KAOLINITE SYNTHESIS. I. CRYSTALLIZATION CONDITIONS AT LOW TEMPERATURES AND CALCULATION OF THERMODYNAMIC EQUILIBRIA. APPLICATION TO LABORATORY AND FIELD OBSERVATIONS

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Abstract—The equilibrium diagrams developed for Al-hydroxide and for kaolinite by Garrels and Christ (1965) have been modified by taking into account the existence of gels. From the stability zones obtained, the "appropriate" concentrations can be deduced and utilized for synthesizing these species, provided the requirements to insure good crystal growth are observed. Among procedures to promote these crystallizations, homogeneous precipitation processes (La Iglesia et al., 1974, 1976) appear to be particularly adequate.

The theoretical considerations provide an explanation for most of the processes observed until now, both successful and unsuccessful syntheses, and also give an explanation for many field observations. The crystallizations, however, remain poorly reproducible, indicating that many factors are still poorly known. Some points requiring further investigation include (i) better values for ΔG_r^0, (ii) the influence of organic complexes, (iii) the effect of preexisting crystalline phases, (iv) those involving dehydration processes in these systems.

Key Words—Aluminum, Hydroxide, Kaolinite, Synthesis, Thermodynamic.

INTRODUCTION

Many experiments set up to synthesize kaolinite at ordinary temperatures led, until recently, to deceptive results, and to amorphous and poorly crystallized phases that did not evolve further even after long aging. This situation has persisted until very recently when a series of independent experiments led finally to positive results (Kittrick, 1970, 1971; Harder, 1970; Linares and Huertas, 1971a, b; La Iglesia and Martín Vivaldi, 1972, 1975; La Iglesia et al., 1974; La Iglesia and Serna, 1974; Hem and Lind, 1974; Lind and Hem, 1975).

The present work attempts to explain the reasons for these successes as well as for the previous failures. Interpretable information can be obtained from the theoretically calculated equilibrium diagrams, which indicate the zones in which kaolinite is stable and is logically bound to appear.

THERMODYNAMIC CONSIDERATION OF STABILITY OF AL-HYDROXIDES AND KAOLINITE

A knowledge of the equilibria involved is obtained from the free energy values calculated from dissolution equilibria, such as those given by Feth et al. (1964), Garrels and Christ (1965), Kittrick (1966, 1970), Gardner (1970), Huang and Keller (1973) (see Table 1). It is easy to deduce from them the systems which evolve with greater ease toward gibbsite (Table 2) and kaolinite

(Table 3), at least theoretically since no indication is obtainable on the energy barriers involved in the intermediate stages (see later). Until now, the data for these equilibrium diagrams have been calculated only for crystalline species but an attempt to complete them by introducing similar constants for gels is made in the present work. Lack of information on starting materials prevents the authors from carrying this work very far, but it becomes evident that consistent changes result and that different and possibly better explanations for the facts observed can be obtained.

The equilibrium diagrams for the Al- and Al-Si-systems

Curve I (Figure 1) corresponds to the equilibrium deduced, considering gibbsite as the only possible solid phase for the pure Al-system (Garrels and Christ, 1965). Curve II is calculated for Al-gels, and is obtained by using the value from Feitknecht and Schindler (1963) (Table 1) in agreement with the treatment from Fritz and Tardy (1973).

The new field of stability for gibbsite appears to be reduced to a narrow, pH-dependent range between curves I and II. *If its crystallization appears possible from acid or from alkaline solutions,* gels are generated if the product of the $(\Sigma Al) \cdot (OH)$ activities is higher than the one indicated by the ΔG_r^0 for gibbsite. It may, however, crystallize out of gels if a procedure is set up
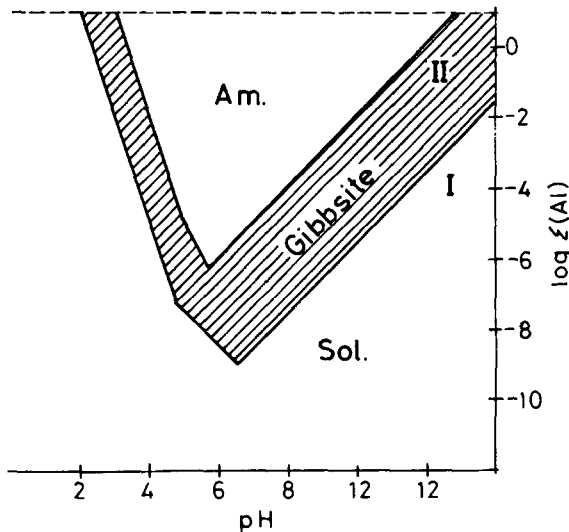
Fig. 1. Stability diagram for the system aluminum-water at 25° and 1 atm as calculated from Table 2 equations (see also text). The solid phases considered are gibbsite (curve I) and amorphous hydroxide (curve II). Curve I is close to the one obtained by Raupach (1963) from dissolution experiments on Al(OH)$^{++}$ and Al(OH)$_2$$^+$ ions.

Table 1. Gibbs' free energies of formation at 25°C and 1 atmosphere for the different species studies.

Species	ΔG_r°kcal moles^{-1}	Sources of data
Al^{3+} (aq)	-115.0	Latimer (1952)
Al OH^{2+} (aq)	-164.9	Raupach (1963)
Al (OH)$_2$$^+$ (aq)	-215.1	Raupach (1963)
Al (OH)$_4$$^-$ (aq)	-311.7	Hem and Roberson (1967)
Al (OH)$_3$ (c) gibbsite	-275.3	Kittrick (1966)
Al (OH)$_3$ (c) amorphous	-271.3	Feitknecht and Schindler (1963)
H$_4$ SiO$_4$ (aq)	-312.7	Polzer and Hem (1965)
H$_3$ SiO$_4$$^-$ (aq)	-299.4	Hem et al. (1973)
Al$_2$ Si$_2$O$_5$(OH)$_4$		
(c) kaolinite	-902.9	Robie and Waldbaum (1968)
(c) halloysite	-898.4	Hem et al. (1973)
amorphous	-897.0	Hem et al. (1973)
H$_2$O (l)	-56.69	Latimer (1952)
OH$^-$ (aq)	-37.59	Rossini et al. (1952)

tainly not far from it. Whatever it may be, the validity of our argument remains unchanged.

Limitations of the diagrams

For the Al-systems, no distinction is made between crystalline species with almost the same ΔG_r° such as gibbsite or bayerite, nor between these crystalline species in the "pregibbsite" and "pseudoboehmite" phases. The amorphizing influence of anionic impurities outlined by several authors (Marboe and Bentur, 1961; Gastuche and Herbillon, 1962; Hsu and Bates, 1964; McHardy and Thomson, 1971) could not be taken into account.

For the Al-Si systems, as outlined, ΔG_r° values for gels cannot be found, nor any variation of it with the Al-ligancy. Data for Al^{IV} forms in Al-Si compounds, either crystalline or amorphous, are lacking so that no argument is possible. Furthermore, silica is considered to form under H$_4$SiO$_4$ in the whole range of pH although the silicate is present in the alkaline range. It has been impossible also to indicate the field of stability deduced for halloysite, which obviously stands between kaolinite and an Al-Si gel. Figure 3 indicates a more elaborate diagram in which other ions such as H$_3$SiO$_4$ and different types of Al ions have been introduced in the calculations, and which possibly is closer to natural conditions than the diagram of Figure 2.

to decrease this product down to the zone in which gibbsite is stable. Some crystallizations of trihydrates can be interpreted in this sense, such as those by dialysis of gels (Gastuche and Herbillon, 1962), from hydrolysis of aluminum in water, in weak acid, or in alkaline dilute solutions, or by the reactions of Al^{3+} ions with exchange resins (McHardy and Thomson, 1971).

A similar correction can be applied to the Al-Si equilibrium diagram by superposing on the one developed by Garrels and Christ (1965) for kaolinite the data for the Al-Si gels. The diagram from Garrels and Christ is built in such a way that kaolinite is supposed to dissolve into Al^{3+} ions at an acidic pH, into aluminate at alkaline pH, and incongruently into gibbsite for a decrease in silica concentration (Figure 2a, curve I′). Similar data from gels lead to curve II′, Figure 2a (see also Table 3).

Once more, the introduction of the data for gels leads to a restriction in the zone of stability for kaolinite, recalling, in its range and extension, the one calculated for gibbsite. If the concentrations are too low in silica, gibbsite and/or Al gels form; if they are too high, Al-Si gels appear.

One problem has been to find ΔG_r° values for the Al-Si gels, which are not available in the literature. The value utilized here considers a gel with composition similar to kaolinite and with all the Al in sixfold coordination. The value introduced is the one given by Hem et al. (1973) (Table 1) for an X-ray amorphous species supposed to be halloysite because its energy of formation "was only 1 kcal less negative than the value for halloysite" (Hem and Lind, 1974). The introduction of this value in our calculation is a first approach, the true value possibly being somewhat different but cer-

Table 2. Free energies of reactions calculated from dissolution equilibria at 25°C and 1 atm for pure Al systems.

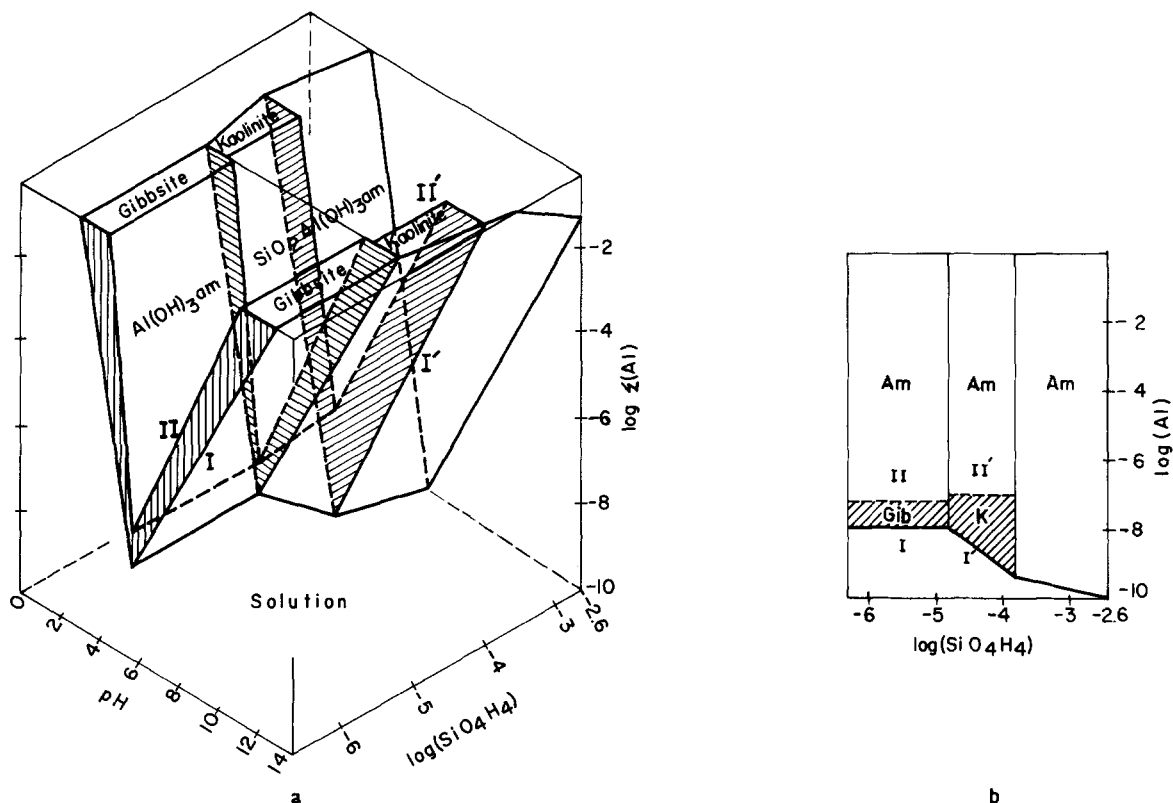| Equilibria		ΔG_r°kcal moles^{-1}
(1) Al(OH)$_3$ (am) ideal compound	= Al(OH)$_3$ (c) gibbsite	-4
(2) Al(OH)$_2$$^+$ (aq) + OH$^-$	= Al(OH)$_3$ (am)	-18.61
(2′) Al(OH)$_2$$^+$ (aq) + OH$^-$	= Al(OH)$_3$ (c)	-22.61
(3) Al(OH)$_4$$^-$ (aq) + H$^+$	= Al(OH)$_3$ (am) + H$_2$O (l)	-16.29
(3′) Al(OH)$_4$$^-$ (aq) + H$^+$	= Al(OH)$_3$ (c) + H$_2$O (l)	-20.29
(4) Al^{3+} (aq) + 2OH$^-$ (aq)	= Al(OH)$_3$ (am)	-18.61
(4′) Al^{3+} (aq) + 3OH$^-$ (aq)	= Al(OH)$_3$ (c)	-22.61

Fig. 2.   a. Stability diagram for the system silica-aluminum-water at 25° and 1 atm calculated according to the explanations given in the text. The solid phases considered are gibbsite (I), amorphous aluminum hydroxides (II), kaolinite (I'), and the corresponding amorphous silico-alumina gel (II'). b. This cut at pH 5,6 from Figure 2a indicates more clearly the evolution of the phases in the third dimension. Hatched zones correspond to the crystalline phases gibbsite (Gib.) and kaolinite (K.). Am. corresponds to the different amorphous phases indicated in Figure 2a.

From these diagrams, the crystallization of kaolinite appears to be possible either from acidic or from alkaline solutions.

THESE REACTIONS CONSIDERED AS CRYSTALLIZATION PROCESSES

The reactions considered here are crystallization processes and thus obey the laws of crystal growth

Table 3.   Free energies of reaction calculated from dissolution equilibria at 25°C and 1 atm for Al-Si systems of the kaolinite type.

Equilibria	ΔG_r° kcal moles^{-1}
(1) $Al_2O_3 \cdot 2SiO_2 - 2H_2O$ (am) ideal compound $= Al_2Si_2O_5(OH)_4$ (c)	-5.7
(2) $2Al(OH)_3$ (c) (gibbsite) $+ 2H_4SiO_4$ (aq) $= Al_2Si_2O_5(OH)_4$ (c) $+ 5H_2O$ (l)	-13.1
(3) $2Al(OH)_3$ (am) (ideal compound) $+ 2H_4SiO_4$ (aq) $= Al_2Si_2O_5(OH)_4$ (c) $+ 5H_2O$ (l)	-17.1
(4) $2Al(OH)_4^-$ (aq) $+ 2H_4SiO_4$ (aq) $+ 2H^+$ (aq) $= Al_2Si_2O_5(OH)_4$ (c) $+ 7H_2O$ (l)	-50.9
(5) $2Al(OH)_4^-$(aq) $+ 2H_3SiO_4^-$ (aq) $+ 4H^+$ (aq) $= Al_2Si_2O_5(OH)_4$ (c) $+ 7H_2O$ (l)	-77.6
(6) $2Al^{3+}$ (aq) $+ 2H_4SiO_4$ (aq) $+ 6OH^-$ (aq) $= Al_2Si_2O_5(OH)_4$ (c) $+ 5H_2O$ (l)	-105.1

(Dekeyser and Amelynckx, 1955). The conditions for the growth of such complex crystals as those investigated are very poorly known, but some indications can be obtained from the laws of crystallization processes in general. Solutions in which crystallizations may occur are those in which a nucleation process is possible. This process is thermodynamically equivalent to a new phase and the conditions allowing its formation can thus be deduced directly from our diagrams. The nucleus, which can be defined as an association of ions as in the crystal, begins to form "potentially" and becomes stable only after attaining a "critical" size (Gibbs, 1928). Nuclei smaller than the critical size dissolve again; the others can grow further and give rise to crystals. However "good" crystals form only in slightly supersaturated solutions in which a slow and regular rate of growth has been insured; otherwise imperfect crystals develop with many defects, such as cracks, inclusions, etc. It is evident that the purity of the mother solution is of outstanding importance, since small amounts of foreign ions disturb or even poison the crystallizations. The size of the crystals being related to the solubility of the ions, the small size of kaolinite is thus easily understandable.

A knowledge of the conditions of supersaturation

helps in setting up "appropriate" conditions able to give birth to kaolinite. This has been done only recently. It is now evident that most of the earlier attempts at low temperature syntheses have been performed in too concentrated media, so that, both logically and as observed, only gels could result, except in some rare cases where definite precautions had been taken.

EXAMPLES OF CRYSTALLIZATION PROCESSES FROM SOLUTIONS IN WHICH THE "APPROPRIATE" CONCENTRATIONS HAVE BEEN SET UP

The conditions required to insure crystal growth involve initially a slightly supersaturated solution and proceed towards the theoretical "appropriate" zone in which this crystal is stable. These conditions can be deduced from the aforementioned thermodynamical equilibrium diagrams and it is evident from Figures 2 and 3 that the concentrations in Al and Si able to generate kaolinite are extremely low. This requirement involves a series of difficulties from the practical point of view: small amounts of products only are obtainable from large amounts of solutions.

The synthesis of kaolinite by slow change at constant rate of one of the leading parameters of the diagram

Kaolinite can be synthesized through a slow change at constant rate of one of the leading parameters of the diagram (either the activities in Si, Al, or in H_3O) or even by a change of all at the same time, provided the sum of their logarithms enters the stability zone.

As already outlined, previous syntheses have been carried out in solutions far too concentrated and gave only gel phases. Kaolinite, however, was obtained in small amounts either by adding slowly one of the reagents on a "crystallization base" (Gillis and Dekeyser, 1962; De Kimpe et al., 1964), or by releasing it slowly at specific rates from previously organized structures (Estéoule, 1969). Both procedures can be interpreted by a mechanism involving slow change in one parameter of the diagram.

A similar procedure is applied in experiments from Van Oosterwyck-Gastuche (this work) and Kittrick (1971). In the first type of experiment, kaolinite is obtained from slow migration of dilute sodium silicate solutions on precrystalline Al gels (Figure 4). Contrary to what is predicted from the equilibrium diagram, kaolinite forms only from acidic solutions; confused crystallizations appear with increasing pH and tectosilicates crystallize from alkaline solutions (Figure 5). In the second, kaolinite crystallizes from solutions supersaturated towards this species and obtained from slow dissolution of montmorillonite. A very high yield in crystalline phase is found in this last experiment.
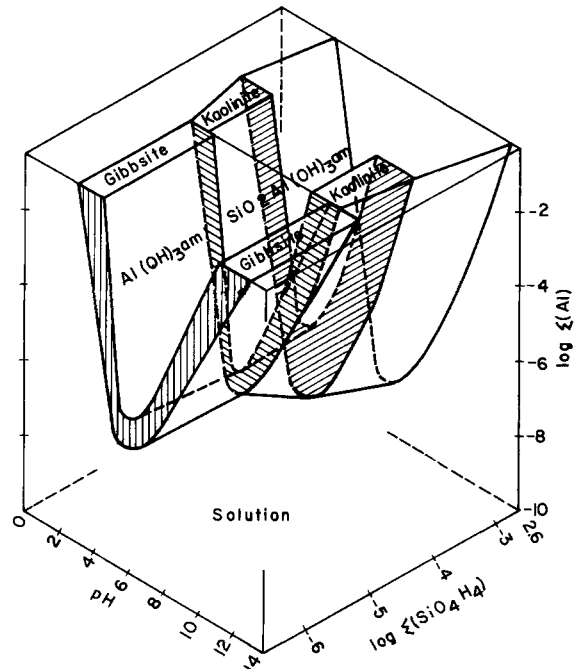

Fig. 3. Stability diagram for the same system in the above mentioned conditions of P and t° considering other ionic species for which thermodynamic data were available, such as all the aluminum ionic species (including polycations) and the $SiO_4H_3^-$ ion (this calculation is not completely explained in the text). This last diagram probably represents a closer approach to the actual situation observed in the natural systems.

Syntheses from ionic solutions

Kaolinite crystallizes from ionic solutions in which the "appropriate" concentrations have been set up, but not in every case. Thus, Harder (1970)* obtained kaolinite, but only at acidic pH (4.5 to 5); experiments at higher pH's do not generate layer lattice structures unless magnesium is added (Harder, 1972).

Experiments by Hem et al. (1973), although carried out in the same kind of "appropriate" conditions,† produced amorphous substances. This failure to crystallize kaolinite possibly is related to the retarding or even inhibiting influence of anionic impurities; high concentrations of sodium perchlorate were added to adjust the ionic strength.

Syntheses from homogeneous precipitation processes

La Iglesia et al. (1974, 1976) utilized a procedure applied in inorganic chemistry and known as "homogeneous precipitation process" (Willard and Tang, 1937)

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* Solutions utilized by Harder were from 10 to 30 ppm in SiO_2 and from 6 to 12 ppm in Al_2O_3.

† Solutions prepared by Hem et al. ranged between 18 and 259 ppm in SiO_2 and from 32 to 450 ppm in Al_2O_3 for pH's comprised between 2.29 and 5.24.
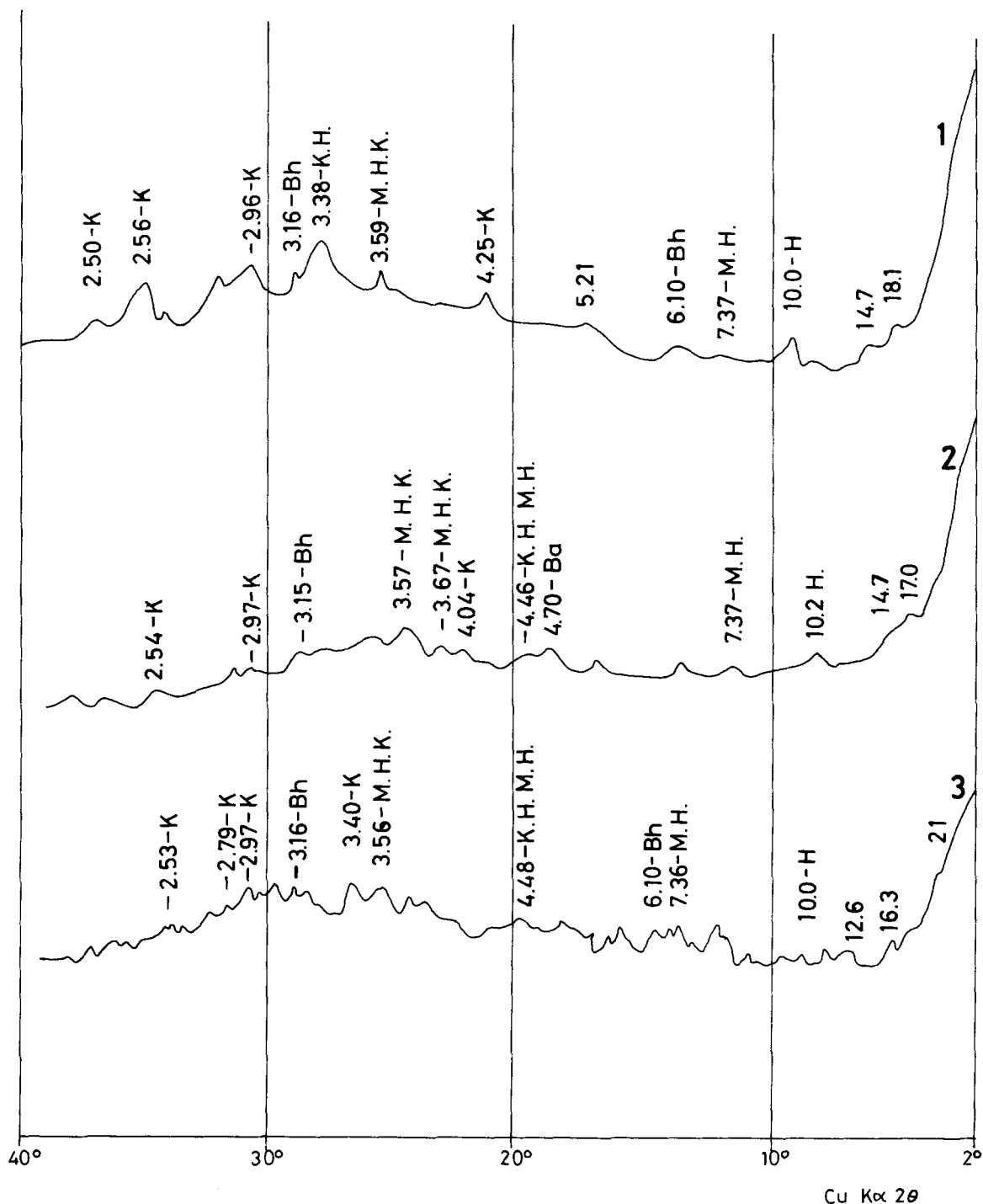
Fig. 4. Pregibbsite and pseudoboehmite gels aged during 45 days at 60° in presence of dilute Na_2SiO_3 solution (~60 ppm SiO_2) show crystallization into kaolin from pregibbsite and more confused crystallizations from pseudoboehmite. H: halloysite, M.H.: metahalloysite, K: kaolinite, Bh: boehmite. 1. Silicified pregibbsite (inner side of the dialysis bag). 2. Silicified pregibbsite (outer side of the dyalysis bag). 3. Silicified pseudoboehmite.

or "precipitation under controlled kinetics" (Kolthoff, 1964). This method consists of a slow and uniform precipitation induced through a slow and uniform change in the conditions of an initially homogeneous solution.

Large quantities of liquids are thus avoided. This technique has a definite beneficial influence on the crystallization process, since this precipitation is obtained by addition of substances which generate the insoluble end
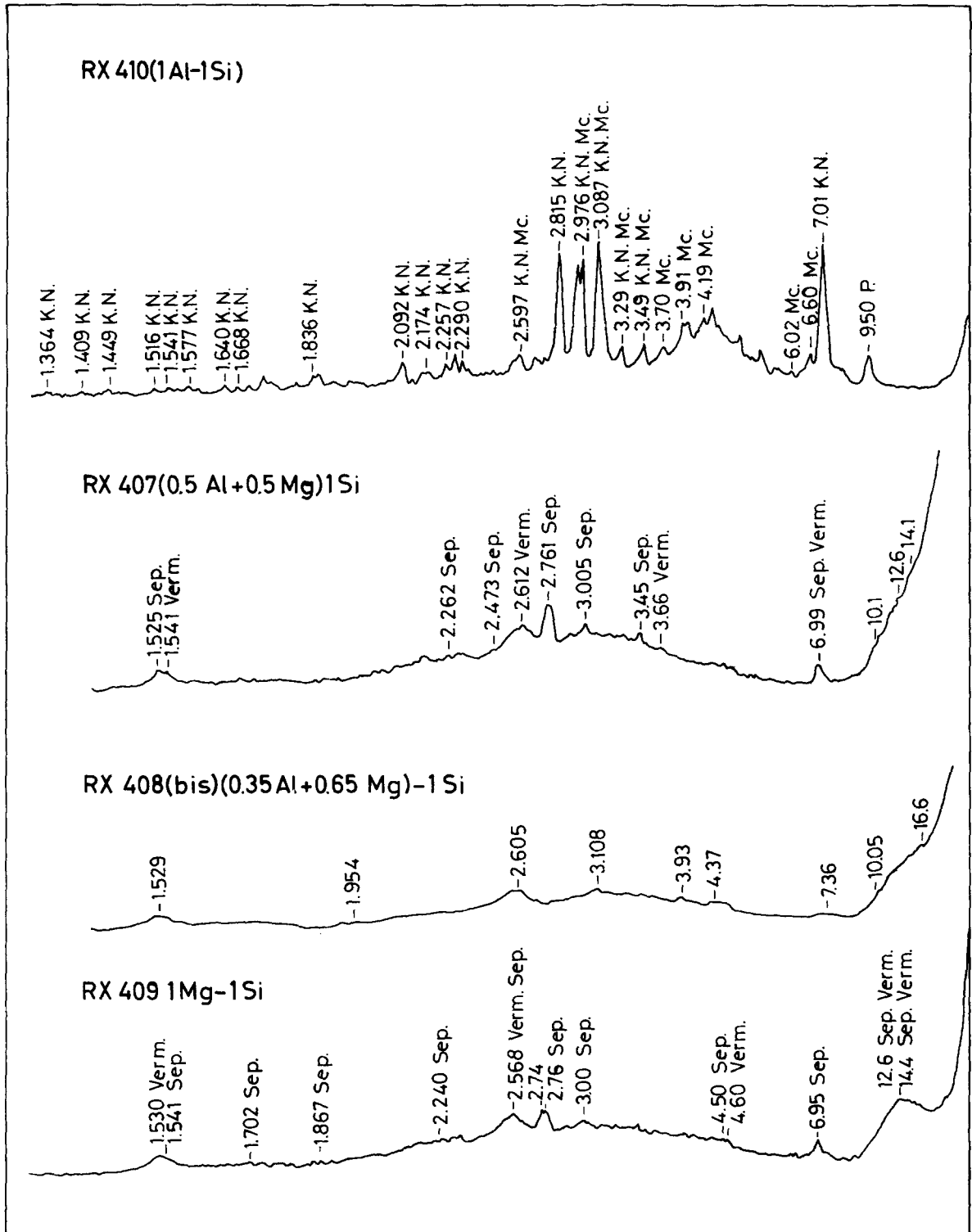
Fig. 5.   Predialyzed Al + Mg/Si systems with ration 1:1 aged during 2 months in KOH N at 60°C. Pure Mg/Si and Al + Mg/Si systems aged in sepiolite-vermiculite, without sign of dioctahedral crystallization, possibly on account of the very high pH conditions. Pure Al system crystallized mainly in tectosilicates: K-natrolite (K-natr.), microcline (Mc), and possibly pyrophillite (P.).

Table 4. Kaolin synthesis through homogeneous precipitation.

1) Synthesis starting from acid solutions (SiO_2 90 ppm, Al_2O_3 90 ppm, pH 4)
   (Al acetate or chloride, Na silicate)

	Al_2O_3 final	SiO_2 final	pH final	Resin	Crystallizations obtained
LA IGLESIA and	4	12	6.55	IRA-401 (Cl^-)	Hall, Kaol., Bayerite.
MARTIN VIVALDI	6	13	5.80	IRA-401 (Ac^-)	Kaol., Hall.
(1975)	5	12	6.60	IRA-402 (Cl^-)	Bayerite.
	6	12	5.74	IRA-402 (Ac^-)	Kaol., Hall.

2) Synthesis starting from alkaline solutions (SiO_2 60 ppm, Al_2O_3 50 ppm, pH 11.2)
   (Al aluminate, Na silicate)

	Al_2O_3 final	SiO_2 final	pH final	Resin	Crystallizations obtained
LA IGLESIA and	2	5	7.8	Amb. IRC-120	traces of Bayerite.
SERNA (1974)	2	7	7.5	Dowex 50W-X8	traces of Bayerite.
	10	12	8.2	Amb. IRC-50	Kaol. and Bayerite.

3) Synthesis through hydrolysis reaction (SiO_2 192 ppm, Al_2O_3 83 ppm, pH 4)
   (Al acetate or chloride, Na silicate)

	Al_2O_3 final	SiO_2 final	pH final	Resin	Crystallizations obtained
	68	159	4.00	Microcline (Ac^-)	Mica, Kaol.
LA IGLESIA	76	166	4.03	Microcline (Cl^-)	Mica, Kaol.
et al. (1974)	70	155	4.10	Adularia (Ac^-)	Mica, Kaol., Smect.
	73	161	4.12	Adularia (Cl^-)	Mica, Kaol., Smect.

product *at a slow and uniform rate at every point of the solution simultaneously* and prevents the formation of gel phases appearing under conditions of local supersaturation (by rough addition of a reagent, for instance).

Several procedures can be utilized to generate such reactions (Burriel Martí, 1967; Cartwright et al., 1967), such as: (1) Slow change in the pH; (2) changes induced through hydrolysis processes or redox reactions; (3) cation (or anion) release at constant pH; (4) cation (or anion) release through change in pH; (5) cation (or anion) release through replacement (from complexes, for example). All these processes are of great interest in mineral syntheses since they are likely to occur in nature. Their efficiency in kaolinite synthesis is illustrated in Tables 4 and 5. Examples from Table 4 are given for slow change in the pH and for some hydrolysis processes.

Kaolinite obtained from slow change in the pH. Acid or alkaline solutions have their pH changed through the influence of ion-exchange resins, either under OH^- or H_3O^+ forms. The solutions are slightly supersaturated with regard to kaolinite and thus enter slowly the region in which this mineral is stable. All the theoretical conditions being thus met, kaolinite should be bound to crystallize. Results obtained show that the crystallization does not appear in all cases nor in similar yields, indicating that still other factors enter in the run.

Kaolinite was obtained for the first time in alkaline medium (La Iglesia and Serna, 1974). The efficiency of H_3O^+ resins in stabilizing the Al^{VI} form‡ in the pH range in which otherwise the Al^{IV} form is stabilized is thus evidenced (see Gastuche and De Kimpe, 1959; De

Kimpe et al., 1961). However, positive results are obtained from carboxylic resins, and not from sulfonic ones.

This fact must still be correlated with data from La Iglesia and Martín Vivaldi (1975) who obtained a far better yield in kaolinite from similar experiments carried out in an acidic medium. Here also more crystalline product is obtained from the carboxylic resins than from the sulfonic ones. This result can be related with the well-known beneficial influence of carboxylic acids in generating gibbsite (McHardy and Thomson, 1971) and with the inhibiting effect of chlorides or sulfates (see references in the paragraph on Al-systems).

Synthesis through hydrolysis processes. In these experiments, La Iglesia et al. (1974, 1976) employ the hydrolysis of feldspars to generate the OH^- ions, but several other ions are released at the same time (such as potassium ions), making the reaction more complex than the previous ones but possibly closer to those observed in nature. In addition to kaolinite, smectites and micas appear.

The nature of the feldspar and its rate of hydrolysis have an influence on the end product. Thus, the fast-decomposing adularia gives a mica-kaolinite ratio of 4/1 and the slow-decomposing microcline, a 1/1 ratio.

Kaolinite syntheses from Al complexes (Table 5). Although kaolinite has been synthesized from some Al complexes, no systematic study has been undertaken. Products complexing aluminum have been utilized that decompose slowly in a solution already containing the "appropriate" concentrations in silica. This procedure deserves a special thermodynamic treatment since aluminum is now introduced in the solution in a relatively concentrated, complexed form, from which only a small part is effectively active. Siffert (1962) and Wey and Siffert (1962) were the first to use this technique by

‡ Through the reaction $2AlO_2^- + 2H_3O^+ \gtreqless Al_2(OH)_6$.

Table 5. Kaolin synthesis starting from Al-complexes.

Author	Procedure	n° sample	pH range	SiO₂/Al₂O₃	X-rays
SIFFERT and WEY (1962)	Slow destruction of Al-oxalate in a solution saturated in SiO_2 (147 ppm) by use of Ca^{++} ions	7 16	6–6.75 7.63–7.98	2.01 0.53–4.08	broad and poor lines of a 1:1 layer lattice
LINARES and HUERTAS (1971)	Slow destruction of Al-fulvic complexes in a solution containing 140 ppm in SiO_2	12 9 9	4–9 6 6	2–10 2 2	Kaol. (poor). Gibbs. Bayer. pseudoboehm.
LA IGLESIA and MARTIN VIVALDI (1973)	Slow destruction through neutralization of Al-fulvic in a solution containing 100 ppm in SiO_2. (pH 4–6 and 8–6)	14	4–8 4–8	3.40 1.70	Kaol. Kaol. (poor).
HEM and LIND (1974) LIND and HEM (1975)	Very dilute solutions of Al and Si aged in solutions containing quercetin at 25°		6.5–8.5	3.45–5.55	Amorphous to X-rays Identification by E. M. and E. D.

decomposing slowly Al-oxalate. Linares and Huertas (1971a, b) obtained kaolinite, gibbsite, bayerite, and pseudoboehmite from fulvic complexes. Gibbsite is generated for the first time from experiments involving neither dialysis processes, hydrolysis ones, nor exchange resins. It has been supposed that the fulvic complexes give rise to octahedral layers with the Al wholly in sixfold coordination upon which silica can fix by means of a surface reaction. Kaolinite was obtained again in a fulvic medium by La Iglesia and Martín Vivaldi (1972). In addition to former characteristics, this acid is also supposed to reduce the hydration of the silica and to favor the layer crystallization through an epitaxy process. The case of the synthesis of kaolinite in the presence of quercitin is comparable (Hem and Lind, 1974; Lind and Hem, 1975). Although the amount of quercitin added is too small to complex all the aluminum present, higher yields in kaolinite (approximating 5%) are obtained, while the similar, but organic-free reagents utilized by Hem et al. (1973) (and already discussed) only generated gels.

DISCUSSION

The diagram developed by Garrels and Christ (1965) brought about the important information that kaolinite and gibbsite could form only from extremely dilute solutions. An obvious explanation is thus obtained for the previous failures: the experiments had been carried out from too concentrated solutions, so that only gels could result. Our diagram reduces the zones of stability previously calculated by introducing the ΔG_r^0 data for gel phases.

The present work draws attention to the importance of considering these reactions as crystallization processes, so that the "appropriate" concentrations in which nucleation is possible can be deduced from our diagrams. The reactions must still be carried out from extremely pure solutions in which a slow and regular rate of growth has been insured.

All successful syntheses performed until now were obtained from solutions obeying the aforementioned conditions. Kaolinite was thus obtained: (1) From direct precipitation from solutions at the "appropriate" concentrations (Harder, 1970); (2) from slow introduction (or slow departure) of ions on a crystallization base originating from (a) slow formation (or dissolution . . .) of gels (Gillis and Dekeyser, 1962; De Kimpe et al., 1964; Van Oosterwyck-Gastuche, this work), (b) slow dissolution of crystalline phase (Estéoule, 1969; Kittrick, 1970), (c) homogeneous precipitation, produced by (i) slow change in pH (La Iglesia and Serna, 1974; La Iglesia and Martín Vivaldi, 1975), (ii) hydrolysis processes (La Iglesia et al., 1974, 1976), (iii) decomposition of complexes (Siffert, 1962; Wey and Siffert, 1962; Linares and Huertas, 1971a, b; La Iglesia and Martín Vivaldi, 1972; Hem and Lind, 1974; Lind and Hem, 1975).

It is of interest that a variation in the rate process is observed when parameters other than temperature (and evidently concentration) change. Attempts to synthesize kaolinite or gibbsite that produced amorphous phases can be related to the presence of large anions inhibiting those crystallizations, such as chlorides, sulfates, or perchlorates. On the contrary, good yields of kaolinite obtained from already organized layer-lattices can be explained by an increase in the rate process through epitaxial heteronucleation (Estéoule, 1969; Kittrick, 1970).

Better yields of kaolinite have been obtained in experiments carried out in apparently equivalent conditions, such as: (a) Those carried out from slow migration of Na-silicate (Van Oosterwyck-Gastuche, this work) rather than $Si(OH)_4$ (De Kimpe et al., 1964) on the same kind of precrystalline Al gels; (b) from electrolyte-rich solutions (NaCl) instead of aqueous ones (Gastuche and De Kimpe, 1959; De Kimpe et al., 1961); (c) from complexing agents for aluminum of high molecular weight—fulvic acids (Linares and Huertas,

1971a, b; La Iglesia and Martín Vivaldi, 1972), flavone-rich solutions (Hem and Lind, 1974, Lind and Hem, 1975)—rather than those of small molecular weight (oxalate), that gave poorer crystallizations (Siffert, 1962); (d) from ions obtained from hydrolysis of crystals (even with tridimensional frameworks) (La Iglesia et al., 1974, 1976) rather than ions precipitated from the solution (Harder, 1970). *The rate process of this reaction is evidently related to the relative ease of formation of the kaolinite nucleus and to the rate of its further growth.*

The present authors consider that insufficient attention has been paid to a relationship between the rate of dehydration of the ions in solution and the rate of crystallization, since the nucleus can form and grow only from dehydrated ions, which in solution are present in very hydrated states. Al^{3+} is one of the more hydrated ions of those involved, and no precise data for Si^{4+} are available. The hydration must be very high at low pH and then decrease until attaining the range in which the SiO_3^{2-} monomer is stable (pH 13; Iler, 1955). Furthermore, under low pH conditions, some hydrogen-bonding will exist in the silica-water system, as shown by the formation of gels and the delaying influence of some electron-donor polar organic compounds on the gelation time (Iler, 1955).

Thus the crystallization of silicates will occur more easily at high than at low pH. However, under these conditions, the Al^{IV} form is stabilized so that, logically, only Al^{IV}-Si crystals appear, as evidenced by the synthesis of zeolites (Van Oosterwyck-Gastuche, this work). Kaolinite will form only from alkaline solutions provided the conditions permit the stabilization of Al^{VI}, as in the experiments of La Iglesia and Serna (1974) from exchange resins, or those of Van Oosterwyck-Gastuche in which very dilute solutions are progressively fixed on Al gels.
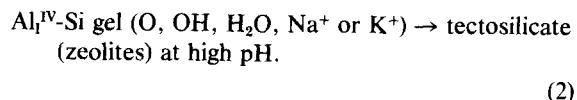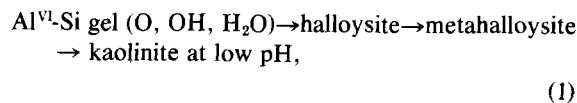
The present work confirms the importance of a preexisting "dynamic" octahedral layer either in the process of forming or of destruction (Gastuche, 1964), that orients the polymerization of the silica layer. This layer may be reduced to a "bidimensional Al^{VI}–OH seed" as evidenced from the experiments related presently.

The easy formation of layer structures from feldspars (La Iglesia et al., 1974, 1976) is probably related to conditions insuring a regular and rather rapid release of ions still poorly hydrated that organize easily into the kaolinite nucleus. Experiments in a fulvic medium involve other factors than the well-known complexing properties of these acids towards aluminum. The authors who performed this research emphasize its ability to induce epitaxial heteronucleation (through layer orientation on this large, sheetlike molecule, see also Kononova, 1961), and to produce conditions for dehydration of gels. But the conditions for the solubility of the other ions in this medium change altogether; of particular importance is the case of Si^{4+} and, again, only few data are available. Ponomareva and Ragim-Zade (1969) who performed experimental chemical weathering with humic and fulvic acids, indicate that their starting solution 0.005 N in fulvic acid contained, in mg/liter: organic carbon 400, SiO_2 8–12, Al_2O_3 15–20. Thus a normal solution in this acid would contain 1.6–2.4g/liter of SiO_2, a value far higher than that of the solubility of SiO_2 in water. The authors further indicate that the attack occurs by the formation of an insoluble colloidal complex between the mineral and the acid, in which a large amount of aluminum remains trapped, whereas the silicon is released. The fulvic type of weathering, therefore, is characterized by "the high mobility of Si and the relative stability of Al in the mineral decomposition products" (Ponomareva and Ragim-Zade, 1969).

The attack on the Si-layer structure of clay minerals (including kaolinite) by humic and fulvic acids has been clearly demonstrated by Tan (1975). It occurs through a chelation mechanism and the amounts of Si released from the HA or FA solutions after attack are very large and higher than the amounts of Al released from the Al-layer.

It is obvious that the conditions of stability deduced from our diagrams are not applicable in this case, but in a general way the evolution towards kaolinite at low temperature will be:

Al^{VI}-Si gel (O, OH, H_2O)→halloysite→metahalloysite → kaolinite at low pH,

$$(1)$$

Al_I^{IV}-Si gel (O, OH, H_2O, Na^+ or K^+) → tectosilicate (zeolites) at high pH.

$$(2)$$

Both of these reactions occur with the loss of large amounts of water.

PEDOLOGICAL AND GEOLOGICAL IMPLICATIONS

All the previously described processes have been observed in nature. The most common occurrence of kaolin minerals results from the hydrolysis of rocks in a strongly leached medium. The pH, which is very high close to the parent rock,§ decreases to 4.5–5.5. Conditions for the Al^{VI}-Si gel formation are thus spontaneously obtained and the evolution generally observed is the one expressed in equation (1), which agrees with the above-calculated equilibrium. Evidence that this gel forms through diffusion of very dilute

§ From dissolution experiments, Huang and Keller (1973) conclude that the primary leachates necessarily must be alkaline.

alkaline silicate solution on $Al^{IV}-OH$ "bidimensional nuclei" is confirmed from observations of kaolinization processes in which the kaolinite is always preceded by the so-called "alkaline front" (Szpila, 1972).

Thus, in the more general case, kaolinite genesis involves a *dynamic equilibrium* related to the degree of leaching by extremely dilute solutions. Strong leaching conditions result in gibbsite, the less strong generate kaolinite, and still weaker ones, sericite or 2:1 layers. The ionic concentration in the leachates depends more on the degree of leaching[¶] than on the nature of the primary minerals, confirming thus the primary importance of the physicochemical conditions of weathering on clay-mineral genesis as evidenced by Pedro (1964) and Keller (1970).

Ponomareva and Ragim-Zade (1969) indicate that the difference between black chernozems (which correspond to a humic-type weathering) and podzols (which result from a fulvic-type one) consists in the fact that the first are soils whose aluminosilicate part remains undifferentiated within their vertical profile, while the second have an Al-rich horizon. This characteristic of podzol profiles has been described everywhere in the world (see also Millot, 1964; Moore, 1964, etc.). A correlation between the amount of gibbsite and fulvic acid has been found recently (Sanchez Camazano et al., 1974).

From the geological viewpoint, the weathering described in the German literature as "Moorverwitterung" that generated gibbsite, kaolinite, or 2:1 phyllosilicates according to the degree of leaching has also been related to the influence of fulvic solutions (Huang and Keller, 1970). The genesis of the "tonstein" beds is also certainly related to a weathering through organic matter of the humic or fulvic type. It is of interest to mention the existence in these beds of very large kaolinite crystals "leverreite" (Moore, 1964), indicating conditions of increased solubility for Al^{3+} and Si^{4+}. Huang and Keller (1970) who studied the weathering by low molecular weight complexing acids, observed a fundamental difference compared with that produced by water or CO_2-rich water. Extrapolating their resuts to those induced by the high molecular weight complexes, they observed: "Weathering of silicate minerals by complexing acids as commonly occurs in soils and lignites may result in a different order of the mineral stability as the traditional one of Goldich." Thus, if the equilibrium diagrams calculated above are obviously

no more applicable, the fundamental mechanism of crystal growth remains.

A further occurrence of kaolinite in nature is connected with the slow addition or release of appropriate ions, at "convenient" rates known as "aggradation" or "degradation" processes (Millot, 1964).

Although the abovementioned mechanisms cover the occurrence of kaolin minerals in their great generality, one must still mention several descriptions of kaolinite formed in acid mediums (see, for instance, Keller et al., 1964) and at least one in a closed, neutral to alkaline medium (Auger, 1972) under conditions recalling possibly those experimented by La Iglesia and Serna (1974).

CONCLUSIONS

The conditions delineated from laboratory experimentation correspond to those observed in natural media and provide a logical explanation for the crystallization observed, as well as for the formation of gel phases. Thus it is concluded that no more experiments on those syntheses are needed.

On the contrary, the processes involved in these complex reactions still remain poorly understood. Many data must still be obtained on ΔG_r^0 values to develop diagrams similar to that of Figure 2 for other silicate minerals and even to complete this one. The "appropriate" rates at which these crystallization processes must be carried out are still unknown and appear to depend on various factors, such as those influencing the dehydration of ions and gels, those acting in epitaxial heteronucleation, those influencing the solubility and the hydration of the Al^{3+} and Si^{4+} ions. Data for this last ion are lacking in many fields. The manifold influence of high molecular weight organic complexes has been evidenced, but the mechanisms involved remain unknown.

It appears evident that experiments to determine all these parameters should be set up in order to obtain a better knowledge of the phenomena and to allow more elaborate treatments, such as kinetic studies of these reactions. At the moment only a general comparison between data from laboratory experimentation and field observation is possible.

ACKNOWLEDGMENTS

[¶] From experiments on potassic feldspar at 200°, Sabatier (1962) observed that, for high leaching rates, the Si/K molar ratio in the percolating solutions was close to 3, corresponding to congruent dissolution; for low leaching rates, the ratio approximated 1. Similar experiments were carried out with complexing organic acids by Huang and Keller (1970).

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Резюме- Диаграммы равновесия,построенные Гаррелсом и Кристом /1965/ для гидроокиси Al и каолинита,были модифицированы с учетом существования гелей. На основе полученных стабильных зон,"надлежащая"концентрация может быть определена и использована для синтезирования этих видов,при условии,что соблюдаются условия,обеспечивающие хороший рост кристаллов. Среди процедур, обеспечивающих такую кристаллизацию,процесс гомогенного осаждения /Ла Иглесия и др. 1974-1976/ представляется особенно подходящим.

Теоретические исследования обеспечивают объяснения большинства процессов, наблюдавшихся до настоящего времени,как успешные так и безуспешные синтезы, а также дают объяснения многим полевым наблюдениям.Кристаллизация,однако, остается плохо воспроизводимой,указывая,что многие факторы еще недостаточно известны. Некоторые вопросы,требующие дальнейших исследований,включают 1) более точные значения для ΔG_r^O , 2) влияние органических соединений, 3) воздействие первоначально существовавших кристаллических фаз, 4) вопросы,включающие дегидратационные процессы в этих системах.

Kurzreferat- Die Gleichgewichtsdiagramme,welche von Garrels und Christ (1965) für Aluminiumhydroxyd und für Kaolinit entwickelt wurden,wurden umgeändert,indem die Existenz von Gelen in Betracht gezogen wurde.Von den erhaltenen Stabilisierungszonen konnten die geeigneten Konzentrationen abgeleitet und zur Synthese benutzt werden,vorausgesetzt,daß die Bedingungen für die Züchtung von guten Kristallen eingehalten werden.Von denen Methoden, die Kristallisation fördern,erscheint das homogene Ausfällungsverfahren (La Iglesia et al.,1974-1976)besonders angemessen.Die theoretischen Erwägungen geben eine Erklärung für die meisten Verfahren ab,die bis jetzt untersucht wurden und erklären auch viele Beobachtungen im Felde.Die Kristallisationen dagegen bleiben schlecht reproduzierbar,was darauf hindeutet,daß viele Faktoren noch nicht ganz verstanden werden.Einige Punkte,welche weitere Untersuchungen verlangen,sind (i)bessere Werte für ΔG_r^0,(ii)die Beeinflußung von organischen Komplexen,(iii)der Effekt von präexistierenden kristallinen Phasen,(iv)und die Dehydratationsverfahren in diesen Systemen.

Résumé-Les diagrammes d'équilibre développés pour l'hydroxide d'Al et pour la kaolinite par Garrels et Christ (1965) ont été modifiés en prenant en considération l'existence de gels.Les concentrations "appropriées" peuvent être déduites des zones de stabilité obtenues et utilisées pour la synthétisation de ces espèces à condition que les exigences pour une bonne croissance de cristaux soient remplies.Parmi les procédés employés pour induire ces cristallisations,ceux de précipitation homogène semblent particulièrement appropriés (La Iglesia et al.,1974-1976).

Les considérations théoriques donnent une explication à la plupart des procédés observés jusqu'à présent, à la fois aux synthèses réussies et ratées,et donnent aussi une explication à beaucoup d'observations sur le terrain.Les cristallisations restent cependant mal reproduisibles,indiquant que de nombreux facteurs sont encore mal connus.Certains points demandant une investigation plus profonde sont(i) de meilleures valeurs pour ΔG_r^O,(ii) l'influence des complexes organiques,(iii) l'effet de phases cristallines pré-existentes,(iv) celles impliquant des procédés de déshydratation dans ces systèmes.