate with approximate composition $K_2Si_{20}O_{41} \cdot xH_2O$ ($x \approx 11$) (Lagaly, 1980). The X-ray powder patterns (Table 3) are very similar if conditions are chosen so that the basal spacings are equal. The relations between kenyaite and $K_2Si_{20}O_{41} \cdot xH_2O$ are best revealed by their intracrystalline reactions. The crystalline silicic acid prepared from the potassium silicate reacts with NaOH and gives a sodium silicate which strongly resembles kenyaite. Thus, kenyaite appears to be the sodium form $Na_2Si_{20}O_{41} \cdot xH_2O$ of the potassium silicate $K_2Si_{20}O_{41} \cdot xH_2O$.

One is not surprised that intracrystalline reactions and dehydration/hydration experiments reveal some differences between kenyaite and the sodium and potassium silicate as well as among the corresponding acids (Table 5). When placed in contact with water the basal spacing of the air-dried potassium silicate expands to nearly 22Å (corresponds to a bilayer of water molecules between the silicate layers) whereas that of the sodium silicate and synthetic kenyaite remains the same (19.8Å) and corresponds to a monolayer of water molecules between the silicate layers. In the air-dried state or after dehydration at higher temperatures the spacings of the three compounds become identical.

Surprisingly, the potassium ions promote a higher hydrated interlayer state. In the titration experiments reported in Figure 4 the sodium ions are not quantitatively exchanged by protons. This reveals a fixation of sodium ions in the interlayer spaces. $K_2Si_{20}O_{41} \cdot xH_2O$ quantitatively exchanges the potassium ions when used in the same procedure. This behavior contrasts with the potassium fixation by higher-charged 2:1 clay minerals such as vermiculites and micas. It should be noted that potassium fixation not only results from the reduced hydration tendency of the potassium ions but also from specific interactions with the silicate surface. One might, therefore, speculate that the sodium fixation and the restriction to a single water monolayer in the $Na_2Si_{20}O_{41} \cdot xH_2O$ and kenyaite structures give evidence of specific interactions with the silicate layer which overcome the increased hydration tendency of the sodium ions.

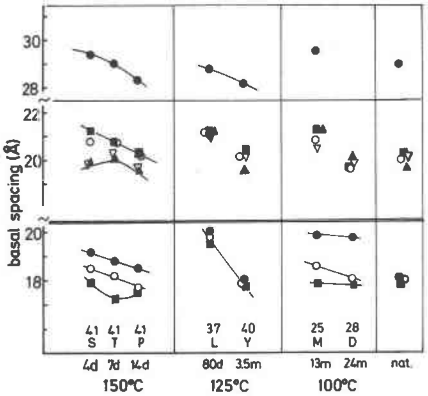

Fig. 5. Basal spacings of H-kenyaites under different conditions and in contact with various liquids. Lower third of figure: ● kenyaites in contact with HCl, ■ H-kenyaites, air-dried, ○ H-kenyaites, rehydrated; upper two thirds of figure: H-kenyaites under dimethyl sulphoxide (○), ethylene glycol (▲), N-methyl formamide (▽), dimethyl formamide (■), ephedrine (●).

Table 5. Basal spacings of kenyaite, sodium and potassium silicate, and the corresponding crystalline silicic acids under various conditions

Sample and run No.	Basal spacings (Å) wet	air-dried 25°C	rehydrated (under water)	KOH,NaOH (≥1m)	heated to 200°C	heated to 200°C, then rehydrated
natural kenyaite		19.7	19.8	—	19.6	19.6
synth. kenyaite* (25M)	19.8	19.8	19.8	—	17.7	18.0**
sodium silicate	19.9-20.4	19.9	19.8	—	17.7	19.6**
potassium silicate (25H)	21.8	19.9	21.6	—	17.7	20.4**
silicic acids from:				NaOH:		
(1) natural kenyaite	18.0	17.9	17.9	19.9	17.6	
(2) synthetic kenyaite (25M)	19.7	17.8	18.6	20.1	17.7	18.2**
(3) sodium silicate (34S)	20.1	18.0	18.0	20.3	17.7	17.7
				KOH:		
(4) potassium silicate (25H)	21.6	19.6	22.1	22.1	17.3	17.8**

* prepared from the potassium silicate (34S), scheme (I), ** after dehydration/rehydration cycles at 200°C: 17.7 Å

The acid form of the potassium silicate has spacings of 21.3–21.8Å which decrease to 19.0–19.7Å by air-drying. Rehydration reconstitutes the 22Å-form. The acid forms of synthetic kenyaite and the sodium silicate have spacings of 19.5–20.8Å, 17.7–18.0Å after air-drying and ≤18.6Å after rehydration. Thus, the transformation of the potassium silicate into the sodium silicate and vice versa proceeds through two acid forms which are very similar but not identical:

$$\begin{tikzcd}
\text{potassium silicate} \arrow[d, shift left, "H^+"] & \text{acid form-II} \arrow[l, "K^+"'] \arrow[d, shift left, "Na^+"] \\
\text{acid form-I} \arrow[u, shift left, "K^+"] \arrow[r, "Na^+"'] & \text{sodium silicate and kenyaite} \arrow[u, shift left, "H^+"]
\end{tikzcd}$$

(scheme I)

Since the spacings of both acid forms become identical after dehydration (≥120°C), the thickness of the silicate layers appears to be the same in all compounds. The interlayer cations probably influence orientation and arrangement of the $[SiO_4]$-tetrahedrons. Scheme I implies that the silicate layers retain some flexibility which allows an adaptation to the interlayer cations.

Conclusion

The reported studies make evident that the chemical composition and the X-ray powder patterns of synthetic and natural kenyaites can be sensitively changed: (1) by variations in the amount of interlayer water, if the physical conditions (for example, relative humidity, temperature) change, (2) by partial or complete exchange of the interlayer sodium ions by protons if kenyaite comes into contact with water. The changes are typical for intracrystalline reactive minerals. Other minerals showing this behavior are magadiite (Lagaly *et al.*, 1975a), kanemite (Beneke and Lagaly, 1977a), krautite (Beneke and Lagaly, 1981), uranium micas (Weiss and Hofmann, 1952), uvanite (Hilke *et al.*, 1973) and clay minerals.

Sodium interlayer cations are exchanged by protons even in alkaline solutions (pH ≥9, Fig. 4). Thus, when kenyaite is brought into contact with water, the water leaches sodium ions out of the structure. In the first stages of exchange (exchange ratio <20%) the basal spacings are only slightly changed. Eugster (1967, 1969) and Eugster *et al.* (1967) report a SiO_2/Na_2O ratio of 22 for kenyaite. The ratio in synthetic kenyaites is about 20 and appears to be confirmed by the composition of the analogous potassium silicate $K_2Si_{20}O_{41} \cdot xH_2O$. A higher ratio for natural kenyaite obviously can result from partial leaching by percolating water.

The variability of the powder pattern complicates the detection of kenyaite in nature. The changes reported in this study may aid in a proper identification of kenyaite even in mixtures with other sodium silicates.

Acknowledgments

Thanks are extended to Dr. Christian Samtleben, Mr. W. Reimann, and Mrs. U. Schuldt, of the Institute of Geology of the University of Kiel for taking the scanning electron micrographs. We are grateful to the "Fonds der Chemischen Industrie" for financial support.

References

Beneke, K. and Lagaly, G. (1977a) Kanemite—innercrystalline reactivity and relations to other sodium silicates. American Mineralogist, 62, 763–771.

Beneke K. and Lagaly, G. (1977b) Pecularities of intercalation reactions of the natural silicic acid silhydrite. Clay Minerals, 12, 363–365.

Beneke, K. and Lagaly, G. (1981) Krautite, $MnHAsO_4 \cdot H_2O$—an intracrystalline reactive mineral. American Mineralogist, 66, 432–435.

Brindley, G. W. (1969) Unit cell of magadiite in air, in vacuo and under other conditions. American Mineralogist, 54, 1583–1591.

Brindley, G. W. and Chang, Tsien-Show (1974) Development of long basal spacings in chlorites by thermal treatment. American Mineralogist, 59, 152–158.

Eugster, H. P. (1967) Hydrous sodium silicates from Lake

Magadi, Kenya: Precursors of bedded chert. Science, 157, 1177–1180.

Eugster, H. P., Jones, B. F., and Sheppard, R. A. (1967) New hydrous sodium silicates from Kenya, Oregon and California; possible precursors of chert. Geological Society of America, Program Annual Meeting, 1967, New Orleans, Louisiana, 60.

Eugster, H. P. (1969) Inorganic bedded cherts from the Magadi Area, Kenya. Contributions to Mineralogy and Petrology, 22, 1–31.

Frondel, C. (1979) Crystalline silica hydrates from leached silicates. American Mineralogist 64, 799–804.

Gude, A. J. and Sheppard, R. A. (1972) Silhydrite, $3SiO_2 \cdot H_2O$, a new mineral from Trinity county, California. American Mineralogist, 57, 1053–1065.

Hilke, K. J., Grosse-Brauckmann, U., Lagaly, G., and Weiss, A. (1973) Zur Chemie von Uranylvanadaten mit Trimetavanadationen und Schichtstruktur. Zeitschrift für Naturforschung, 28b, 239–245.

Iler, R. K. (1964) Ion exchange properties of a crystalline hydrated silica. Journal of Colloid and Interface Science, 19, 648–657.

Johan, Z. and Maglione, G. F. (1972) La kanemite, nouveau silicate de sodium hydraté de néoformation. Bulletin de la Société francaise de Minéralogie et de Cristallographie, 95, 371–382.

Kalt, A., Perati, B. and Wey, R. (1979) Intercalation compounds of $KHSi_2O_5$ and $H_2Si_2O_5$ with alkylammonium ions and alkylamines. Proceedings International Clay Conference, Oxford 1978, Elsevier, Amsterdam, 1979, 509–516.

Lagaly, G. (1979) Crystalline silicic acids and their interface reactions. Advances in Colloid Interface Science, 11, 105–148.

Lagaly, G. (1980) Kristalline Kieselsäuren, ihr Kaliumsalz, Verfahren zu ihrer Herstellung und ihre Verwendung. German Patent, P 2742 912 (August, 23, 1977).

Lagaly, G. and Matouschek, R. (1980) Die kristallinen Kieselsäuren aus Apophyllit, Carletonit und Gillespit. Neues Jahrbuch für Mineralogie, Abhandlungen 138, 81–93.

Lagaly, G., Beneke, K., and Weiss, A. (1973) Organic complexes of synthetic magadiite. Proceedings International Clay Conference, Madrid 1972, Division de Ciencias C.S.I.C., Madrid 1973, 663–673.

Lagaly, G., Beneke, K. and Weiss, A. (1975a) Magadiite and H-magadiite: I. Sodium magadiite and some of its derivatives. American Mineralogist, 60, 642–649.

Lagaly, G., Beneke, K., and Weiss, A. (1975b) Magadiite and H-magadiite: II. H-magadiite and its intercalation compounds. American Mineralogist, 60, 650–658.

Lagaly, G., Beneke, K. und Kammermeier, H. (1979) Neue Modifikationen des Siliciumdioxids. Zeitschrift für Naturforschung, 34b, 666–674.

Liebau, F. (1964) Über Kristallstrukturen zweier Phyllokieselsäuren, $H_2Si_2O_5$. Zeitschrift für Kristallographie, 120, 427–449.

McAtee, J. L., House, R., and Eugster, H. P. (1968) Magadiite from Trinity County, California. American Mineralogist 53, 2061–2069.

Pabst, A. (1958) The structure of leached Gillespite, a sheet silicate, American Mineralogist, 43, 970–980.

Sheppard, R. A., Gude, A. J., and Hay, R. L. (1970) Makatite, a new hydrous sodium silicate mineral from Lake Magadi, Kenya. American Mineralogist, 55, 358–566.

Schwarz, R., and Menner, E. (1924) Zur Kenntnis der Kieselsäuren (I). Chemische Berichte 57, 1477–1481.

Weiss, A. and Hofmann, U. (1952) Reaktionen im Innern des Schichtgitters von Uranglimmern. Zeitschrift für Naturforschung, 7b, 362–363.

Werner, H.-J., Beneke, K. und Lagaly, G. (1980) Die Acidität kristalliner Kieselsäuren. Zeitschrift für anorganische und allgemeine Chemie, 470, 118–130.

Wey, R., and Kalt, A. (1967) Synthèse d'une silice hydratée cristallisée. Comptes Rendues d'Academie de Sciences francais, Paris, 265, 1437–1440.

Manuscript received, April 23, 1982;
accepted for publication, December 8, 1982.