IONIC COORDINATION IN ALUMINO-SILICIC GELS IN RELATION TO CLAY MINERAL FORMATION

C. De Kimpe, M. C. Gastuche* and G. W. Brindley†

ABSTRACT

Syntheses of aluminum and magnesium silicates have been carried out at low temperatures and normal pressures, with the production of various proportions of gels and crystalline phases. With aluminum, the gel phase is the more abundant and identification of the crystals is possible only by electron diffraction; with magnesium, the yield in crystals is much higher and x-ray identification is possible. It is shown that the properties of the gels influence the kind of crystals synthesized. The main factors are pH, salt concentration and the ratio of aluminum or magnesium content to the silica content. For aluminum, the change from six-fold to four-fold coordination increases with pH. Kaolinite has been identified at low pH and mica-like structures at higher pH. Serpentine minerals have been obtained in an intermediate pH range. The better yield of magnesium-bearing minerals may be attributed to the six-fold coordination of this cation.

INTRODUCTION

According to Hénin, Caillère and their collaborators (1953), the formation of clay minerals under ordinary conditions of temperature and pressure appears to be determined by the existence of a brucite-type hydroxide layer which, even in solution, induces the SiO_4 tetrahedra to develop a layer lattice. Various clay minerals are formed depending on the type of cation involved and on the pH of the solution, with high pH's (8–9) favoring formation of 2:1 lattices and lower pH's (6–7) favoring 1:1 lattices. In the pH range 6–7, precipitation of aluminum hydroxide occurs but, according to these authors, its rapid recrystallization to boehmite prevents the formation of kaolinite under these conditions.

The present experiments were undertaken with a view to studying the influence of simultaneous additions of Al and Si in the pH range of aluminum hydroxide precipitation with the hope that the recrystallization of the hydroxide might be retarded and the formation of a layer silicate structure facilitated. Experiments were also carried out with magnesium with a view to obtaining additional information on clay mineral formation.

Part of the present study carried out in the University of Louvain has been described by Gastuche and De Kimpe (1959) but subsequent work

* Laboratoire des Colloïdes des Sols Tropicaux, I.N.E.A.C., Institut Agronomique, Héverlé-Louvain, Belgium.

† Department of Ceramic Technology, The Pennsylvania State University, University Park, Pa. (U.S.A.).

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at the Pennsylvania State University, utilizing additional techniques, now enables an integrated account to be given of these investigations.

PROCEDURE

The influence of the following factors on clay mineral formation was studied (see also Table 1):

a) *pH control:* Daily additions were made of normal solutions of either NaOH or HCl to maintain constancy of pH in a desired range between pH 4 and 9.

b) *Salt concentration:* Two series of experiments (experiments IIIa and IIIb) were run with and without a solution saturated with NaCl. High salt concentration favors gel flocculation but no evidence of preferential orientation is found.

c) *Aluminum in solution:* Initially (experiments I and IIa) aluminum was brought into solution by slow dissolution of a metallic plate, but subsequently (IIa, III) by daily additions of an ionic form, $AlCl_3.6H_2O$.
   The experiments were made in a constant volume of 2 l which was maintained constant by evaporation of excess water; concentration increased, therefore, as the the experiments progressed.

d) *Silica sources:* Either the sol, 'Ludox SM,' (exp. I) or ethyl silicate (expts. II & III) was added daily in small amounts. In one experiment (exp. I) no silica was added apart from that extracted from the Pyrex flask.

e) *The ratio $Al_2O_3/(Al_2O_3+SiO_2)$*: In the first experiment, where the amount of aluminum dissolved from the plate depends on the pH, the relative content of this element is always low. Subsequently in order to keep this ratio as nearly as possible 50%, Al ions were used.

Each experiment lasted for at least two months. Afterwards, the samples were removed, washed and oven-dried at 105° C.

STUDY OF THE GELS

Alumina-silica gels

The slow addition of both Si and Al ions in the pH range studied was thought to be favorable to the fixation of SiO_4 tetrahedra at the time of formation of the aluminum hydroxide framework. *X*-ray studies of such gels give no indication of crystallized aluminum hydroxide, while in a similar experiment carried out at pH 4.2 with the Pyrex glass as the only source of silica, boehmite was found as the final result, as proved by both electron and *x*-ray diffraction techniques.

To explain the lack of *x*-ray reflections in most experiments, it can be supposed that silica controls the development of the sample, imposing mainly its three-dimensional framework.

A closer study provides further information. It has been concluded by Tamele (1950) and by Milliken, *et al.* (1950), that in fresh alumina-silica gels, obtained by coprecipitation, the aluminum is involved in the four-fold coordinated silica framework, provided the (Al_2O_3/Al_2O_3

TABLE 1. SURVEY OF EXPERIMENTS AND OF RESULTS

Exp.	Silica source	Aluminum source	pH	Solution	$\dfrac{Al_2O_3}{SiO_2+Al_2O_3}$ %	Gel H_2O %	B.E.C. meq.g.	So m²/g.	X-ray data	Electron microscope and diffraction data
0	Pure Ludox, ppt. by propyl alcohol	—	—	—	—	5	—	400	Gel	Gel
I_a	Ludox	Al "Merck" plate	4.2	H_2O	15.7	14.1	0.5	—	Gel	Gel+kaolinite (fire-clay)
			5.5		2.6	8.15	0.26	—	Gel	Gel+kaolinite
			7.5		1.3	7.33	0.15	—	Gel	Gel+kaolinite or mica
			9.0		12.3	5.5	0.29	—	Gel	Gel+mica
I_b	Pyrex flask	Al "Merck" plate	4.5	Sat. NaCl	88.1	26.5	0.18	—	Gel+boehmite	Boehmite+kaolinite
II_a	Ethyl silicate	Al "Merck" plate	4.5	Sat. NaCl	14.7	15.2	1.61	99.3	Gel	Gel+kaolinite
		Al "Merck" plate	4.5	H_2O	20	—	—	—	Gel	Gel alone
		Al^{+3}	4.5	H_2O	31.1	31.1	0.72	31.8	Gel	Gel+kaolinite
II_b		Metallic magnesium	6.7	Sat. NaCl		21.0	0.20	156.3	Platy serpentine	Gel+platy serpentine
	Ethyl silicate	Metallic magnesium	6.7	H_2O		20.2	0.18	193.1	Brucite	Gel+platy serpentine +chrysotile
		Mg^{+2}	4.5	H_2O		8.6	0.21	—	Gel	Gel+antigorite
III_a	Ethyl silicate	Al^{+3}	5.0	Sat. NaCl	32.4	16.2	1.07	128	Gel	Gel+kaolinite or mica
			6.5		28.1	15.9	1.63	37	Gel	
			8.0		27.1	17.6	2.32	40.9	Gel	
III_b	Ethyl silicate	Al^{+3}	5.0	H_2O	29.6	15.4	1.11	110.8	Gel	Gel+kaolinite or mica
			6.5		29.6	12.9	1.41	114.5	Gel	
			8.0		29.7	13.6	1.87	63.0	Gel	

$+SiO_2$) ratio remains less than 30–40%. As the ratio increases, the excess aluminum may take six-fold coordination. According to Iler (1955), the the following equilibria can be considered:
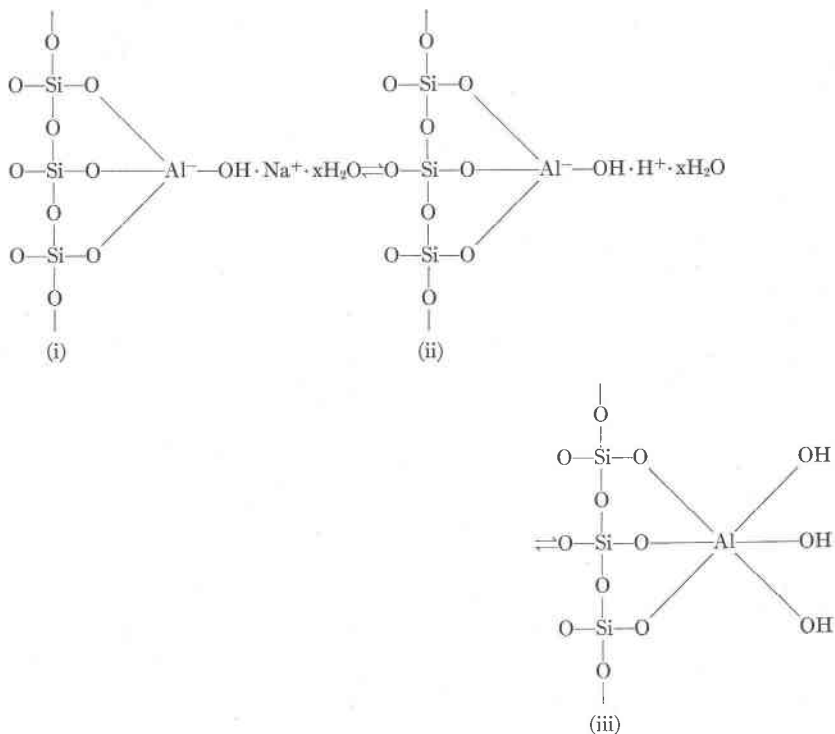
For each four-fold coordinated aluminum ion in formula (i), one negative charge arises, which is balanced by a cation. Gels of this form are stabilized under conditions of high pH and high salt concentration. With decreasing pH, at about pH 4.5, the unstable acid form of the gel, formula (ii), transforms quickly into an arrangement having uncharged six-fold coordinated aluminum, formula (iii).

a) The change in the base exchange capacity (B.E.C.) with respect to the relative content in Al_2O_3 (Fig. 1), shows a maximum as already proved by several authors, Tamele (1950), Milliken, *et al.* (1950), Bosmans and Fripiat (1958). It can be interpreted as follows: As long as the ($Al_2O_3/Al_2O_3+SiO_2$) ratio is small enough to allow the formation of tetrahedral aluminum, the charge will increase with aluminum content; when the ratio reaches the upper limit above which there are no further steric possibilities of Al-tetrahedra sharing corners with Si-tetrahedra, the charge decreases, and the excess aluminum adopts octahedral coordination.
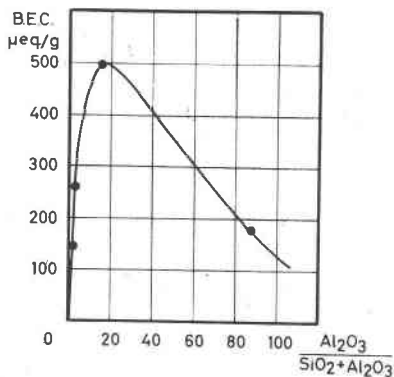
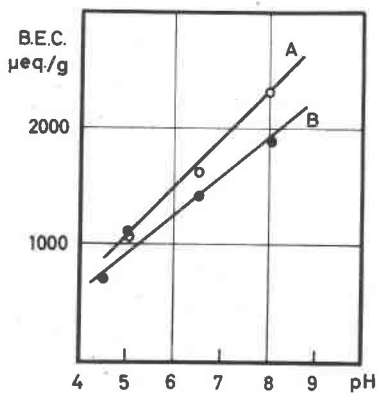FIG. 1. Change in B.E.C. following relative aluminum content for experiment I_a.

FIG. 2. Variation of B.E.C. according to pH of gel formation for the same relative aluminum content. A. Experiment III_a (in solution saturated in NaCl). B. Experiments II_a and III_b (in dilute solution).
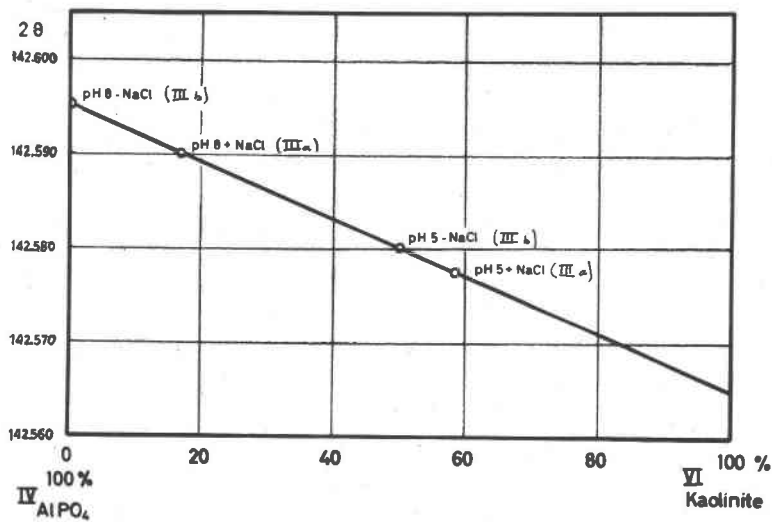

FIG. 3. Change in the diffraction angle 2θ with aluminum coordination.

b) In experiments II and III, where the aluminum content was kept constant, one observes the influence of pH and salt concentration on the transformation of aluminum coordination. In Fig. 2, it is seen that the B.E.C. of the gels increases with the pH of gel formation. For gels prepared in dilute solutions, the B.E.C. values are always smaller (*cf.* Fig. 2, line B) than those for gels prepared in more concentrated media (line A). This can be explained in terms of the equilibria discussed above.

To obtain more direct evidence for the interpretations (*a*) and (*b*), the aluminum coordination number was determined by *x*-ray fluorescence, following the method described by White, *et al.* (1958). In effect, one measures the emission wavelength of $AlK\alpha$, using a reflection from an EDT crystal in the region of $2\theta = 142.5°$. A General Electric XRD-5 *x*-ray unit with a flow-proportional counter and helium path was employed. Small but significant shifts in the angular position of the $AlK\alpha$ line are obtained for different corrdination states. The results are calibrated by reference to $Al^{IV}PO_4$ and $Al_2^{VI}Si_2O_5(OH)_4$ (kaolinite). A calibration line is drawn between the 2θ-values obtained with $AlPO_4$ and
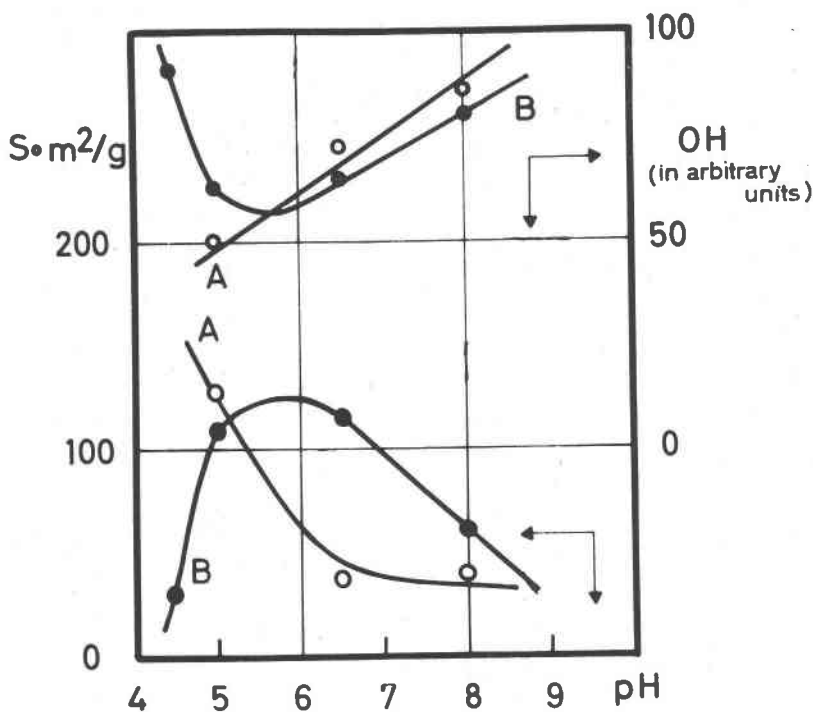

FIG. 4. Evolution of surface area and OH content following the pH of gel formation. A. Gels prepared in concentrated NaCl solution. B. Gels prepared in dilute solution.

with kaolinite, as in Fig. 3, from which an estimate is obtained of the proportions of Al ions in the two coordination states in a mixture. Although high accuracy cannnot be claimed for these estimates of Al^{IV} and Al^{VI}, nevertheless when the results for the gels are inserted in the diagram a clear trend is seen towards six-fold coordination as the pH conditions become more acidic.

c) Valuable data also are provided by surface area (S_0) measurements, which are compared with the OH content of the gels (Fig. 4). The former determinations were made following the Brunauer, Emmett and Teller (B.E.T.) method, by adsorption of nitrogen at low temperature. The OH contents of the gels were obtained by infra-red spectrophotometry; the intensity of the OH stretching vibration band at 2.85μ was compared with the intensity of the H_2O deformation band at 6μ, and this ratio, when multiplied by the total water content of the gel determined by chemical analysis, gives a value related to the total OH content of the sample.

The curve for the specific surfaces of gels obtained under conditions of great dilution (see lower part of Fig. 4), shows a maximum around pH 5.5 which, according to Iler (1955), is the pH of maximum instability for a silica gel. It is noticeable that this disorganization appears also in the formation of mixed gels.
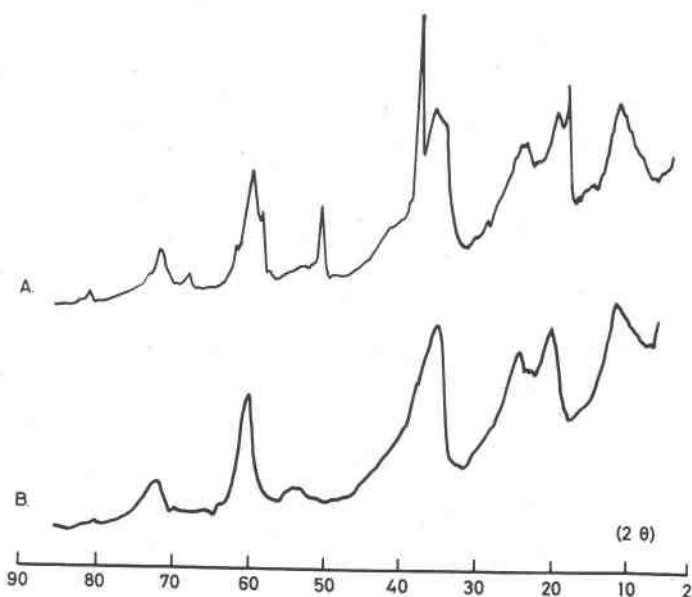

Fig. 5. X-ray patterns of the magnesium products. A. Serpentine mineral, plus brucite. B. Serpentine mineral; in the presence of NaCl, the reaction is complete and brucite is wholly transformed.
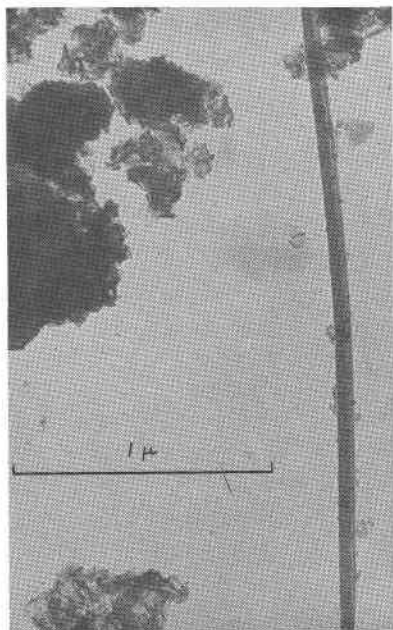
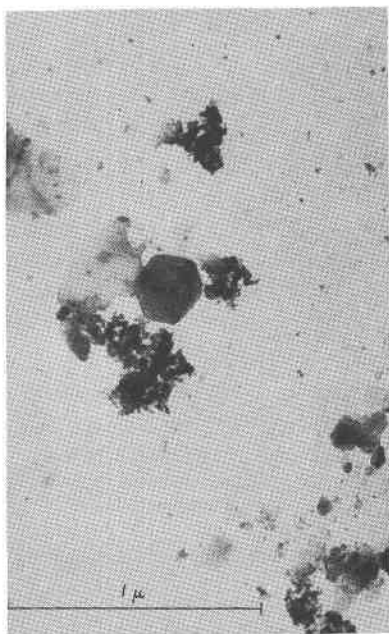FIG. 6. Example of a fiber formed in the experiment with magnesium and ethyl silicate, in dilute solution.

FIG. 7. Formation of kaolinite crystals. Notice the variable thickness of the platy crystals. Experiment II_a; ionic aluminum and ethyl silicate at pH 4, 5.

The decrease in surface area observed at high pH can be explained by a strain due to the water held by the cations. Iler (1955) admits this possibility for alumina-silica gels. Bosmans and Fripiat (1958) observe also, for such freshly coprecipitated gels, that the maximum in B.E.C. at about 30 to 40% of relative aluminum content is connnected with the minimum in surface area, measured by the B.E.T. method.

The slow increase in OH groups along with increasing B.E.C. for these samples (compare data in upper part of Fig. 4 with data in Fig. 2), comes from the stabilization of the tetrahedral aluminum form. The low surface area measured for the gel prepared at pH 4.5 comes along with a sharp increase in OH groups and a very low B.E.C.; in this case, the six-fold coordinated aluminum is stabilized.

Magnesia-silica gels

Experiment II_b was performed in order to investigate the formation of gels starting from a cation which takes only the six-fold coordination.

Two kinds of magnesium sources have been used. The ionic form, $MgCl_2 \cdot 6H_2O$, was added slowly along with ethyl silicate at pH 5.5. Two

other experiments were performed with metallic magnesium; one in a solution saturated in NaCl, the other in dilute solution. The metal quickly transformed into hydroxide; the reaction was more rapid in presence of NaCl.

Though the pH had to be kept constant in the acid pH range, the rapid dissolution of magnesium into hydroxide increased the pH up to 7.5.

The products obtained in these experiments are characterized by very high specific surface, high water content and very low B.E.C.

THE CRYSTALLINE PHASE

Magnesium products

For the reasons given above, the yield in crystalline phase is important and good x-ray patterns of a 1:1 serpentine mineral were obtained.

The presence of NaCl promoted considerably the result; in the case of dilute solutions, the brucite pattern is still present (Fig. 5).
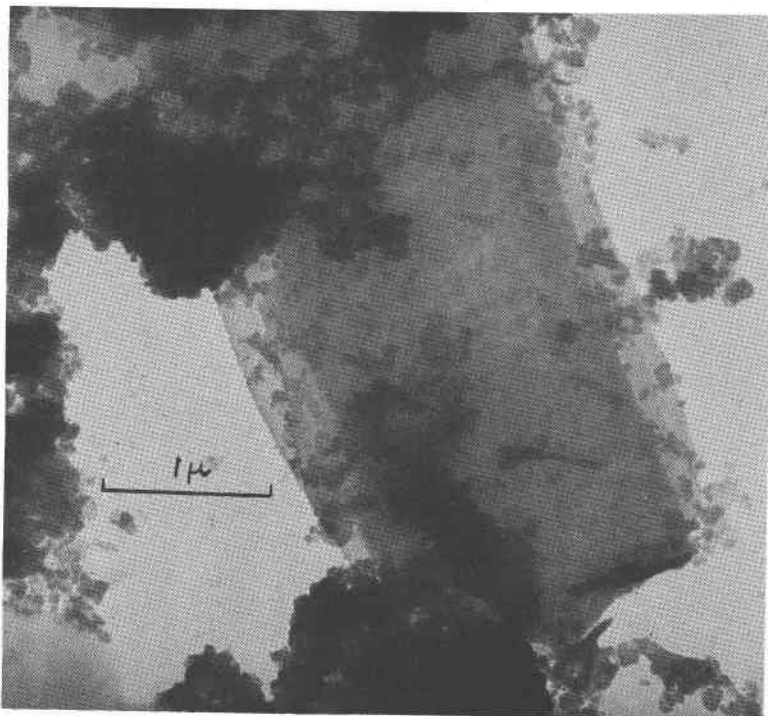

FIG. 8. Formation of mica-like plates. Crystal coming from experiment I$_a$, with Ludox and metallic aluminum at pH 9.
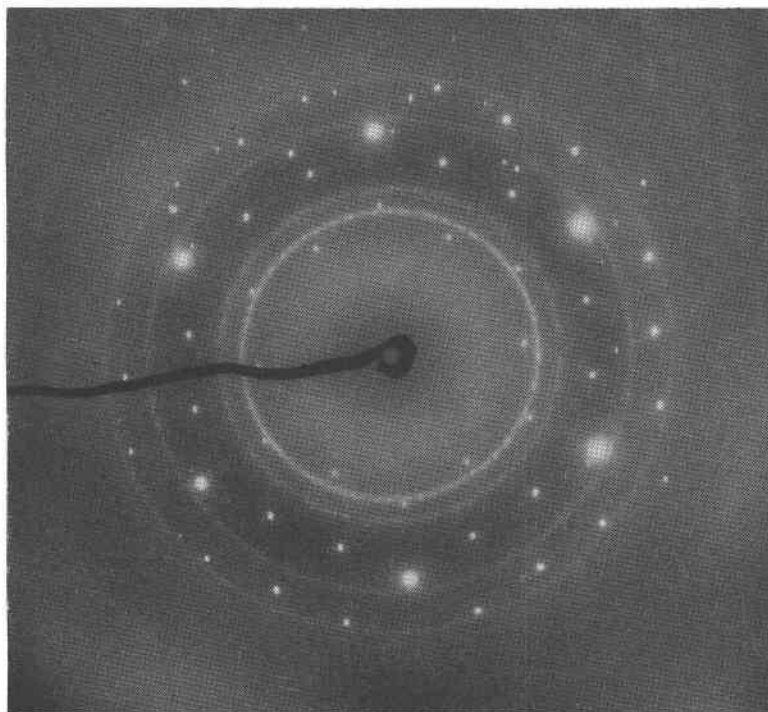
FIG. 9. Example of diffraction by pseudo-hexagonal crystal found at low pH, kaolinite. Ring pattern formed by aluminum metal used as internal standard.

Under the electron microscope, two different crystalline forms were observed. A platy form was obtained which yielded an electron diffraction pattern showing a hexagonal distribution of spots with *no* evidence for the long *a*-parameter of antigorite found by Zussman, *et al.* (1957). This form is therefore a platy serpentine, possibly lizardite, but complete identification is not possible. At least it can be said that the platy form is *not* antigorite in the strict sense of this term. Fibrous forms are also observed in the electron microscope and these appear to be chrysotile (Fig. 6).

Aluminum products

As said previously, the yield in crystalline phase was never sufficient to give a useful *x*-ray pattern. Therefore, all the determinations on these crystals were made using electron microscope and electron diffraction techniques.

In most cases, the first step in the crystalline process appears to be the formation of plates with a widely variable thickness. Their development in the 001 plane depends on the pH. In the low pH range, several pseudo-hexagonal crystals were found (Fig. 7) some showing 120° angles, very similar to those of a well crystallized kaolinite. In the high pH range, the crystals are better developed in the 001 plane, but their morphology is less well defined. They do not show any obvious geometrical form except that occasionally they are platy in appearance (Fig. 8).

The diffraction unit of the R.C.A. microscope E.M.U. 2D was used, equipped with an aperture specially designed by Charteron and Oberlin (1956) which permitted selected area diffraction. Single-crystal patterns were obtained showing $hk0$ reflections. Identification on the basis of these reflections is difficult and has been discussed fully by Brindley and De Kimpe (1961). They find that a clear distinction between the $hk0$ diagrams of different layer lattices is possible only by accurate measurement of the lattice parameters, using metallic aluminum shadowing as an internal standard. By this method it is possible to measure the b-parameter with an accuracy better than $\pm 0.2\%$, which is sufficient to distinguish between the principal clay lattices (see Fig. 9).

Using this method, b-parameters were measured for crystals among the gel phase: At pH 4.5, the b-parameter is 8.93 ± 0.03 Å. It can be correlated with kaolinite. At higher pH, a value of b equal to 9.02 ± 0.02 Å corresponds to a mica or mica-like mineral. The sodic mica, paragonite, is a possible explanation.

CONCLUSIONS

Though the yield of crystalline phase is very poor in the experiments carried out in the presence of aluminum, a detailed study of the gel phase shows its tendency to organization, confirmed by the crystalline phase study. Kaolinite appears at low pH, where the six-fold coordinated structure of aluminum is stabilized. At higher pH, a mica-like clay mineral appears, while the four-fold coordinated aluminum increases in the gel structure.

The low yield in crystalline phase can be attributed to:

(i) The insolubility of silica at the pH studied induced the polymerization of an alumina-silica gel.

(ii) The aluminum ion easily gives an isomorphous substitution with silicon, the hexacoordinated form being stable only at low pH.

The latter difficulty does not arise with magnesium ions and in consequence magnesian clays are developed more easily.

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