KAOLINITE SYNTHESIS: THE ROLE OF THE Si/Al AND (ALKALI)/(H$^+$) RATIO IN HYDROTHERMAL SYSTEMS

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Abstract—The Si/Al ratio of an hydrothermal system plays an important role in kaolinite synthesis. If the atomic Si/Al ratio of a system is greater than 2·0, kaolinite will disappear at 345 $\pm$ 5°C and 2 kbars water pressure according to the reaction kaolinite + 2 quartz → pyrophyllite + H$_2$O. If the atomic Si/Al ratio is less than 2·0, however, kaolinite will persist until 405°C where it will react according to the equation 2 kaolinite → pyrophyllite + 2 boehmite + 2 H$_2$O. The Si/Al ratio of the system and temperature are also factors in determining whether *b*-axis ordered or disordered kaolinite will crystallize. The ordered variety is favored by a lower Si/Al ratio and a higher temperature than is the disordered form.

Hydrothermal experiments also show that kaolinite can be synthesized at 150°C and 5 bars pressure in distilled water from amorphous starting materials. Previous investigators were unsuccessful in forming kaolinite under these conditions because their systems were contaminated with alkalis.

Attempts to synthesize halloysite and dickite failed, but halloysite was converted to kaolinite at 150°C, suggesting that halloysite can be synthesized only at low temperatures.

INTRODUCTION

Although minerals of the kaolinite group are among the most frequently studied clay minerals, knowledge of the physico-chemical conditions necessary for their formation remains unclear. The hydrothermal experiments reported here, which grew out of a larger study on experimental diagenetic reactions (Eberl, 1971), help to elucidate the following problems: (1) the temperature for the upper stability of kaolinite; (2) the

reasons why kaolinite is difficult to synthesize at low temperatures; and (3) the nature of the stability relationships between ordered kaolinite, *b*-axis disordered kaolinite, halloysite and dickite.

EXPERIMENTAL TECHNIQUES

The starting compositions listed in Table 1 were prepared by the Ludox gel method of Luth and Ingamells (1965). Two types of hydrothermal experiments were performed: (1) those carried out in small welded tubes (see Table 2); and (2) those run in large volume teflon reaction vessels (see Table 3).

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Table 1. Starting compositions

Comp. No.	Atomic proportions of the elements:				Mineral with analogous comp.	Crystallinity of starting comp.
	Si	Al	Na	K		
II	1.0	0.64	0.00	0.093	K-smectite	amorphous
V	1.0	0.64	0.056	0.038	Na$_{0.6}$-K$_{0.4}$ smec.	amorphous
VII	1.0	0.64	0.093	0.000	Na-smectite	amorphous
X	1.0	0.50	-----	-----	pyrophyllite	amorphous
XV	1.0	1.0	-----	-----	kaolinite	contains mullite
XVI	1.0	1.0	-----	-----	kaolinite	contains corundum
XVIII	1.0	1.5	-----	-----	1/2 kaolinite 1/2 gibbsite	contains corrundum
XIX					halloysite	natural sample that contains some gibbsite; sample from near Bloomington, Indiana.

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Table 2. Welded gold tube runs at 2 kbars water pressure. In this table and in subsequent tables Boeh = boehmite, Fs = feldspar, Gib = gibbsite, Halloy = halloysite, Hyd = hydralsite, I/S (80%) = a randomly mixed-layer illite/smectite that is 80% expandable, (I/S) ord. (35%) = an ordered mixed-layer illite/smectite that is 35% expandable (see Reynolds and Hower, 1970), Kao = kaolinite, Py = pyrophyllite, and Q = quartz

Run* No.	Starting Comp.	Temp. °C.	Run time (days)	Final pH at 25°C	Run products
7	II	343	23	4.6	I/S (80%), Kao
*8	II	347	88	3.8	(I/S) ord. (35%), Q, Fs
9	II	338	99	4.7	(I/S) ord. (25%), Q (?)
*14	II	394	169	---	(I/S) ord. (15%), Q, Py
76	X	253	99	6.0	Kao (disordered)
154	X	337	12	---	Kao (disordered)
77	X	347	74	4.4	Py
*78	X	379	169	4.7	Py, Q
79	XV	215	167	---	Kao (ordered)
80	XV	250	167	5.2	Kao (ordered)
81	XV	330	74	---	Kao (ordered)
*82	XV	285	74	---	Kao (ordered)
83	XV	358	28	---	Kao (ordered)
84	XVI	253	18	---	Kao (ordered)
85	XVI	360	28	---	Kao (ordered)
86	XVI	363	16	---	Kao (ordered) - 175 bars pressure
87	XVIII	310	28	---	Kao (ordered), Boeh
88	XIX	302	28	---	Kao (disordered)
*89	XIX	312	28	---	Kao (disordered)

* X-ray powder diffraction data for these runs can be found in Eberl (1971).

Table 3. Teflon bomb runs

Run Ref. No.	Starting Comp.	Temp. °C	Days	Initial Soln. Comp.	Final pH at Run T	Final Soln. (ppm) Na	K	Run Products
101	II	100	101	H_2O	7.3	2.3	17.0	No reaction
102	II	100	101	NaCl 2×10^{-3}M KCl 2×10^{-3}M KOH 10^{-4}M	6.7	19.0	145.0	No reaction
103	II	100	101	4×10^{-3} NKCl 10^{-4} NKOH	5.9	14.0	265.0	No reaction
104	II	126	85	H_2O	7.2	2.7	28.0	No reaction
105	II	152	101	H_2O	6.6	9.0	50.0	tr. Kao (?)
106	II	152	82	H_2O	7.4	4.0	44.0	No reaction
107	II	152	101	4×10^{-3}M NaCl 10^{-4} KOH	6.5	155.0	70.0	tr. Kao
109	V	100	101	H_2O	7.4	15.0	3.5	No reaction
110	V	126	85	0.1MNaCl 0.1MKCl 10^{-5}HCL	4.5	6.3×10^3	8.2×10^3	No reaction
111	V	152	82	H_2O	7.4	33.0	8.0	No reaction
112	V	152	101	KCl 2×10^{-3}N NaCl 2×10^{-3}N KOH 10^{-4}N	6.4	208.0	175.0	No reaction
113	V	152	82	KCl 0.1N NaCl 0.1N HCl 10^{-5}N	4.1	5.7×10^3	9.5×10^3	No reaction

Table 3. *cont.*

Run Ref. No.	Starting Comp.	Temp. °C	Days	Initial Soln. Comp.	Final pH at Run T	Final Soln. (ppm)		Run Products
						Na	K	
114	VII	100	101	H_2O	6.9	25.0	0.2	No reaction
115	VII	126	85	NaCl 0.1N KCl 0.1N HCl 10^{-5}N	4.5	$6.3x$ 10^3	$8.2 x$ 10^3	No reaction
116	VII	152	101	H_2O	6.9	60.1	1.0	tr. Kao
117	VII	152	82	H_2O	7.7	48.0	2.5	tr. Kao
118	VII	152	101	KCl $4x10^{-3}$N KOH 10^{-4}	6.0	101	245	No reaction
120	X	100	101	H_2O	5.9	5.5	2.7	No reaction
121	X	126	85	H_2O	6.2	5.0	8.0	tr Kao (?)
122	X	155	20	H_2O	4.0	13	1	poor Kao
*123	X	152	101	H_2O	5.9	23	1	Kao (disord)
124	X	152	82	HCl 10^{-4}N	4.5	23	3	Kao (disord)
125	X	152	82	HCl 10^{-4}N	3.8	19	1	Kao (disord)
126	X	152	82	1N NaCl 10^{-4} HCl	2.1	high	1	poor Kao
127	X	152	82	1N NaCl	2.3	high	1	poor Kao
128	X	152	78	1M KCl	2.1	----	----	No reaction
129	X	152	78	0.4M KCl 10^{-5} HCl	2.1	38	high	No reaction
130	X	152	78	$3.2x10^{-2}$M KCl 10^{-5}M HCl	2.7	16	160	Kao (disord)
131	X	159	78	10^{-2}M KCl 10^{-4}M HCl	2.6	16	960	Kao (disord)
132	X	159	78	H_2SO_4(2 drops)	0.6	----	----	tr. (?)
133	XV	152	82	H_2O	---	----	----	No reaction
134	XVI	155	20	H_2O	5.4	5	1	poor Kao
135	XVI	152	78	H_2O	4.7	----	----	Kao
137	XVIII	158	60	H_2O	4.6	---	---	Kao slightly ordered
138	XVIII	158	60	HCl (1 drop)	2.0	---	---	Kao (disord)
139	XX	155	20	H_2O	4.5	8	0.2	poor Kao
140	XIX	152	78	HCl 10^{-4}N	3.8	---	---	Kao + Halloy + Gib + Boeh
141	XIX	158	78	H_2O	5.2	---	---	same as 140

Pressure at 100°C = 1 bar, pressure at 126°C = 2 bar, pressure at 152°C = 5 bars.

The gold tube hydrothermal runs were made by putting 30 mg of the powdered starting materials into 1·90 cm long gold tubes (3·05 mm o.d., 2·54 mm i.d.) containing 35 μl of distilled water that had been introduced into the tube with a micro-syringe. The tube was then welded shut and placed in a stainless steel rod-type reaction vessel of the Tuttle-type. The water pressure in the bomb was controlled at 2 kbars by equilibration with a 2-l. reservoir connected to the reaction vessel. The reaction vessel was sealed from the reservoir when it reached the desired temperature. In several experiments the reaction vessels were run as autoclaves at low pressures.

Temperatures were maintained in horizontal resistance-type furnaces by on–off regulators; the furnace temperature was measured by an external thermocouple located in a well in the side of the vessel. The temperatures were corrected for temperature differ-

ences between the exterior and interior of the vessel and are accurate to within ± 5°C.

The teflon vessel runs were made by putting 100 mg of starting material and 25 ml of solution into teflon reaction vessels made by boring out solid teflon rods. These vessels were sealed with a teflon screw-type top and reinforced with hose clamps. The vessels were then placed in large boiling flasks which contained ethylene glycol–water mixtures that boiled at the desired temperatures. The flasks were topped with reflux condensers and left to boil on hot plates.

The solid run products were identified by X-ray powder diffraction methods. The pH of the final solution for the teflon bomb runs was measured with a Beckman SS-3 pH meter immediately on opening the vessel. These pH values were then corrected to the pH at run temperature by calculation (Krauskopf, 1967). The pH of the gold tube runs was measured

Table 4. Runs for which the reaction kaolinite + 2 quartz → pyrophyllite + H_2O was determined to be 345 ± 5°C at 2 kb water pressure

Starting Comp.	Temp. Degrees C	Run Time (days)	Run Products	Run No.
X	253	99	Kao	76
II	338	99	Kao, I/S, Q (?)	9
II	343	23	Kao, I/S	7
X	337	12	Kao (disordered)	154
II	347	88	I/S, Fs, Q	8*
X	347	74	Py	77
X	379	169	Py,Q	78
II	394	169	Py, I/S, Q	14*

from the damp to wet run product by using a single drop electrode. These pH values are reported as measured at 25°C. The teflon bomb final solutions were analyzed for sodium and potassium by flame emission with a model 303 Perkin-Elmer atomic absorption spectrophotometer.

THE UPPER STABILITY OF KAOLINITE

In the experiments presented in Table 4, the disappearance of kaolinite and the appearance of pyrophyllite occurs at 345 ± 5°C with 2 kbars water pressure in systems that have a Si/Al ratio similar to that of pyrophyllite. This temperature, however, is not the upper synthesis limit for kaolinite. As will be shown, kaolinite may persist to 405°C if the Si/Al ratio of the system is low.

Previous attempts to determine the upper temperature stability limit of kaolinite are given in Table 5. These temperatures center about two values; (1) 345°C if the Si/Al ratio of the experimental system is that of pyrophyllite and (2) 405°C if the Si/Al ratio is that of kaolinite. The former temperature is most likely the synthesis temperature for the reaction; kaolinite + quartz → pyrophyllite + H_2O. The latter temperature is probably the synthesis temperature for the reaction; 2 kaolinite → pyrophyllite + 2 boehmite + $2H_2O$.

Table 5. Temperatures of the upper stability of kaolinite from the data of various authors. (nat) = natural sample

| Reactants	Products	Temperature °C (at 2 kb unless otherwise noted)	Author
Py (nat), Kao (nat) Q (nat)	solution study	350 ± ?(1 kb)	Hemley, et. al. (1964)
Py (nat), Kao (nat) Q (nat)	ppt. study	345 ± 10	Thompson (1970)
Kao (nat), excess SiO_2 (amorphous)	Py	355 ± 8	Carr, et. al. (1960)
Kao (nat), excess SiO_2 (amorphous)	Py	340 ± ?	Carr (1963)
glass of Py composition (X)	Py	345 ± 5	this study
Kao (nat), 2Q (nat)	Py	420 ± 5	Winkler (1957)
Kao (nat), 2Q (nat)	Py	414 ± 7	Carr, et. al. (1960)
glass of Py composition	Py	311 ± 8	Velde, et. al. (1969)
Kao (nat), excess Q	Py	390 ± 10	Althaus (1956)
Kao polymorphs (natural)	Py, Hyd	405 ± 10 (1 kb)	Roy, et. al. (1954)
glass of Kao composition	Hy	405 ± 10 (1 kb)	Roy, et. al. (1954)
glass of Kao composition	Py, Boeh	405 ± 10 (4 kb)	Aramaki, et. al. (1963)
glass of Kao composition	Py, Boeh, Hyd	398 ± 10	Velde, et. al. (1969)
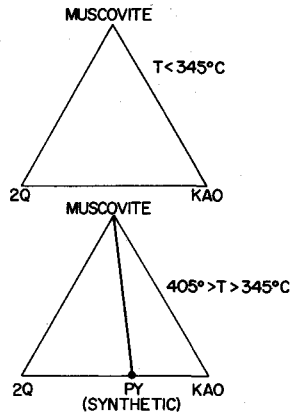
Fig. 1. Synthesis relations in the system muscovite–quartz–kaolinite–water, showing the appearance of synthetic pyrophyllite at 345°C. An illite stability field has been omitted for clarity.

Synthesis relations for the disappearance of kaolinite can be visualized by referring to Fig. 1. Below 345°C in this system, kaolinite is crystallized regardless of the amount of silica present. Between 345 and 405°C, however, kaolinite appears only if the starting composition has less silica than synthetic pyrophyllite. As is discussed in Eberl and Hower (in press) synthetic pyrophyllite may contain more aluminum than the ideal pyrophyllite composition. Above 405°C, kaolinite reacts to form pyrophyllite and hydralsite, a meta-stable phase which, with time, decomposes to pyrophyllite and boehmite (or diaspore).

The high temperatures given in Table 5 by Winkler (1957), Althaus (1956) and Carr et al. (1960) for the unreversed reaction of natural kaolinite and quartz to pyrophyllite are probably a function of slow reaction rates: quartz is slow to decompose and does not participate in the reaction. These authors are, in effect, determining reaction temperature in a system with a Si/Al ratio of kaolinite. If the reaction is monitored by observing changes in the solution composition (Hemley et al., 1964), or by weight changes in quartz crystals (Thompson, 1970), then the onset of reaction can be determined more precisely. The temperature determined in these ways for the reaction of natural quartz and kaolinite is about 345°C, the same temperature obtained by crystallization from amorphous starting materials.

The low temperature determined by Velde et al. (1969) for the upper stability of kaolinite in a system of pyrophyllite composition may be due to the mis-identification of pyrophyllite. Pyrophyllite was identified by its (003) diffraction peak in the range 3·03–3·10 Å. The pyrophyllite first order reflection was not seen in most of their diffraction patterns. The 3·03–3·10 Å peak could have resulted from a phase other than pyrophyllite.

The temperatures of 345 and 405°C found for the reactions previously discussed should not be taken as equilibrium temperatures. Since none of the reactions reported in Table 5 were reversed, it can only be said

that these temperatures are accurate for runs of relatively short duration (e.g. less than 100 days). Thus Fig. 1 is a synthesis diagram rather than an equilibrium phase diagram.

THE CRYSTALLIZATION OF KAOLINITE AT LOW TEMPERATURE

It was shown in the previous section that kaolinite will crystallize in water at elevated temperatures directly from glasses of pyrophyllite and kaolinite composition. Kaolinite synthesis at lower temperatures, however, has met with exceptional difficulties (De Kimpe, 1967; 1969; De Kimpe et al., 1961; 1968). Prior to 1970, no appreciable yield of kaolinite had been obtained from amorphous starting material below 250°C, although individual kaolinite-like crystals were detected by electron diffraction in runs with temperatures as low as 25°C (Polzer et al., 1967). This difficulty in synthesizing kaolinite is surprising since field evidence suggests that kaolinite forms abundantly in nature at low temperature and slightly acid pH. Many frustrated attempts to synthesize kaolinite led one investigator to conclude that, "The direct transformation from the gel into a clay mineral (kaolinite) using an acid solution or water is not feasible." (De Kimpe, 1969).

De Kimpe (1969), however, crystallized b-axis disordered kaolinite in a sealed Pyrex tube starting with an alumino–silicic gel heated at 175°C for 16 days. The initial pH, which he considered critical to the synthesis, was 13 with NaOH. After completion the pH was 6. He proposed that the kaolinite formed from an undetected intermediate zeolitic phase which forms readily at high pH. In another experiment, Brindley and De Kimpe (1961) synthesized a poorly crystalline b-axis disordered kaolinite in a Pyrex tube starting with gibbsite and amorphous silica (Ludox) at 150°C with a pH below 1·5 with HCl.

The most successful experiment prior to 1970 was that of Roy and Osborn (1954). Using gold envelopes as reaction containers, they ran purified alumino–silica gels in water at 155°C and 5 bars pressure. After 11 days they obtained a poorly crystalline kaolinite mineral, but their X-ray pattern was to diffuse to identify the polymorph.

In the present experiments, which were performed in teflon reaction vessels, a well-developed b-axis disordered kaolinite (Fig. 2) was synthesized from glasses with the composition of pyrophyllite (composition X) and kaolinite (composition XVI) in distilled water (runs 123, 135) and in slightly acidic water (runs 124, 125) at 152°C after 80–100 days, as is shown in Table 3. After 20 days these glasses had formed only a poorly crystalline kaolinite (runs 122, 134). An extremely poorly crystalline kaolinite–like mineral, identifiable only by diffuse hkl X-ray reflections, was synthesized in water at 126°C (run 121). Glasses treated at 100°C did not crystallize (runs 120, 101–103, 109, 114). Glass compositions that contained sodium or potassium (compositions II, V, and VII)
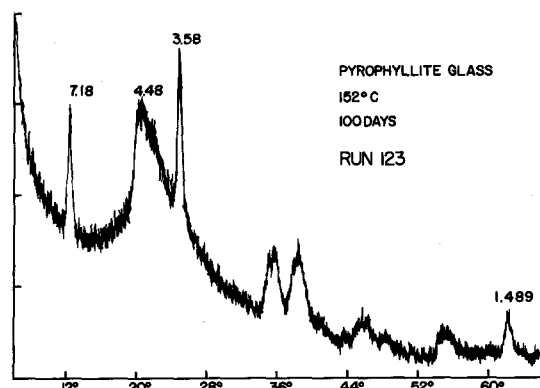
Fig. 2. X-ray powder diffraction pattern (Cu Kα; degrees
2θ) of a b-axis disordered kaolinite formed in a teflon
bomb run from composition X after 100 days at 152°C
and 5 bars water pressure. Sample prepared from random
orientation of crystallites.

run in either water or NaCl and KCl solutions also
did not crystallize (runs 105–118). This study demon-
strates that disordered kaolinite can be crystallized
directly from amorphous starting material in a
nearly neutral solution at relatively low temperatures
provided the run time is long enough (greater than
20 but less than 80 days), and the activity of Na^+
and K^+ in the system is low.

Hemley and Jones (1965) have shown that kaolinite
stability in the system Na_2O–K_2O–Al_2O_3–SiO_2–
H_2O depends on the ratio of alkali activity to hydro-
gen ion activity. This relationship is manifested in the
following equation for the breakdown of muscovite:

$$2 \text{ muscovite} + 2\,H^+ \rightarrow 3 \text{ kaolinite} + 2\,K^+$$
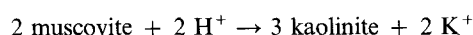
for which the equilibrium constant is:

$$K\text{-equil.} = \frac{(K^+)}{(H^+)}.$$

A similar reaction can be written for paragonite,
yielding an equilibrium constant equal to $(Na^+)/(H^+)$.
Using thermodynamic data for these and similar reac-
tions in the system HCl–H_2O–Al_2O_3–K_2O–Na_2O–
SiO_2 at 150°C, Helgeson et al., (1969) have con-
structed an activity diagram that shows the stability
fields for kaolinite, Na–montmorillonite, muscovite,
and feldspar as a function of the $(alkali)/(H^+)$ ratio
of the solution (Fig. 3). The calculated final solution
compositions of some of the 150°C teflon bomb ex-
periments reported in Table 3 are plotted on this dia-
gram. It is apparent from this figure that those glasses
from which crystallized a good kaolinite had solution
compositions that lay well within the kaolinite stabi-
lity field. With two exceptions, those runs which did
not crystallize or which crystallized only a trace of
kaolinite had solution compositions which lay on the
fringes or outside of the kaolinite field as defined by
Helgeson et al. (1969). The exceptions were pyrophyl-
lite glasses run in concentrated KCl solutions (runs 128
and 129) which had final pH's that were low enough
for their solution compositions to fall within the kao-

linite field. Thus it appears either that the phase
boundary in this region of the diagram is incorrect,
or that even if the solution composition lies within
the kaolinite field, large amounts of alkali or chlorine
can retard kaolinite formation.

The data in Table 3 demonstrate that kaolinite is
easily crystallized at 150°C in nearly neutral condi-
tions from an alumino–silicic glass if the $(alkali)/(H^+)$
ratio is low. The failure of previous attempts may
be attributed to contamination of the system with
alkali. Previous experiments were conducted in Pyrex
glass tubes rather than the teflon bombs used here.
Pyrex contains 3% sodium that could be leached from
the walls of the tube during the experiment and so
move the solution composition out of the kaolinite
stability field if the pH of the system is near neutra-
lity. Thus Brindley and De Kimpe (1961), in an exper-
iment mentioned previously, were able to form kao-
linite in Pyrex tubes at 150°C only if the pH of the
solution was below 1·5. In contrast, Roy and Osborn
(1954), in an experiment also mentioned previously,
were able to crystallize a kaolinite mineral at 155°C
by using alkali-free gels heated in gold reaction
vessels.

The starting glasses used in the experiments
reported here were contaminated with sodium
because the colloid Ludox, which was used as a
source of amorphous silica, is stabilized with NH_4OH
which contains a small amount of sodium: the Ludox
used was 6·1 M with respect to silica and 0·02 M with
respect to sodium. The large (250:1) water to sample
ratio employed, however, reduced the $(Na^+)/(H^+)$
ratios to values that lay within the kaolinite stability
field.

As mentioned previously, this successful synthesis
of kaolinite was carried out at 150°C starting with
amorphous material and water. With different initial
conditions, however, a significant amount of kaolinite
can be formed even at room temperature. In a recent
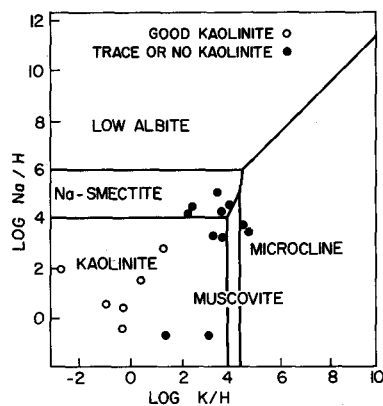paper, Kittrick (1970) reports the formation at room

Fig. 3. Stability diagram for the system Na_2O–K_2O–HCl–
Al_2O_3–SiO_2–H_2O at 150°C (after Helgeson et al., 1969) on
which are plotted the final solution compositions and solid
productions of some teflon bomb runs.

temperature of kaolinite from montmorillonite in a solution that was supersaturated with respect to kaolinite after a run of 3–4 yr. The result of this experiment was not surprising since montmorillonite can weather to form kaolinite (Altschuler *et al.*, 1963). In other recent papers, Linares and Huertas (1971) synthesized a 'pre-kaolin'-type mineral at room temperature in just one month from solutions of monomeric silica and aluminum–fulvic acid, and Hem and Lind (1974) synthesized some well crystallized material of kaolinitic appearance at 25°C after 6–16 months in solutions that contained quercetin, an organic flavone. Huang and Keller (1970) have shown that the solubility of aluminum and silica can be enhanced by complexing with organic acids. The presence of organic compounds in the experiments of Linares, *et al.* and Hem, *et al.* probably served to mobilize aluminum, which would otherwise have been highly insoluble at such a low temperature, so that it could participate in the reaction. Thus the formation of kaolinite at low temperatures in nature may be catalyzed by the presence of organic compounds.

THE SYNTHESIS OF ORDERED KAOLINITE

The genetic relationship between ordered and *b*-axis disordered kaolinite is not well understood. Experiments were undertaken to determine the effect of the Si/Al ratio of the system on the crystallization of these two polymorphs. As is shown in Table 6, starting glass X of pyrophyllite composition (Si/Al = 2·0) formed disordered kaolinite regardless of the run temperature. Starting compositions XV and XVI of kaolinite composition (Si/Al = 1·0) crystallized ordered kaolinite at all but the lowest temperature. Starting material XVII with a composition equivalent
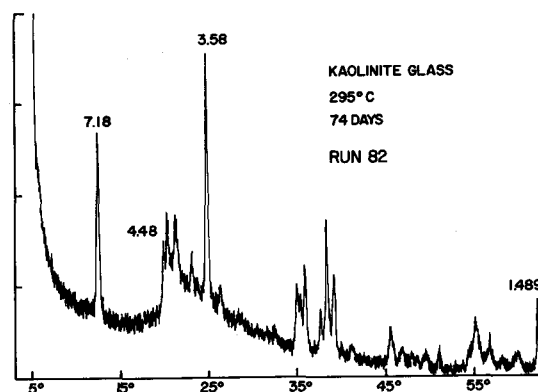

Fig. 4. X-ray powder diffraction pattern (Cu Kα; degrees 2θ) of an ordered kaolinite formed from composition XV held at 285°C and 2 kbars water pressure for 74 days. Sample prepared for random orientation of crystallites.

to 1/2 kaolinite and 1/2 gibbsite (Si/Al = 0·67) began to show signs of ordering even at 158°C. Figure 4 is a typical X-ray powder diffraction pattern of the synthesized ordered kaolinites.

These data suggest that the formation of ordered kaolinite in an experimental system is favored by a low Si/Al ratio and a high temperature. A third factor also may be important: there is field evidence to suggest that the formation of ordered kaolinite in nature often results from the alteration of certain high temperature minerals. Sand (1956), in a study of kaolin deposits in the southeastern United States, found ordered kaolinite to be pseudomorphous after muscovite. In the same deposits he observed that feldspar had altered to endellite. Thus minerals in the original rock may exert structural control over the type of kaolinite formed on alteration.

Table 6. The synthesis of *b*-axis disordered and ordered kaolinite. The 152 and 158°C runs were made in teflon bombs at 5 bars water pressure. All other runs were made in gold tubes at 2 kb water pressure

Composition	Si/Al	Temp °C.	Run Time (days)	Run Product	Run No.
X	2.0	152	80–100	Kao (disordered)	122–125* 130–131
		253	99	Kao (disordered)	76
		337	12	Kao (disordered)	
XV	1.0	152	80	No reaction	133
		215	167	Kao (ordered)	79
		285	74	Kao (ordered)	82*
		358	28	Kao (ordered)	83
XVI	1.0	152	78	Kao (disordered)	135
		253	18	Kao (ordered)	84
		363	16	Kao (ordered)	86
XVII	0.67	158	60	Kao (slightly ordered)	137
		310	28	Kao (ordered)	87

Pre-existing high-temperature structures, however, were probably not important in these hydrothermal experiments. Starting compositions XV and XVI have the same Si/Al ratio, but XV initially contained mullite and XVI contained a small amount of corundum. These high-temperature phases formed when the gels were fired during preparation of the starting glasses (see Luth and Ingamells, 1965). Despite this difference in initial crystallinity, the ordered kaolinites that formed from XV and XVI appear to be identical. The only difference in behavior between the two compositions was that composition XV could not react at 152°C due to the large activation energy for the breakdown of mullite.

HYDROTHERMAL INVESTIGATIONS OF HALLOYSITE AND DICKITE

Unsuccessful attempts were made to synthesize halloysite. Keller has suggested that halloysite formation may depend on the presence of sulfate (Keller et al., 1968), K^+ (Keller, 1963) and excess aluminum (Keller, 1970). All of these components were tried in teflon bombs containing glass of pyrophyllite composition and water at 150°C: a run containing H_2SO_4 crystallized only a trace of an unidentified phase (run 132, Table 3); various concentrations of potassium in the system either produced disordered kaolinite or remained amorphous (runs 128–131); and kaolinite rather than halloysite was crystallized in runs with aluminum in excess of that required to produce kaolinite (runs 137–138).

In another experiment, a natural sample of halloysite (composition XIX) was treated hydrothermally at 152 and 312°C (runs 140 and 88) and was converted to a non-hydrated b-axis disordered kaolinite. This experiment suggests that halloysite synthesis should be attempted at low temperatures (that is, somewhere below 150°C). Indeed, the most successful attempt to synthesize halloysite to date was made at 78°C: Parham (1969) artificially weathered feldspars at this temperature for 140 days and produced tube-like structures reminiscent of halloysite. In another study, Hem et al. (1973) outlined the apparent stability field at 20°C of an aluminosilicate precipitate having an Si/Al ratio of one. The precipitate was amorphous and had a higher solubility product than kaolinite. Hem et al. concluded, on the basis of several lines of evidence, that the amorphous material was protohalloysite.

Attempts were also made to synthesize dickite. Schroeder and Hayes (1967) have offered field evidence that dickite is a high temperature form of kaolinite. The starting material of kaolinite composition was run at temperatures ranging from 285 to 363°C at various pressures (runs 82–86). All of these runs produced ordered kaolinite. The conditions for run No. 86 are nearly identical to a run made by Ewell and Insley (1936) in which they claim to have synthesized dickite.

CONCLUSIONS

The Si/Al ratio and the (alkali)/(H^+) ratio of hydrothermal systems are important factors in kaolinite synthesis. If the Si/Al ratio lies between the values for pyrophyllite and quartz, kaolinite disappears above 345°C. If the Si/Al ratio lies between the values for pyrophyllite and kaolinite, kaolinite persists until 405°C. Crystallization of the ordered variety of kaolinite is favored by a lower Si/Al ratio and a higher temperature than is the disordered form.

At low temperatures, kaolinite can be synthesized at 150°C and 5 bars pressure in distilled water from amorphous starting materials if the (alkali)/(H^+) ratio of the experimental solution is low. Kaolinite formation at still lower temperatures may be catalyzed by the presence of complexing organic compounds which serve to mobilize aluminum.

Attempts to synthesize halloysite and dickite failed, but halloysite was converted to kaolinite at 150°C, indicating that halloysite is a low temperature polymorph.

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