

# PRECIPITATION OF KAOLINITE AT 25°C AND 1 ATM\*

J. A. KITTRICK

Department of Agronomy, Washington State University, Pullman, Wash. 99163

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**Abstract**—The 0.2–5 $\mu$  particle size fraction of montmorillonite from three sources was equilibrated with various solutions at room temperature. After 3–4 yr, kaolinite was found in some of the samples that were supersaturated with respect to kaolinite, but not in any of the undersaturated samples or in the original montmorillonite. X-ray diffraction analysis of the precipitated kaolinite showed no inter-layer expansion of glycerated, oriented samples. Random powder samples indicated a poor crystallinity. The thermal stability of the precipitated material was indistinguishable from that of crystalline kaolinite. The electron microscope did not reveal any distinctive sizes or shapes.

Equilibration behavior of several samples defined a single kaolinite solubility line at or above which kaolinite apparently begins to precipitate. The solubility line is equivalent to a standard free energy of formation ( $\Delta G$ ) of -904.2 kcal per mole of kaolinite. This represents highly crystalline kaolinite. The stability of kaolinite actually precipitated at room temperature probably depends upon precipitation conditions. Thus kaolinite stability could range from poorly crystalline up to the equivalent of the kaolinite solubility line at which initial precipitation begins.

## INTRODUCTION

THE PROCESS of kaolinite formation has attracted considerable study because kaolinite is so commonly formed in soils and sediments. DeKimpe and Fripiat (1968) point out that one can synthesize kaolinite in the laboratory at high temperature and pressure from almost any mixture of hydrated alumina and silica (see, for example, DeKimpe, Gastuche and Brindley, 1964). When the temperature and pressure are lowered, the prerequisite conditions with regard to starting materials become progressively more restrictive.

As an example of more restrictive conditions, Van Moort, DeKimpe, Herbillon and Fripiat (1966) and Poncelet and Brindley (1967) were able to synthesize kaolinite from montmorillonite at 220°C and above. However, kaolinite could not be synthesized from montmorillonite at 175°C (Van Moort *et al.*, 1966) unless the montmorillonite was interstratified with poly-nuclear

aluminum complexes (Poncelet and Brindley, 1967). More recently, DeKimpe (1969) synthesized kaolinite at 175°C from an aluminosilicic gel in just 3 days.

Whether the requirements for the synthesis of kaolinite in a short time at higher temperatures can be projected to the lower temperatures and longer times available in nature is not known. To help answer this and many other questions about the formation of kaolinite in nature, one must first synthesize kaolinite at room temperature. Polzer, Hem and Gabe (1967), may have come the closest to synthesizing kaolinite at room temperature so far. They synthesized amorphous tubular or lathlike particles at room temperature that had an Al/Si ratio close to unity.

## DESIGN OF THE PRECIPITATING SOLUTION

From a suitable equation and the known thermodynamic stability of kaolinite, one can determine the characteristics of a solution saturated with respect to kaolinite. Consider the precipitation of kaolinite from  $\text{Al}^{3+}$  and  $\text{H}_4\text{SiO}_4$  in solution,



The equilibrium constant,  $K$ , for this reaction is

$$K = (\text{H}^+)^6 / (\text{Al}^{3+})^2 (\text{H}_4\text{SiO}_4)^2$$

where ( ) denote activities and assuming the activity of kaolinite and water to be unity. Taking negative logarithms of activities

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$$pK = 6pH - 2pAl^{3+} - 2pH_4SiO_4 \quad (2)$$

Dividing by 6 and rearranging

$$pH - 1/3pAl^{3+} = 1/3pH_4SiO_4 + 1/6pK \quad (3)$$

This is the equation of a straight line on  $pH - 1/3pAl^{3+}$  vs.  $pH_4SiO_4$  ordinates, with a slope of 1/3 and an intercept of 1/6 pK. This solubility line is shown in Fig. 1 for a kaolinite whose stability will be described later. All solution compositions above this line are supersaturated with respect to kaolinite. Solution compositions below the line are under-saturated.

The stability range of kaolinite in Fig. 1 is limited by the solubility of amorphous silica (shaded area), thus the dashed portion of the kaolinite solubility line represents a metastable extension. Kaolinite is stable and likely to be precipitated exclusively only at  $pH_4SiO_4$  values for which the kaolinite solubility line is solid.

Presumably, the greater the degree of supersaturation, the faster will be the rate of kaolinite precipitation. However, a solution that is considerably supersaturated with respect to kaolinite is also likely to be supersaturated with respect to

other minerals\*. The risk of precipitating phases other than kaolinite can be lessened by using only slightly supersaturated solutions. To maintain the supersaturation of such solutions as kaolinite precipitation depletes them, the slow dissolution of some solid-phase aluminum-silicate ion source is required. Thus, kaolinite was found to precipitate in montmorillonite samples equilibrated under conditions of undersaturation with respect to montmorillonite, but supersaturation with respect to kaolinite. These results are the substance of this investigation.

#### MATERIALS AND METHODS

The montmorillonites used were from Belle Fourche, South Dakota; Otay, California; and Aberdeen, Mississippi. No kaolinite (or chlorite) could be detected by X-ray diffraction analysis in the 0.2–5  $\mu$  particle size fraction of these montmorillonites. A. P. I. samples from these same montmorillonite deposits showed no kaolinite (or chlorite) impurities (Kerr, 1951).

After iron removal treatment, the 0.2–5  $\mu$  size fraction of these montmorillonites was equilibrated in approximately 200 ml of solution in polyethylene bottles. The samples, ranging in size from 1 to 18 g, were gently shaken almost continuously for 3–4 yr. The supernatant liquid was sampled periodically, after centrifuging until clear to a Tyndall beam. The supernatant liquid was analyzed colorimetrically for Al,  $Fe^{2+}$ ,  $Fe^{3+}$  and Si. Mg was determined with the atomic absorption spectrometer, Na with the flame photometer, and  $Cl^-$  with the Buchler-Cotlove chloridometer.

Most pH measurements were made on a Corning Model 12 meter. The instrument was calibrated to within  $\pm 0.02$  units of two (and sometimes three) buffers prior to determinations. Ion activities were computed from the Debye-Hückel equation (Klotz, 1964). The pH at which the samples were run was sufficiently low so that corrections for hydrolysis of the  $Al^{3+}$  ion were found to be within analysis precision.

The minimum precision of solution analyses was estimated by comparing analyses for pSi, pAl, and pH for 14 montmorillonite samples. Analyses approximately 2 months apart were compared. The average differences were  $\pm 0.023$  pSi,  $\pm 0.016$  pH, and  $\pm 0.018$  pAl. The samples had been equilibrating over 2 yr and were changing very slowly, so most of these differences may be attributed to analysis error.

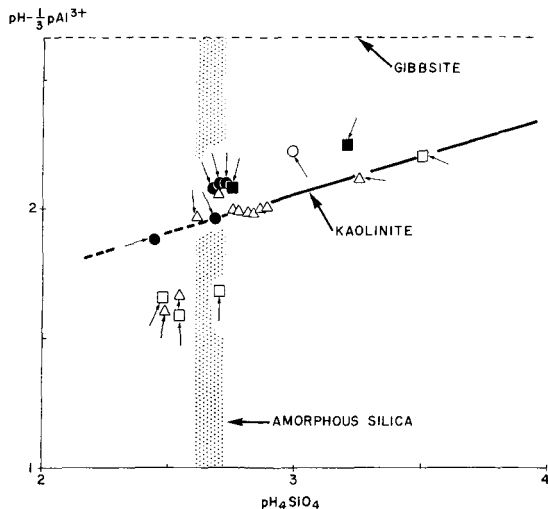


Fig. 1. Analyses of solutions equilibrated with montmorillonites from Belle Fourche, South Dakota ( $\square$ ), Otay, California ( $\circ$ ) and Aberdeen, Mississippi ( $\triangle$ ) after three to four years of equilibration. Solid symbols indicate kaolinite formation, whereas open symbols indicate no detectable kaolinite. Size of the symbols is based upon analysis precision. Arrows show the direction of sample equilibration as indicated by previous analyses. Solubility lines are dashed where metastable. Placement of the amorphous silica solubility area (shaded) and the gibbsite solubility line is from Kittrick (1969).

\*Calculations by the author from the data of Polzer *et al.* (1967) show the solution from which the lath-like particles precipitated was supersaturated with respect to gibbsite.

The montmorillonite samples were initially acidified with HCl. At the last analysis, pH values ranged from 2.60 to 3.47. A range in  $\text{pH}_4\text{SiO}_4$  of 2.38–3.53 and in  $\text{pAl}_m^{3+}$  (where  $m$  denotes molar concentration) of 2.15–4.09 was obtained at the last analysis by initially adding small amounts of Si (as  $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$ ) and Al (as  $\text{AlCl}_3$ ) to some samples.

Each sample solution was analyzed 6 times or more over a 3–4 year period. The time between analyses was short (a week to a month) near the beginning of equilibration when the samples were changing relatively rapidly. A year or more may have elapsed prior to the last analysis points shown in Fig. 1.

To illustrate the placement of analysis points in Fig. 1, consider the sample with the highest  $\text{pH}_4\text{SiO}_4$  ( $\square$  at the far right). At the last analysis, this sample had a pH of 3.47, a  $\text{pSi}_m$  of 3.53 and a  $\text{pAl}_m$  of 3.59. The Si in solution at this pH is essentially all  $\text{H}_4\text{SiO}_4$ , a neutral molecule. Thus,  $\text{pSi}_m$  can be taken as  $\text{pH}_4\text{SiO}_4$ . From the first hydrolysis constant for Al (Schofield and Taylor, 1954), the Al in solution is calculated to be 97%  $\text{Al}^{3+}$ . Thus  $\text{pAl}_m$  corresponds to a  $\text{pAl}_m^{3+}$  of 3.60 (this negligible change exceeds that for the other samples in Fig. 1 which all have lower pH values). The ionic strength of this sample is calculated from solution analyses to be 0.0021, which engenders a  $\text{pAl}^{3+}$  of 3.78. Finally,  $\text{pH} - 1/3\text{pAl}^{3+} = 3.47 - 1.26 = 2.21$ . Thus, the coordinates of the point in question are  $\text{pH}_4\text{SiO}_4$  3.53 and  $\text{pH} - 1/3\text{pAl}^{3+}$  2.21.

## RESULTS AND DISCUSSION

### *Kaolinite formation in relation to common ion activities*

The open symbols in Fig. 1 indicate the solution composition of samples in which no kaolinite was detectable by X-ray diffraction analysis. The solid symbols indicate the solution composition of samples in which kaolinite formation took place. The formation of kaolinite in these samples suggests that the high temperatures and stringent conditions necessary for the synthesis of kaolinite in short-term laboratory investigations are essentially devices to increase reaction rates.

All analysis points in Fig. 1 lie below the gibbsite line and thus represent solution compositions undersaturated with respect to gibbsite. Kaolinite formation took place only in those samples that were saturated or supersaturated with respect to kaolinite. The arrows in Fig. 1 show the general direction of sample equilibration as indicated by previous analyses. With one exception, the solution composition of all samples that are supersaturated with respect to kaolinite is altering downward toward the kaolinite solubility line. The solution composi-

tion of all samples that are undersaturated with respect to kaolinite is altering upward toward the kaolinite solubility line. Solution compositions already on the kaolinite solubility line tend to move along it. The outstanding example of this is an Aberdeen montmorillonite sample ( $\Delta$ ), where all six closely spaced analyses are shown.

### *Kaolinite formation in relation to the montmorillonite ion source*

*Belle Fourche montmorillonite samples* ( $\square$ ) that are supersaturated with respect to kaolinite have formed large amounts of kaolinite as indicated by the left X-ray diffraction trace in Fig. 2.

No kaolinite has formed in the Belle Fourche montmorillonite samples that are undersaturated with respect to kaolinite (X-ray trace in Fig. 2, right). The original 0.2–5  $\mu$  fraction of Belle Fourche montmorillonite (and a second stock sample prepared in the same way) also shows no kaolinite by X-ray diffraction.

*Otay montmorillonite* ( $\circ$ ). Kaolinite has formed in five of the Otay samples that are saturated or supersaturated with respect to kaolinite (Fig. 1). As indicated in Fig. 2, the amount of kaolinite formed in the Otay samples is much less than in the Belle Fourche samples. The one Otay sample that has produced no X-ray detectable kaolinite was initially undersaturated with respect to kaolinite. It has remained at its present degree of supersaturation for over 2 yr. Kaolinite is also absent in the original 0.2–5  $\mu$  Otay montmorillonite.

*Aberdeen montmorillonite samples* ( $\Delta$ ) are uniformly free of kaolinite detectable by X-ray diffraction analysis, including samples that are supersaturated with respect to kaolinite. Dehydration of the material at 60°C prior to X-raying did not yield indications of kaolinite. Electron microscope examination of the equilibrated Aberdeen montmorillonite samples did not reveal any unusual shapes.

### *Nature of the kaolinite formed*

X-ray diffraction data are given for one of the Belle Fourche montmorillonite samples, in which kaolinite peaks were large enough to characterize accurately. An oriented glycerated sample gave spacings of 7.15 Å for the (001), 3.575 Å for the (002) and 2.38 Å for the (003), when peak positions were determined as accurately as possible. These are spacings commonly given in the literature for kaolinite. The crystallinity of the kaolinite was determined from X-ray diffraction analysis of random powder samples (Fig. 3). Resolution in shaded triple-peak areas (Brindley *et al.*, 1963) indicates that the crystallinity of the precipitated kaolinite was relatively poor.

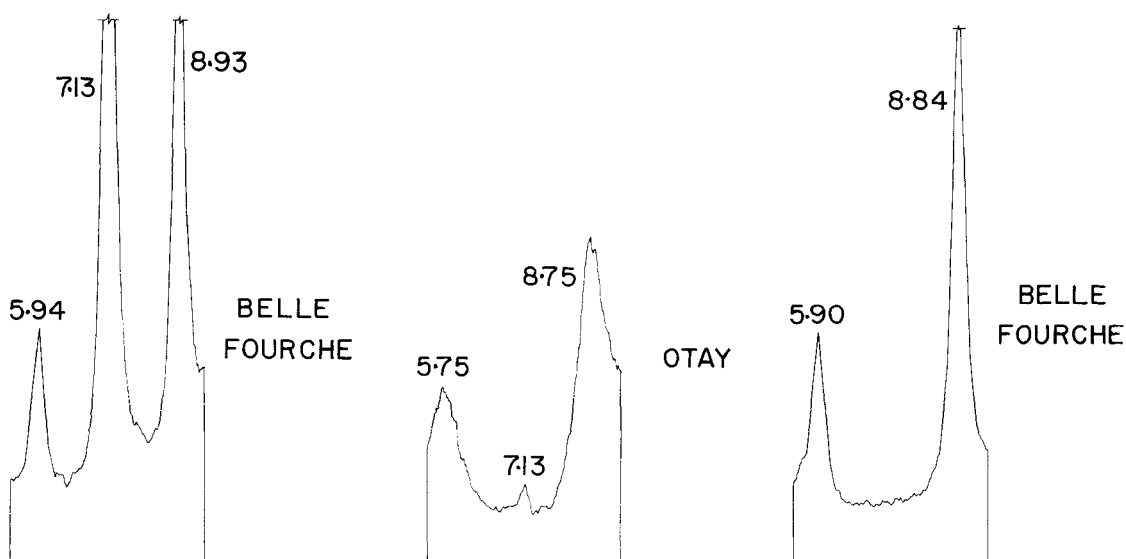


Fig. 2. A portion of the oriented X-ray diffraction patterns typical of three levels of kaolinite formation (from the left, much, little, and none). With respect to the kaolinite solubility line, the left Belle Fourche sample was supersaturated, the middle Otay sample was supersaturated also, and the right Belle Fourche sample was undersaturated. The (001) kaolinite peak at 7.13 Å is bracketed by the (002) and (003) montmorillonite peaks. The samples were run under identical conditions (glycerated slide,  $Al^{3+}$  saturation,  $1^\circ 2\theta/\text{min}$ , scale factor  $1 \times 10^2$ , time constant 8,  $CuK_\alpha$ , Ni filter).

The crystallinity of the precipitated kaolinite is actually close to that of halloysite\*. However, the oriented glycerated samples showed no nonmontmorillonite spacings greater than 7.15 Å. A relatively crystalline kaolinite equilibrated with Belle Fourche montmorillonite under similar conditions for the same length of time still showed good crystallinity (Fig. 3).

*Thermal stability* of the (001) peak of the kaolinite precipitated in Belle Fourche montmorillonite was first investigated by heating the oriented slide for 2 hr prior to X-raying at room temperature. Under these conditions, the (001) peak remained at 400°C, but almost completely disappeared at 500°C.

An effort was made to determine the thermal stability of the precipitated kaolinite more accurately, by observing the (001) peak as the sample was heated in an MRC diffractometer furnace. The sample was sedimented directly upon the surface of the heating element. The thermocouple attached to the heating element was previously calibrated with a series of seven Tempilstiks. It was found that there was a considerable time dependence with regard to the stability of the (001)

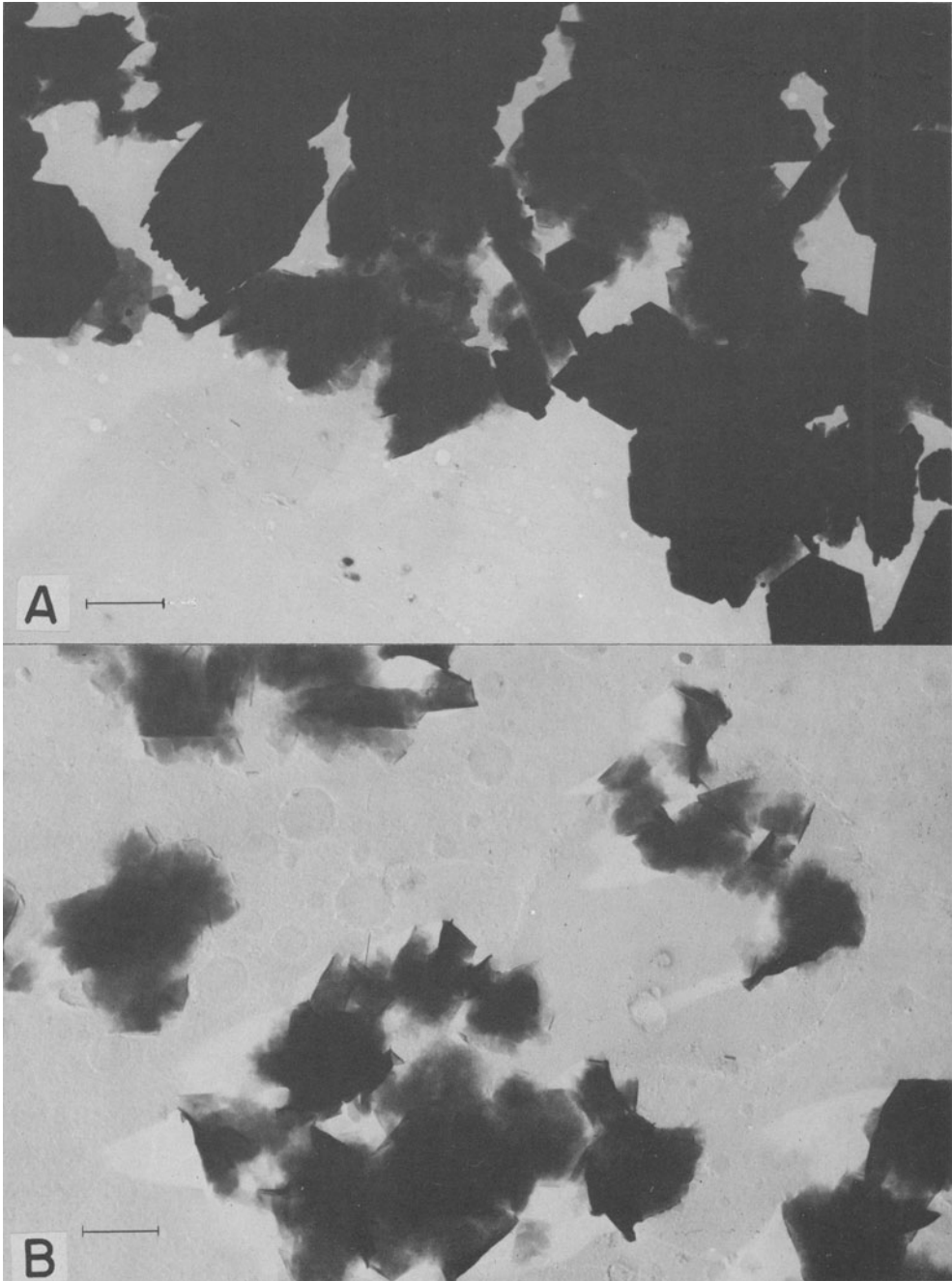
peak of several relatively crystalline kaolinite samples. When the sample temperature was close to 450°C, the intensity of the (001) peak decreased over a period of several days. At approximately 480°C, the (001) peak intensity decreased over a period of hours. Closer to 500°C the (001) peak intensity decreased over a period of minutes. Since the (001) peak of the precipitated kaolinite acted essentially the same way, about all that could be concluded was that the thermal stability of the precipitated kaolinite was indistinguishable from that of crystalline kaolinite.

*Electron micrographs* of typical areas of all samples were obtained\*. Samples were prepared by drying a drop of a diluted well-mixed portion of the sample suspension on a Formvar-covered grid. The samples were lightly shadowed at 15° with chromium. Results for Belle Fourche montmorillonite samples are presented as typical for the three montmorillonites (Fig. 4).

The kaolinite added to and equilibrated with Belle Fourche montmorillonite (Fig. 4A) was quite distinctive, with many thick, flat, euhedral, six-sided crystals with an included angle of 120°. Fig. 4B displays only Belle Fourche montmorillonite, but does not differ appreciably from Fig.

\*The halloysite used in Fig. 3 was collected from the Benson Pit, Latah County, Idaho by Mr. E. W. Hope. Benson Pit halloysite is described by Ponder and Keller (1960).

\*Electron micrographs were taken at the Electron Microscope Laboratory, Washington State University.



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Fig. 4. Electron micrographs of equilibrated Belle Fourche montmorillonite samples. A has crystalline kaolinite added initially. B formed no kaolinite. C formed considerable kaolinite. The line indicates  $1\ \mu$  in all photos.

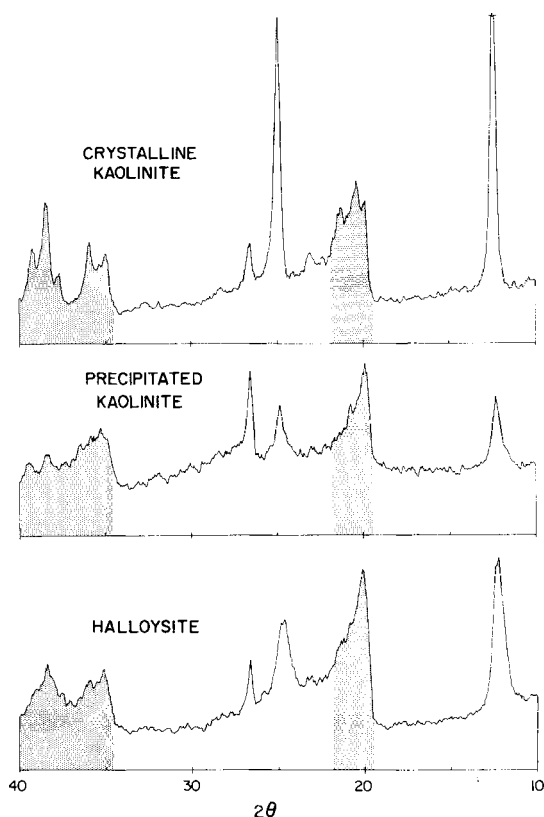


Fig. 3. A portion of the random powder X-ray diffraction patterns of Belle Fourche montmorillonite samples, where relatively crystalline kaolinite was added prior to equilibration (upper) and where kaolinite was precipitated during equilibration (middle). The lower X-ray pattern is from Benson Pit halloysite. Resolution of peaks in shaded areas indicates degree of crystallinity. Diffraction conditions were the same as Fig. 2.

4(C) where large amounts of kaolinite were formed. Evidently the morphology of the precipitated kaolinite is neither halloysite-like tubes, nor that of well formed kaolinite crystals. This negative morphological evidence is in accord with the X-ray evidence, which indicates poorly crystalline kaolinite.

*The stability level at which kaolinite precipitates*

Placement of the kaolinite solubility line in Fig. 1 is based upon sample behavior as discussed previously. Most solution compositions tend to alter toward this line, or move along it. This line was drawn with a slope of 1/3 as required by equation (3) and appears to represent the solution composition at which kaolinite precipitation begins. Since the slope of the initial precipitation line is known,

the position of the line is defined by its intercept (the  $\text{pH}-1/3\text{pAl}^{3+}$  at zero  $\text{pH}_4\text{SiO}_4$ ). The intercept of the line can be determined by using equation (2) and the solution composition of the point at the far right in Fig. 1. Thus

$$\text{p}K = 6(3.47) - 2(3.78) - 2(3.53) = 6.20.$$

From equation (3), the intercept of the kaolinite solubility line is  $1/6\text{p}K$  or 1.03.

To facilitate comparison with kaolinite stability determinations in the literature, the  $\Delta G$  of kaolinite that is equivalent to this kaolinite solubility line may be calculated. From equation (1)

$$\Delta G_r = \Delta G_{(\text{kaolinite})} - 2\Delta G_{\text{Al}^{3+}} - 2\Delta G_{\text{H}_4\text{SiO}_4} - \Delta G_{\text{H}_2\text{O}}$$

where  $\Delta G_r$  is the standard free energy of reaction. Further,  $\Delta G_r = 1.364 \text{ p}K$  or 8.46, so that

$$\begin{aligned} \Delta G_{(\text{kaolinite})} &= 8.46 + 2(-115.0) + 2(-313.0) \\ &\quad + (-56.7) \\ &= -904.2 \text{ kcal per mole.} \end{aligned}$$

The  $\Delta G$  of  $-904.2$  kcal represents a kaolinite of slightly greater stability than does the  $\Delta G$  of  $-903.8$  kcal, which is thought to represent a kaolinite of near maximum crystallinity\* (Kittrick, 1966).

Kaolinite sufficient to permit an estimation of crystallinity was precipitated in only 2 samples. In both samples the kaolinite was derived from Belle Fourche montmorillonite. Both samples were supersaturated with respect to kaolinite to about the same extent and the crystallinity of the precipitated kaolinite was poor in both. The range of solution conditions and results was thus too restricted to determine if the crystallinity of the precipitated kaolinite corresponds inversely to the degree of supersaturation with respect to kaolinite. Other conditions of precipitation and recrystallization may also determine kaolinite crystallinity and stability. Whatever the factors influencing kaolinite stability, it seems likely that the measured  $\Delta G$  values of kaolinite precipitated at room temperature in soils and sediments will range from that

\*These  $\Delta G$  values are dependent upon other  $\Delta G$  values (the  $\Delta G$  values of  $\text{Al}^{3+}$  and  $\text{H}_2\text{O}$  are taken from Garrels and Christ (1965) and that for  $\text{H}_4\text{SiO}_4$  was calculated from the data of Van Lier *et al.* (1960) and Wise *et al.* (1963)). The position of the kaolinite solubility line in relation to  $\text{pH}-1/3\text{pAl}^{3+}$  vs.  $\text{pH}_4\text{SiO}_4$  axes is not similarly dependent.

of halloysite at  $-989.6$  kcal (Barany and Kelley, 1961; corrected for revised heat of formation of quartz) up to the initial precipitation level of  $-904.2$  kcal.

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**Résumé**—La fraction de particule de  $0,2$  à  $5\mu$  de montmorillonite provenant de trois sources différentes a été équilibrée avec des solutions variées à la température ambiante. Trois ou quatre ans après, de la kaolinite a été trouvée dans certains échantillons qui étaient supersaturés par rapport à la kaolinite, mais pas dans les échantillons sous-saturés ou dans la montmorillonite d'origine. L'analyse par la diffraction des rayons X de la kaolinite précipitée n'a montré aucune expansion de la couche intermédiaire des échantillons orientés et glycérisés. Des échantillons de poudre pris au hasard indiquaient une pauvre cristallinité. La stabilité thermique du matériau précipité n'était pas indistincte de celle de la kaolinite cristalline. Le microscope électronique n'a pas révélé des tailles ou formes distinctives.

Le comportement de l'équilibrage de plusieurs échantillons a tracé une simple ligne de solubilité de la kaolinite à laquelle ou au-dessus de laquelle la kaolinite commence apparemment à se précipiter. La ligne de solubilité est équivalente à une énergie libre standard de formation ( $\Delta G$ ) de  $-904,2$  kcal par mole de kaolinite. Ceci représente une kaolinite hautement cristalline. La stabilité de la kaolinite actuellement précipitée à température ambiante dépend probablement des conditions de la précipitation. Ainsi la stabilité de la kaolinite pourrait s'étendre de très peu cristalline jusqu'à l'équivalent de la ligne de solubilité de la kaolinite à laquelle commence la précipitation initiale.

**Kurzreferat**—Eine Fraktion mit  $0,2$  bis  $5\mu$  Teilchengröße von Montmorilloniten aus drei Quellen wurde mit verschiedenen Lösungen bei Zimmertemperatur abgeglichen. Nach 3-4 Jahren konnte in einigen der Proben, die in Bezug auf Kaolinit übersättigt waren, Kaolinit festgestellt werden, nicht jedoch in den untersättigten Proben oder in dem ursprünglichen Montmorillonit. Röntgenbeugungsanalyse des ausgefällten Kaolinit zeigte keine Zwischenschichtaufblähung von glyzerierten, orientierten Proben. Stichproben deuteten geringe Kristallinität an. Die Wärmebeständigkeit des ausgefällten Materials ließ sich von der eines kristallinen Kaolinit nicht unterscheiden. Das Elektronenmikroskop zeigte keine ausgeprägten Größen oder Formen.

Das Abgleichungsverhalten verschiedener Proben ließ eine einzige Kaolinit Löslichkeitsgrenzlinie hervortreten, bei und oberhalb welcher Kaolinit scheinbar anfängt auszufallen. Die Löslichkeitsgrenzlinie entspricht einer normalen freien Bildungsenergie ( $\Delta G$ ) von  $-904,2$  kcal pro Mol Kaolinit. Das stellt hoch-kristallinen Kaolinit dar. Die Beständigkeit des bei Zimmertemperatur ausgefällten



Kaolinitis hängt vermutlich von den Ausfällungsbedingungen ab. Der Bereich der Kaolinitstabilität könnte sich vom gering kristallinen Zustand bis zu dem Äquivalent der Löslichkeitsgrenze des Kaolinitis, bei welcher die Ausfällung beginnt, erstrecken.

**Резюме**—Частицы монтмориллонита фракции 0,2–5 мк из трех различных источников обрабатывались различными растворами при комнатной температуре. После старения суспензий в течение 3–4 лет каолинит был обнаружен лишь в некоторых образцах, которые первоначально были “перенасыщены” в отношении каолинита, но не был обнаружен ни в “ненасыщенных” им образцах, ни в образцах первоначально “насыщенных” монтмориллонитом. Рентгенографический анализ осажденных каолинитов не выявил наличия разбухающих при насыщении глицерином ориентированных образцов. Неориентированные порошковые образцы характеризовались невысокой степенью кристалличности. По термической устойчивости осадки из суспензий не отличаются от кристаллического каолинита. Исследование под электронным микроскопом не выявило различия в размерах и форме частиц.

Равновесные свойства нескольких образцов позволили определить линию уровня растворимости каолинита, при котором или выше которого каолинит начинает осаждаться. Этот уровень эквивалентен стандартной свободной энергии образования каолинита ( $\Delta G$ ), равной 904, 2 ккал/моль (высокая степень кристалличности). Устойчивость каолинита осажденного при комнатной температуре, вероятно, в какойто степени зависит от условий, осаждения. Она может изменяться от устойчивости, свойственной плохо окристаллизованным образцам, до устойчивости, эквивалентной уровню растворимости каолинита, при котором начинается первичное осаждение.