

## KAOLINITE CRYSTALLIZATION AT ROOM TEMPERATURE BY HOMOGENEOUS PRECIPITATION—III: HYDROLYSIS OF FELDSPARS

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**Abstract**—The kaolinite crystallization by homogeneous precipitation with previous hydrolysis of the feldspars added has been followed by pH and potassium concentration measurements. The synthesized products were studied by X-ray powder diffraction and electron microscopy and consist of kaolinite and mica, accompanied occasionally by traces of smectite. The relative quantities of the synthesized minerals depend fundamentally on the supply rate of the alkaline ions.

### INTRODUCTION

Clay mineral synthesis at room temperature has been achieved by using the genesis conditions of these minerals in the edaphic and sedimentary environments. The synthesis of kaolinite has been carried out by considering distinct aspects, for example, the facility to build the gibbsite layer (Caillere and Henin, 1948–1962), the duality of aluminium coordination (Gastuche *et al.*, 1962) and the necessity to form complexes with a tightly bound shell of water molecules and/or the formation of insoluble Al–polycations (Siefert and Wey, 1972).

Considering this last idea Linares and Huertas (1971) realized the kaolinite synthesis with fulvic acids as complexing agents. La Iglesia and Martin Vivaldi (1972) observed that kaolinite precipitation with fulvic acids occurs when there is a pH variation in the solution, assuming that this variation is the cause of the crystallization. Taking into account that the progressive and slow pH variation vs time is one of the ways of homogeneous precipitation, these authors apply this technique to synthesize kaolinite in two systems; (a) acid solutions of silica, aluminium ions and anionic resins in OH<sup>-</sup> form and (b) alkaline solutions of silica, aluminium ions and cationic resins in H<sup>+</sup> form. Good results were obtained in both systems (La Iglesia and Martin Vivaldi, 1975) and (La Iglesia and Serna, 1974). In the present paper, kaolinite crystallization is studied with previous hydrolysis of the added reagent to generate the active ion precipitant.

### EXPERIMENTAL

The experimental conditions were as follows: (a) acid solutions (pH ~ 4) containing sodium silicate and aluminium chloride or acetate, with a silica concentration of 83 ppm and an alumina concentration of 192 ppm, and (b) acid solution (pH ~ 4) containing aluminium chloride or acetate, with an alumina concentration of 211 ppm.

The OH<sup>-</sup> ions, necessary for homogeneous precipitation, were obtained by hydrolysis of microcline and adularia with particle sizes between 0.2–0.1 mm and 0.1–0.053 mm. Five g of feldspars were added to 330 ml of the above solutions. Mixtures in polyethylene flasks were left for 30 days with occasional stirring and after this period the precipitates were separated from the feldspars by decantation and centrifugation and then identified by X-ray powder diffraction and electron microscopy.

The feldspars, microcline of Zarzalejo (Madrid, Spain) and adularie of Saint Gotarde (Switzerland), were previously purified with a Franz isodynamic separator and were identified by X-ray powder diffraction and chemical analysis (Table 1).

### RESULTS

Hydrolysis of the feldspars was followed by pH and potassium concentration measurements. These measurements are summarized in Table 2. The variation of both parameters is linear after the first day. Figure 1 shows the pH values in relation to the potassium concentrations. The linear relation corresponds

TABLE 1

Chemical analyses of the feldspars used, in weight percent

	Microcline	Adularia
SiO <sub>2</sub>	65.16	63.72
Al <sub>2</sub> O <sub>3</sub>	21.52	20.81
Fe <sub>2</sub> O <sub>3</sub>	0.15	0.41
CaO	tr.	tr.
MgO	0.06	0.04
Na <sub>2</sub> O	2.23	1.11
K <sub>2</sub> O	10.18	13.36
H <sub>2</sub> O <sup>+</sup>	0.16	0.08
H <sub>2</sub> O <sup>-</sup>	0.14	0.12
Total	99.60	99.65

TABLE 2  
Hydrolysis of feldspars in H<sub>2</sub>O. A few pH and potassium concentration measurements

Time in days		1	7	12	19	22	29	43	45
Microcline 0.2-0.1 mm	pH	6.70	6.91	6.82	6.86	6.80	6.82	7.0	7.0
	K <sup>+</sup>	38.88	48.60	58.32	77.76	97.20	102.06	106.92	140.94
Microcline 0.1-0.053 mm	pH	6.64	6.7	6.75	6.76	6.82	6.90	6.98	7.0
	K <sup>+</sup>	87.48	92.34	97.20	116.64	136.08	155.52	174.96	174.96
Adularia 0.2-0.1 mm	pH	6.75	6.65	6.75	6.75	6.70	6.90	7.20	7.0
	K <sup>+</sup>	116.64	126.36	145.80	165.24	179.82	199.26	204.12	218.70
Adularia 0.1-0.053 mm	pH	6.50	6.82	6.90	7.05	7.10	7.15	7.20	7.50
	K <sup>+</sup>	111.64	126.36	130.56	145.80	155.52	170.68	184.68	204.12

to one proton of the solution exchanging with one potassium from the feldspar.

In Figs. 2 and 3, the pH and [K<sup>+</sup>] variations versus time are represented for the 16 systems studied. While there is an increase of the potassium concentration there is no pH variation, even though such variation occurs in the feldspar-H<sub>2</sub>O systems (Fig. 1).

The pK variations vs time are straight lines indicating a first order reaction. The constant rates calculated from the slope of the straight lines, for all studied systems, are listed in Table 3. These values clearly show that the reaction rates are influenced by the type of feldspar, the particle size and the nature of the anion (chloride or acetate).

Measurements of SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> concentration in the different systems were made after 60 days, con-

sidering that after this period equilibrium has been established. Results are summarized in Table 4.

The X-ray powder diffraction study of the precipitates indicates the presence of kaolinite and mica, occasionally accompanied by smectite and basic aluminum acetates. Using calcite as an internal standard, an estimate of the clay mineral content was made. Samples containing acetates were heated at 300°C in order to eliminate this anion. The percentage of clay mineral varies between 6 and 10% in the microcline systems and between 5 and 9% in the adularia systems. The relative estimate between the different clay minerals is summarized in Table 5. Figures 4 and 5 show some of the diagrams obtained.

In order to study the morphology of the obtained crystals, different precipitates have been observed under the electron microscope. The identification of crystals by this technique is difficult since they are embedded in amorphous material. The distinction between kaolinite and mica crystals is based on the kind and size of the observed crystals. It is considered that the crystals with hexagonal morphology (120° angles) and a particle size between 0.1 and 1 micron (Figs 6a, b and c) are kaolinites, while irregular crystals with a particle size larger than 3 μm and sufficient thickness to produce Kikuchi's bands correspond to micas (Fig. 6d).

#### DISCUSSION

La Iglesia and Martin Vivaldi (1974) pointed out that crystallization of kaolinite is possible by homogeneous precipitation, independent of the method used. In fact, as our results show, this crystallization is possible with the proposed conditions. However, under these conditions, mica and occasionally smectites also are crystallized.

In the different experimental systems a homogeneous precipitation has been obtained, since the previous hydrolysis of the reagents added to the ionic solution, in order to generate the active ion, has been practically realized in a progressive form and simultaneously at all points of the solution. In fact, the hydrolysis of feldspars produces K<sup>+</sup> and OH<sup>-</sup> at a rate, which permits their diffusion in the solution.

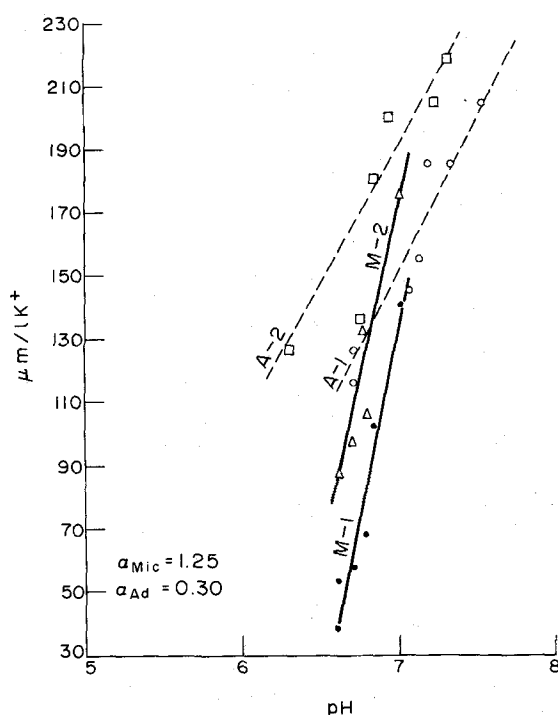


Fig. 1. Relation between pH and potassium concentration in the feldspar-H<sub>2</sub>O systems.

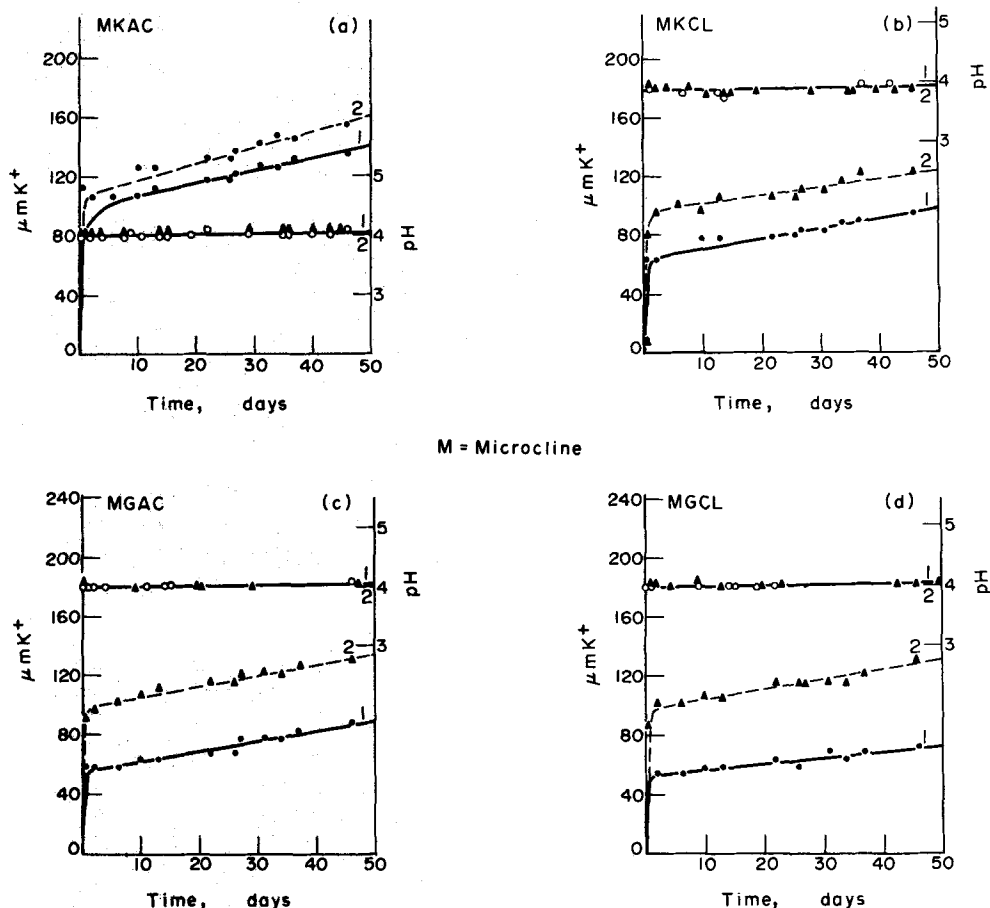


Fig. 2. pH and potassium concentration variations vs time for the microcline systems.

This last assumption is supported by the following experimental data:

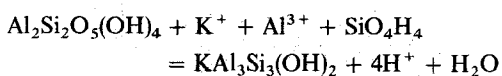
(a) A concentration gradient of potassium and pH does not exist in the different solutions.

(b) The increase of the potassium concentration and the pH variation occur linearly as a function of time. The dispersion of the experimental values is within the range of measurement errors.

(c) In the feldspar-H<sub>2</sub>O systems the pK and pH variations are proportional independently of the particle size. However, the evolution is different according to the kind of feldspar.

In the aluminium-silica-feldspar and aluminium-feldspar systems, the increase of potassium concentration does not produce a pH variation. This is due to the fact that OH<sup>-</sup> ions are used in the formation of different aluminium hydroxylic species and demonstrates that homogeneous precipitation occurs with previous hydrolysis of the reagent added to the solution.

According to Huang's diagrams (1973) for SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>-K<sub>2</sub>O-H<sub>2</sub>O systems and taking into account the mica-kaolinite equilibrium given by the reaction:

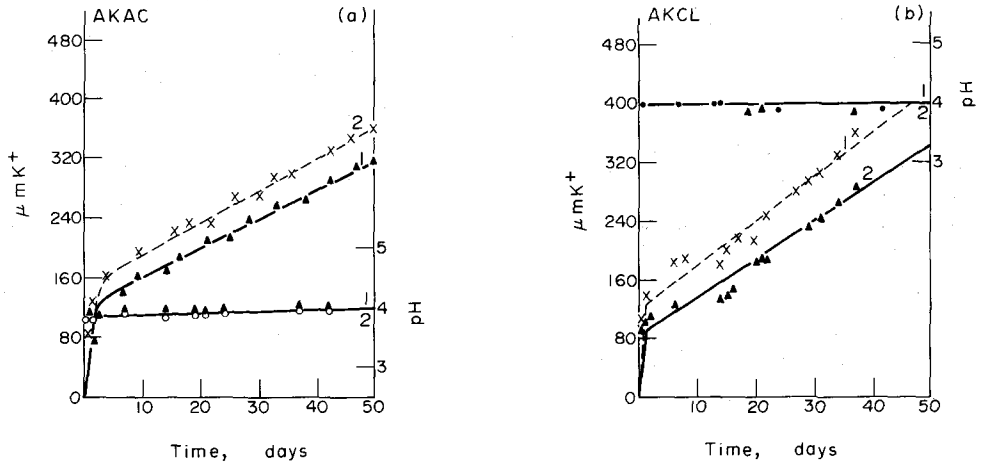


it is possible to represent, for a fixed pH, the mica and kaolinite stability fields, as a function of the pK and pAl-pSiO<sub>4</sub>H<sub>4</sub>. In our case the pH considered has been 4.0, however in all the experimental systems the pH oscillates between 3.9 and 4.1. This pH has been chosen according to the kaolinite solubility diagram calculated by Huang and Keller (1973), since in this range the kaolinite is more soluble and consequently the obtained products are more crystalline. A more acid pH has not been chosen because under these conditions there is a displacement of the feldspar hydrolysis equilibrium to greater potassium concentrations and therefore the homogeneous precipitation would take place in the mica stability field.

Equilibrium constants (K) for the above reaction have been obtained by the known values of the standard free energies of formation ( $\Delta G_f^\circ$ ) (Huang, 1973). Then the following relations are obtained for the mica-kaolinite and mica-halloysite equilibria:

$$6.48 - \log[\text{K}^+] - 4\text{pH} = \log[\text{Al}^{3+}] + \log \text{SiO}_4\text{H}_4 \\ 3.26 - \log[\text{K}^+] - 4\text{pH} = \log[\text{Al}^{3+}] + \log \text{SiO}_4\text{H}_4.$$

Figure 7 is a plot representing these equations and shows the stability fields of halloysite, kaolinite and mica.



A = Adularia

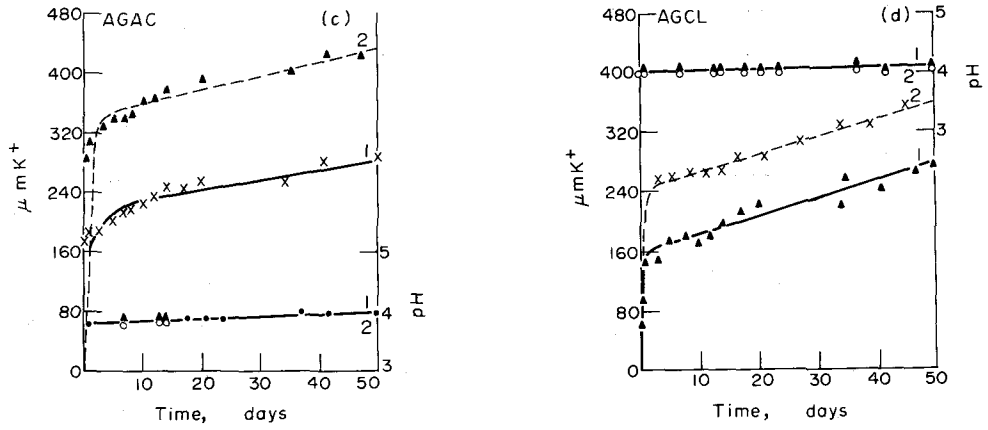


Fig. 3. pH and potassium concentration variations vs time for the adularia systems.

TABLE 3

Rate constants ( $\text{days}^{-1}$ ) calculated by ( $K^+$ ) measurements

Solution	Feldspars	
	Microcline	Adularia
KAc-1	0.0070 ± 0.0001	0.0171 ± 0.0003
KAc-2	0.0080 ± 0.0001	0.0183 ± 0.0002
KCl-1	0.0076 ± 0.0002	0.0209 ± 0.0001
KCl-2	0.0051 ± 0.0002	0.0232 ± 0.0002
GAc-1	0.0087 ± 0.0001	0.0053 ± 0.0001
GAc-2	0.0061 ± 0.0001	0.0048 ± 0.0001
GCl-1	0.0063 ± 0.0003	0.0105 ± 0.0002
GCl-2	0.0056 ± 0.0002	0.0081 ± 0.0001

K = with silica and aluminium in solution

G = with aluminium in solution

Ac = with acetate anions

Cl = with chloride anions

1 = particle size between 0.2-0.1 mm.

2 = particle size between 0.1-0.053 mm.

TABLE 4

SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> concentrations (ppm) in the systems studied at equilibrium (60 days).

	Microcline		Adularia	
	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>
KAc-1	68	159	76	100
KAc-2	71	169	73	111
KCl-1	76	166	68	173
KCl-2	77	169	66	189
GAc-1	53	152	63	133
GAc-2	56	169	n.a.	n.a.
GCl-1	52	176	60	189
GCl-2	57	176	59	200

The log K values, as calculated by us, are different from those obtained by Huang (1973) because the stability boundaries he used represent the maximum in an ideal system, while in ours the errors in the standard free energy determinations were considered. The resulting diagram (Fig. 7) in which the position of both stability boundaries has been displaced upward, allows qualitative estimation of the mineralogical composition of the reaction products.

In Fig. 7 point A represents the initial concentration of silica, aluminium and potassium in the feldspar-silica-aluminium systems if pK is the minimum detection limit of the photometer used. Point D corresponds to the initial concentration of similar ions in the feldspar-aluminium systems, when pAl is the minimum detection limit of the atomic absorption

spectrophotometer used. For example in the MKAc-1 system the concentration of SiO<sub>4</sub>H<sub>4</sub>, Al<sup>3+</sup> and K<sup>+</sup> changes during the first day from point A to point B. The evolution from B to C occurs in the remaining 49 days. In the first stage, either there is no precipitation or it takes place so quickly that there is no crystal formation. In the second stage, crystallization occurs by homogeneous precipitation. The evolution of all systems is similar and the crystallization by homogeneous precipitation takes place always within the microcline and adularia rectangles of the diagram.

The rectangles have been drawn according to the potassium, aluminium and silica equilibrium concentrations (Table 4). Adularia systems are displaced to the left with respect to the microcline systems because the potassium concentration in the hydrolysis of adularia is greater. This fact explains why the weathering of these two feldspars in similar environments is different. The evolution of the microcline systems occurs at the boundary of the stability fields of kaolinite and mica while, in the adularia systems, it occurs practically at the mica stability field. This different evolution does not indicate necessarily that the standard free energies of formation of the feldspars are different. It does indicate that the hydrolysis rate of the adularia in the initial period is so rapid and consequently the potassium concentration so high, that it displaces the homogeneous precipitation to the mica stability field. Therefore, these results support the hypothesis that the alteration products of both feldspars do not depend on the final equilibrium of the solution but on the kinetics of the hydrolysis.

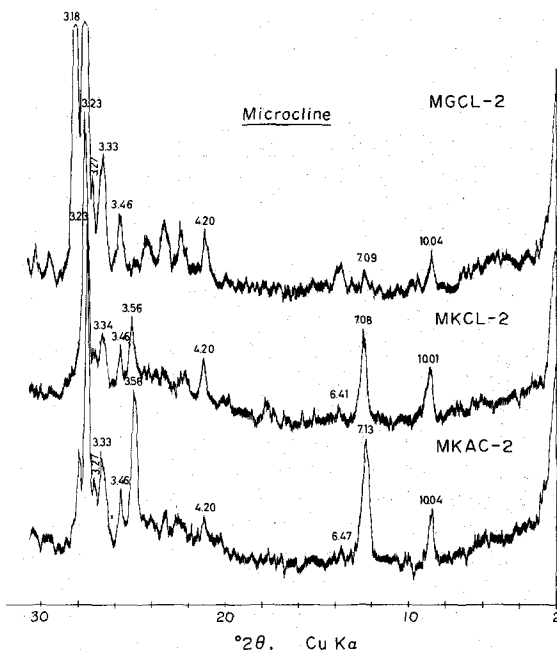


Fig. 4. Some X-ray powder diffraction diagrams correspondent at the microcline systems.

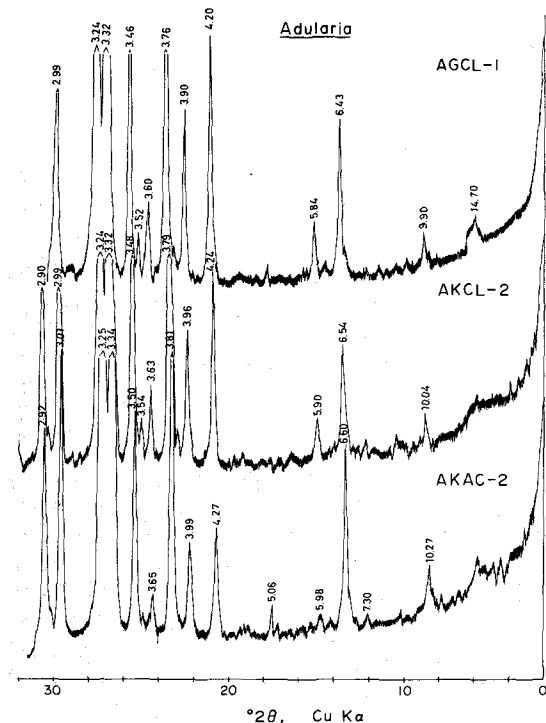


Fig. 5. Some X-ray powder diffraction diagrams correspondent at the adularia systems.



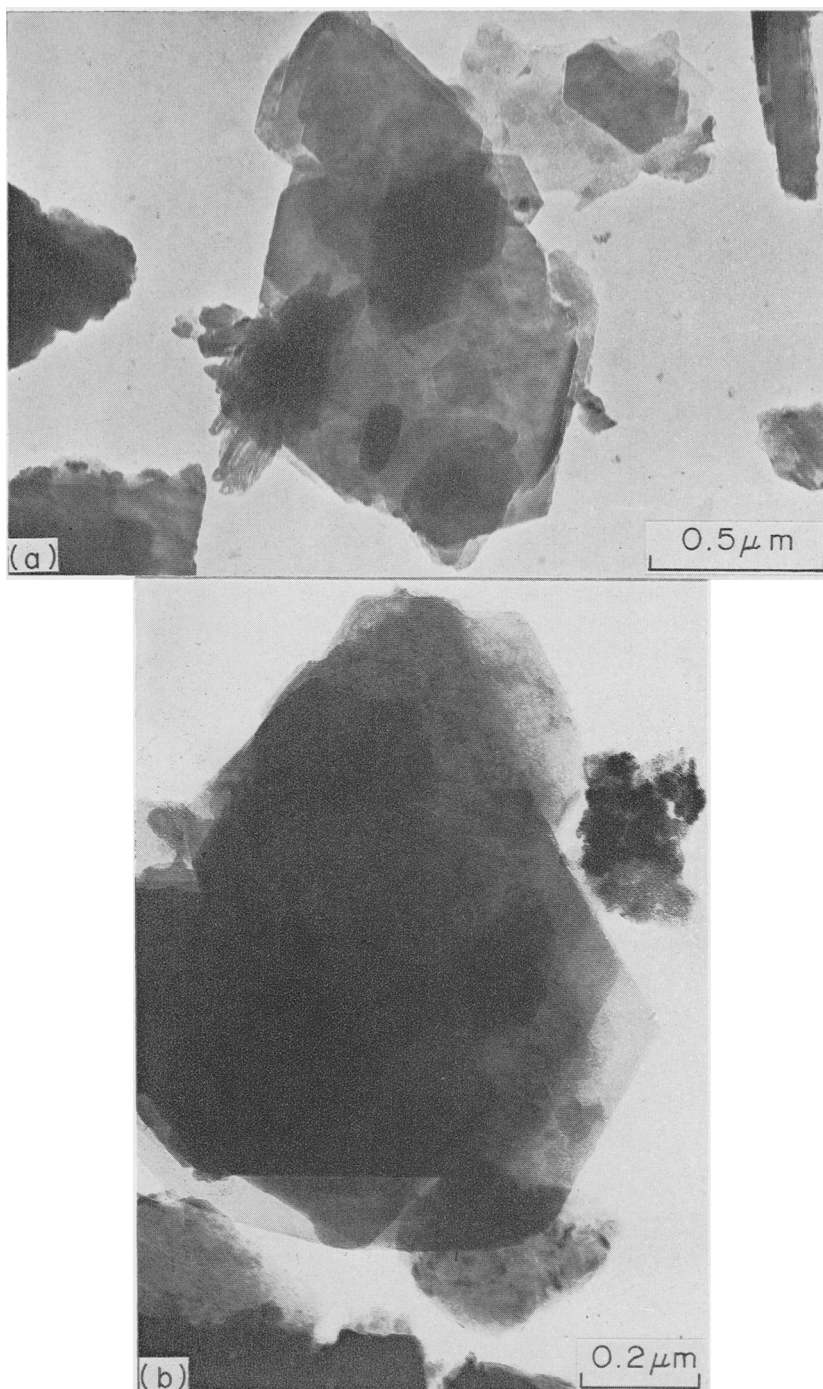


Fig. 6. Electron micrographs of some crystals of kaolinite and mica (a) kaolinite crystals correspondent at the MKCl-1 system (b) kaolinite crystals correspondent at the MGCl-2 system (c) kaolinite crystals correspondent at the AKCl-1 system (d) crystal of mica correspondent at the MGCl-2 system.

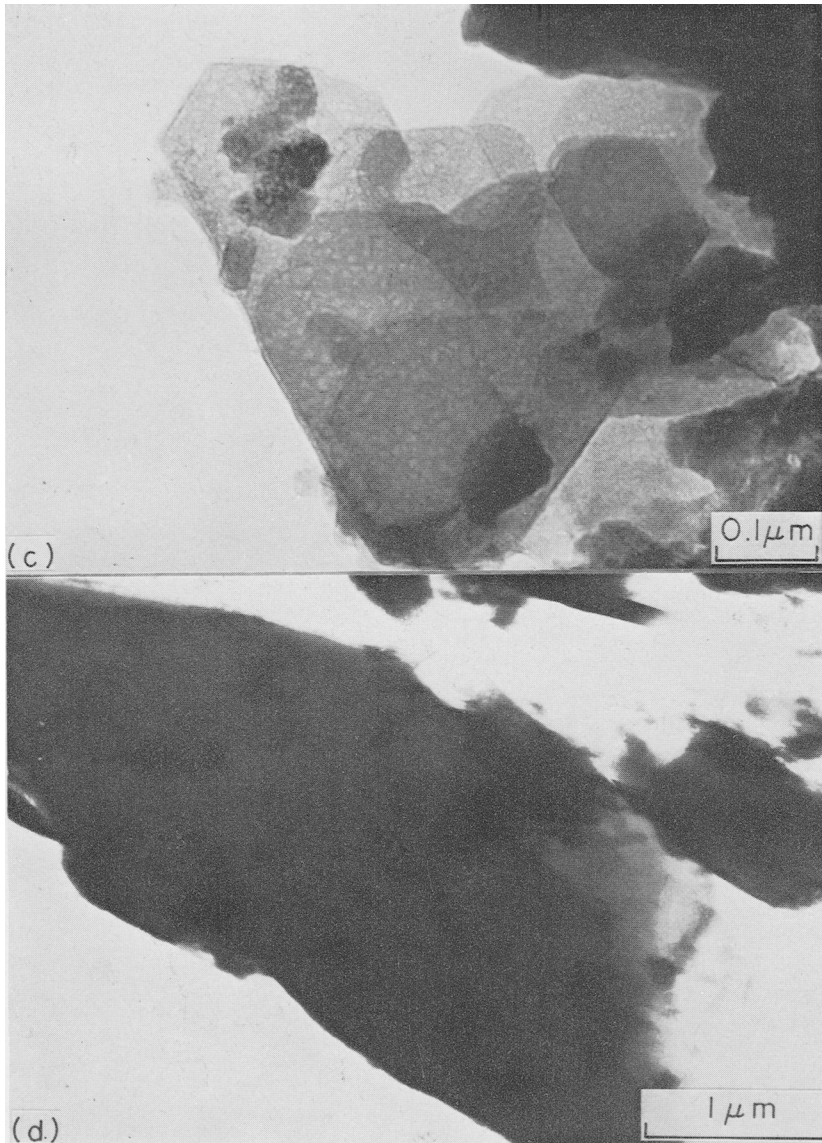


Fig. 6 (c-d).

TABLE 5  
Relative percentage between the different clay minerals

Particle size	with silica in solution											
	Microcline						Adularia					
	Acetate			Chloride			Acetate			Chloride		
	Mic	Kaol	Smect	Mic	Kaol	Smect	Mic	Kaol	Smect	Mic	Kaol	Smect
0.2-0.1 mm	54	46	--	60	40	tr.	75	25	--	74	26	tr.
0.1-0.053 mm	45	55	--	47	53	--	90	10	tr.	89	11	tr.
without silica in solution												
0.2-0.1 mm	74	26	--	61	39	--	100	tr.	--	100	--	--
0.1-0.053 mm	87	13	--	64	36	tr.	100	--	--	100	--	--

Considering the evolution of the experimental systems studied, it is possible to establish that the precipitation order of the clay minerals is: kaolinite—mica or kaolinite—smectite—mica, depending on the  $\text{Na}^+$  concentration in the system.

The estimated errors of the experimental measurements confirm the validity of the proposed hypothesis regarding the type and order of the precipitation. Thus, for example the point C in the diagram represents the end of the homogeneous precipitation of the MKAc-1 system. The coordinates of this point are:  $3.85 \text{ pK}$  and  $5.43 \text{ pAl} + \text{pSiO}_4\text{H}_4$  with errors in the determinations of  $\pm 0.0042$  and  $\pm 0.0182$  respectively.

X-ray powder diffraction data confirm the hypothesis proposed. In all experimental microcline systems, the synthesized products consist of kaolinite and mica, accompanied occasionally by traces of smectite. The kaolinite/mica ratio is about 1 in the systems in which the silica initially is in solution, while in the remaining systems there is more mica than kaolinite.

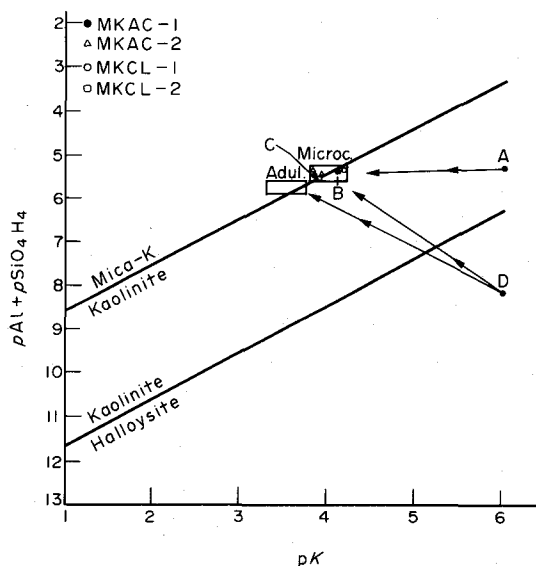


Fig. 7. Stability diagram of halloysite, kaolinite and mica in term of  $\text{pAl} + \text{pSiO}_4\text{H}_4$  plotted against  $\text{pK}$  at  $\text{pH} = 4$  and room temperature. The drawn rectangles represent the potassium, aluminium and silica concentrations in the equilibrium for all the systems.

These changes in the relative proportion of minerals can be explained by considering the concentration product of the ions at the crystallization moment. When silica has not been introduced into the solution, the silica and aluminium concentrations necessary for the kaolinite crystallization are reached when the potassium concentration is also sufficient to crystallize mica. Consequently the kaolinite proportion is small. This is valid for all adularia systems.

Several different processes have been proposed to explain kaolinite genesis and evolution in nature. The most accepted have been the transformation from feldspar to kaolinite with an intermediate stage of mica (Garrels and Howard, 1959), the transformation through amorphous stages (allophanes), hydrated halloysite and metahalloysite (Kinoshita and Muchi, 1954; Sudo and Takahashi, 1956; Ponder and Keller, 1960; Galan and Martin Pozas, 1971). The direct precipitation of kaolinite by feldspar hydrolysis, theoretically possible, seldom has been considered as a probable formation mechanism.

However, according to our results, it is suggested that this mechanism is possible in nature, because these results are an experimental confirmation that the only necessary and sufficient condition for direct crystallization of kaolinite is an adequate rate of supply of the ions. If direct precipitation is possible it will depend on the nature of the environmental conditions. In well drained environments the potassium drainage would permit a direct kaolinite formation, while with insufficient drainage both minerals may be precipitated.

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