

# OBSERVATIONS ON THE ORIGIN OF ENDELLITE IN KENTUCKY, AND THEIR EXTENSION TO “ INDIANAITE ”

by

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## ABSTRACT

ENDELLITE is being formed south of Stanford, Kentucky, in an acid environment (pH 3.0–3.7; acidity at source, pH 1). Parent materials are principally a weathered residuum, derived presumably from the Brassfield Limestone that lies between the illitic, Devonian New Albany (Chattanooga) Shale and illitic, Ordovician Richmond Shale, and added Si and Al dissolved from the New Albany Shale. The source of the acid is the weathering iron sulfide in the New Albany Shale.

Apparent standard free energies of formation, calculated from aqueous solution data measured from the shales, endellite, and residual clays, indicate that essentially equilibrium conditions developed between the endellite, the illite of the New Albany Shale, and the permeating solution. Illites yield a range of values in  $F_f$ , owing presumably to variation in chemical composition and physical disorder in the crystals, which also may be polymorphic; hence, illites likewise vary in susceptibility to alteration and/or conversion of kaolin minerals.

It is suggested that Indiana endellite (“indianaite”) was formed at the Mississippian–Pennsylvanian unconformity in an environment similar to that (Ordovician–Devonian) yielding the Stanford, Kentucky, endellite.

## INTRODUCTION

ENDELLITE–HALLOYSITE was reported from occurrences in Lincoln County, Kentucky, in 1963 by Crawford and McGrain, and in Hart County by McGrain (1960), and McGrain and Hamlin (1962). The purpose of this paper is to describe the geological and geochemical conditions significant to the formation of endellite in the Lincoln County area. Also, similarities between the occurrence of the Kentucky endellite with the endellite (“indianaite”) in Indiana will be pointed out.

## STRATIGRAPHY AT THE ENDELLITE OCCURRENCE

South of Stanford, Kentucky, in an east-facing road cut on U.S. Highway 27, 2.2 miles south of its intersection with U.S. 150 (south edge of Stanford

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7 1/2' Quadrangle Map), white to light-gray endellite\* occurs that appears to be forming in lenses and stringers within what is interpreted as clayey residuum from dissolved Silurian Brassfield Limestone. The stratigraphic section exposed in this road cut is shown in Table 1.

TABLE 1.—STRATIGRAPHIC SECTION.

pH of Moist clay		Thickness
June 1963	June 1964	
		Surface soil, bevelled at road cut.
<1-1.0	1.5-2.0	New Albany (Chattanooga) Shale; dark, abundant iron sulfide
		4 ± feet
		Unconformity beneath Devonian rocks
3.5	3.0-3.5	Brassfield (Silurian) residuum; contains lenses, stringers, irregular masses of granular to porcellanous endellite; variable thickness
		nil to 4 feet
		Unconformity above Ordovician rocks
3.0	1.0	Richmond Shale; altered, greenish
		1 to 1½ feet
4.5		Richmond Shale; gray to brown, irregularly oxidized, light efflorescence
		8 feet
		Talus covered Richmond Shale above, and in, road ditch
		Variable interval

The Devonian New Albany (Chattanooga) and Ordovician Richmond Shales are recognized in the field on straightforward, objective geological evidence. The intervening mudstone is interpreted as an insoluble residuum from the Silurian Brassfield Limestone because of its unconformable position on the Richmond Shale, lithological and mineralogical dissimilarity to both the New Albany and Richmond Shales, and lithological similarity to residuum occurring above and about remnants of clearly defined unweathered Brassfield Limestone present in nearby exposures (but absent in this road cut).

In the first road cut to the north of the endellite-bearing location and separated from the subject endellite-containing road cut by only a small, eastward-draining valley, a sharp, clean unconformable contact separates the New Albany and Richmond Shales. Neither residuum nor endellite is present here—none having been developed in, or from, the upper part of the Richmond Shale. Thus, between the Richmond and New Albany shales there may occur, alternatively, (1) no intervening rocks, (2) remnant Brassfield Limestone accompanied by its residuum, or (3) residuum devoid of limestone association. Endellite has been observed only in the limestone-free Residuum Zone.

\* Endellite refers to the highly disordered kaolin mineral that yields a 10 Å spacing when glycolated and originally moist but which collapses irreversibly to 7 Å when dried.

The stratigraphy of the pH of the moist mudstones, measured in the field by pressing Hydrion paper between freshly broken and then rejoined fragments, is recorded at the left of Table 1. These systems are well into, or below, the minimum pH found necessary by DeKimpe, Gastuche and Brindley (1964) for the synthesis of kaolin minerals at low temperature. The main source of the acid is the oxidizing iron sulfide in the New Albany Shale.

## MINERALOGY OF THE ENDELLITE AND MUDSTONES ADJACENT TO IT

*New Albany Shale* The New Albany Shale in bulk sample contains abundant quartz, clay mineral, dark organic material, iron sulfide and secondary limonite, in varying quantities.

A clay-size fraction ( $<2 \mu$  equivalent spherical diameter by Stokes' Law) of the shale yielded an X-ray diffractogram of illite, apparently 1Md, and a small amount of quartz. Essentially no expanding layers (with ethylene glycol) were registered. A slight elevation in the diffractogram of the glycolated clay, from about 7 Å to about 9 Å spacing where the 10.04 Å peak of illite basal spacing began to rise, is faintly suggestive of the diffractogram produced by endellite undergoing dehydration to halloysite during a diffraction run.

*Endellite* Whitish endellite occurs within the brownish to brownish-gray, somewhat gritty, plastic Brassfield residuum as spots, veins lensing beds and ameboid-shaped irregular bodies. Endellite veins, which tend to follow pre-existing fractures, are commonly a fraction to several inches in width. They may merge with other narrow veins, or with wider lens-to-layer-like shapes or connect with irregular bodies that are 6–12 in. across, vertically or horizontally. Most of the endellite is moderately plastic and finely granular. Other endellite occurrences are small pockets and lenses, commonly up to about 6 in. across, in which the endellite is exceedingly fine-textured, compact, and partly pearly or opalescent: "porcellanous" endellite.

Some contacts, especially between the opalescent endellite and the earthy residuum, appear relatively sharp to the unaided eye. The granular plastic endellite may butt either sharply against the residuum or grade into it across an interval  $\frac{1}{2}$  in. wide.

The endellite was identified by its characteristic X-ray diffractogram (Fig. 1). In thin section it is typically cryptocrystalline and slightly clouded and yields hazy and very low, first-order interference gray. A chemical analysis of a sample collected from this region by T. J. Crawford in 1961, Kentucky Geological Survey Analysis No. 225, is presented in Table 2. It accords with endellite.

Electron micrographs (Plate 1) of the Stanford endellite show its morphology to be elongate tubes and/or rolls best developed in the porcellanous variety (Plate 1a). The surfaces of mortar-pulverized particles, (Plate 1b), are

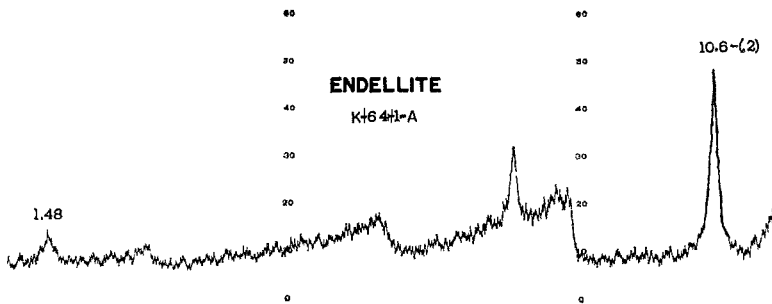


FIG. 1. X-ray diffractogram of Stanford, Kentucky, endellite treated with ethylene glycol. Ni-filtered Cu radiation.

slightly ragged with extended tubular crystals. The more plastic endellite is less elongate and tends to clump into small, cohesive-appearing flocs (Plate 1c, d). Globular shapes—allophane (?)—are abundant in the plastic material.

*Residuum* The enclosing mudstone in which the whitish endellite is developing is dark brown to gray when wetted and plastic, but commonly gritty or accompanied by a slightly granular feel. Much of it is relatively homogeneous and massive in texture and structure. Occasional crustlike, limonitic forms, up to 3 in. in thickness, that are relatively porous and harsh may lie adjacent to some endellite masses. X-ray diffractograms from the predominant, not-harsh residuum show high Fe fluorescence (in Cu radiation), a slight single quartz peak ( $26.7^\circ$ ), but scarcely anything else crystalline. No change in pattern occurs on glycolation.

In thin section (Plate 2), this residuum undergoing endellitization shows typically cryptocrystalline, clouded, low birefringent (and low first-order gray interference color) endellite, containing within it spots of higher interference colors that represent parent clay residue partly transformed to endellite. This sample of residuum is intermediate genetically between final, purest endellite, and the first-stage clay residue described in the next paragraph. A chemical analysis of the intermediate residuum, shown in Plate 2, is presented in Table 2.

A second suite of samples from the same stratigraphic position (between the Richmond and New Albany Shales) was collected from a road cut approximately 2 miles south of the first one described. At this southern road cut, highly decomposed, sandy textured, as well as entirely fresh, Brassfield Limestone several feet thick, is exposed. Laboratory prepared, acid-insoluble residues ( $<2\text{-}\mu$  particles) from the fresh limestone treated separately with 10–15 per cent acetic acid or 10–15 per cent HCl, yielded only very weak  $10\text{ \AA}$  reflections (not expanded by glycol or collapsed by heating) interpreted as illite, and the two strongest reflections, weakly developed, from quartz. Thus, most of the fine fraction of this acid-insoluble clay residue is X-amorphous.

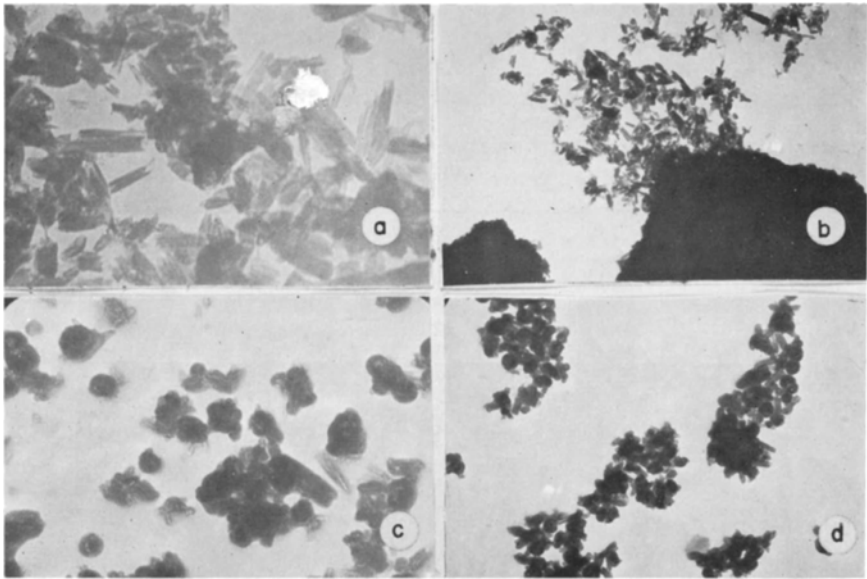


PLATE 1. Electron micrographs of Stanford endellite

- a. Porcellanous endellite, original magnification  $30,000\times$ . Note rolled tubular morphology with "swallow tail" ends. A "double-barrelled" tube in open space in left center may consist of two tubes—or is it one sheet rolled toward the center from two sides?
- b. Porcellanous endellite, original magnification  $8,000\times$ . On the ragged edge of mortar-pulverized fragments are seen protruding (?) or absorbed (?) tubular crystals.
- c. Plastic endellite, original magnification  $30,000\times$ . These crystals are shorter and blockier than those of the porcellanous variety; associated globular shapes are interpreted to be allophane.
- d. Plastic endellite, original magnification,  $16,000\times$ . The plastic endellite clumps together more tightly than does the porcellanous type

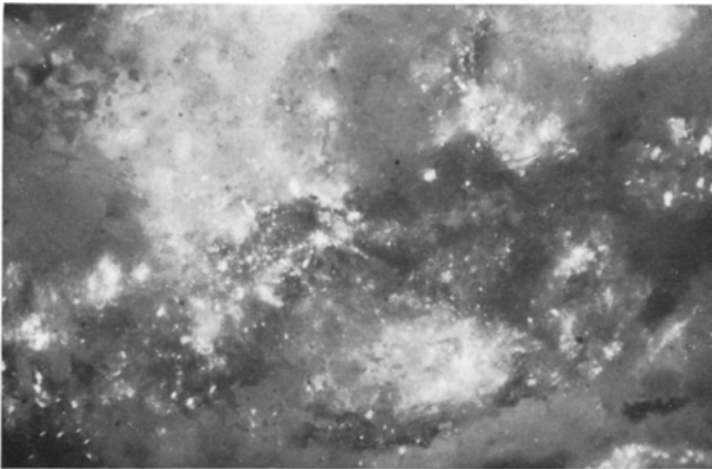


PLATE 2. Photomicrograph of partly endellitized parent residuum of Stanford endellite between crossed polars, original magnification about  $100\times$ . Note low, first-order interference gray color of cryptocrystalline endellite containing light (bright) spots of partly endellitized, otherwise highly birefringent clay mineral.

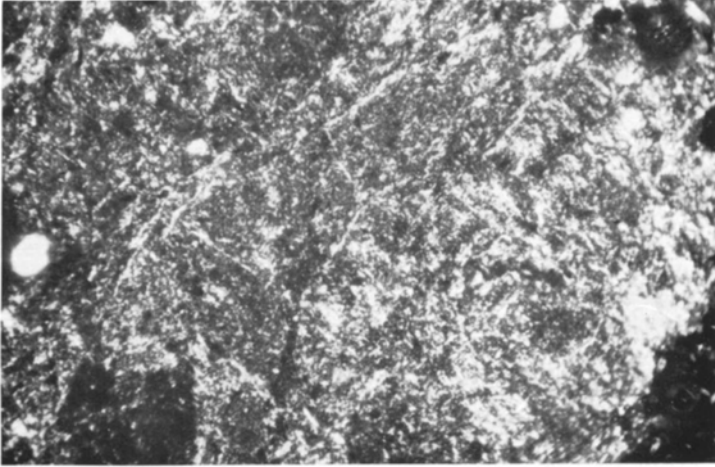


PLATE 3 Photomicrograph of Brassfield red clay residue between crossed polars, original magnification about  $100\times$ . Note criss-cross pattern of randomly oriented, highly birefringent clay flocs and plates mixed with low (dark) interference colour of kaolin-group (?) minerals. Not all of the dark part of the slide is due to extinction positions of the minerals.

TABLE 2.—ANALYSES OF (a) STANFORD ENDELLITE,\* AND (b) ASSOCIATED PARENT RESIDUUM†

	(a)	(b)
SiO <sub>2</sub>	41.50	37.27
Al <sub>2</sub> O <sub>3</sub>	35.89	25.82
Fe <sub>2</sub> O <sub>3</sub>	0.86	10.48
FeO	0.20	1.26
TiO <sub>2</sub>	0.02	0.10
CaO		nil
MgO	Trace	0.59
Na <sub>2</sub> O	0.0	0.37
K <sub>2</sub> O	0.18	1.96
Ig loss	21.55	22.10
Total	100.39	99.95
C	0.09	
S	0.19	
Moisture at 140°C	7.15	
Ratio:	Al <sub>2</sub> O <sub>3</sub> : SiO <sub>2</sub> : H <sub>2</sub> O (Ignition loss)	
(a)	1 : 1.96 : 3.40	
(b)	1 : 2.46 : 4.85	
	1 : 2.0 : 4.0 Ideal endellite	
	1 : 2.0 : .67 : 0.33K <sub>2</sub> O Muscovite	

\* Analysis by Norris Laboratory, U.S. Bureau of Mines.

† Analysis by Bruce Williams Laboratory, Joplin, Mo.

At this same locality, within solution-eroded concavities in the limestone, a reddish-brown clay residue from the naturally weathered limestone remains *in situ*. This clay has been regarded and studied as a prototype of the residuum parent material from which the Stanford endellite developed. It is in first-stage accumulation after release from dissolving limestone and has not undergone subsequent intense reaction with H<sub>2</sub>SO<sub>4</sub> as has elsewhere developed endellite.

A thin section of this clay shows, in addition to the dominant clay mineral matrix, small spots of concentrated iron oxide, and approximately 10–15 per cent of quartz-silt particles, usually up to 0.2 mm and rarely up to 0.7 mm in diameter. The clay mineral, between crossed polars, shows brilliant interference colors, reddish-stained, transmitted from coarse aggregates of floc, shred, and platy shapes that extinguish randomly in an interlocking pattern (Plate 3). This texture, and/or fabric, in contrast to that typical of shale, resembles the random, interlocking pattern exhibited commonly by sedimentary plastic fire clays (Keller, 1946) wherein the dark-gray interference color of "fire clay mineral" is interspersed with brilliant interference light arising from illite, or possibly from the Wiener effect from colloidal clay plates oriented parallel in aggregates. The X-ray diffractograms of this naturally

weathered clay yield quartz peaks but, like the laboratory-prepared residues, no other reflections independently definitive of clay minerals.

*Richmond Shale, altered green zone at top* The bulk, altered Richmond shale contains dominantly quartz and clay mineral. The clay-size fraction ( $<2 \mu$  e.s.d.) of the altered, green, upper zone of the Richmond Shale is dominantly illite (10.04 Å basal spacing) showing slight mixed layering by skewed tailing of the peak toward the high-spacing side. A minor peak at 7.1 Å that does not disappear when the clay is heated to 500°C for 4 hr is interpreted as chlorite in small amount. Quartz peaks are present in moderate intensity. No evidence of endellite, confirmed by glycolation and heat treatments, could be detected.

### GEOCHEMISTRY OF THE ARGILLIZING SYSTEM

The geochemistry and apparent free-energy relations of the argillizing reactions in the Stanford road cut were examined in six systems: (1) New Albany Shale, (2) plastic endellite and (3) porcellanous endellite from the residuum zone, (4) the upper, altered (greenish) zone of the Richmond Shale, (5) non-harsh parent residuum, and (6) the recent, naturally weathered residue from the Brassfield Limestone. The apparent standard free energies of for-

TABLE 3.—DISSOLVED IONS AND COMPOUNDS IN CENTRIFUGATE FROM AQUEOUS SUSPENSIONS

	K	Na	Element Si	Al	SO <sub>4</sub>	H
New Albany Shale						
Dissolved, ppm	0.61	0.37	78	68	225	pH 3.0
log activity	-4.864	-4.849	-2.560	-2.653	-2.685	-3.0
Plastic endellite						
Dissolved, ppm	1.28	6.40	16.20	30	150	pH 3.6
log activity	-4.527	-3.597	-3.239	-2.995	-2.848	-3.6
Porcellanous endellite						
Dissolved, ppm	1.19	2.75	18.6	4.45	36	pH 3.7
log activity	-4.536	-3.942	-3.178	-3.802	-3.446	-3.7
Richmond Shale altered greenish upper zone						
Dissolved, ppm	0.99	0.2	93	120	1000	pH 2.5
log activity	-4.682	-5.142	-2.479	-2.431	-2.062	-2.5
Non-harsh parent residuum						
Dissolved, ppm	1.52	1.26	48.5	65.0	—	pH 3.6
log activity	-4.464	-4.313	-2.810	-2.669	—	-3.6
Recent, Brassfield residue						
Dissolved, ppm	3.300	0.75	22.7	46.0	—	pH 3.3
log activity	-4.122	-4.533	-3.12	-2.814	—	-3.3



mation of the clay minerals were calculated from analyses of the aqueous solute from the clays.

Ten to fifteen grams of disaggregated, outcrop-wet shale or clay were gently shaken in 150 ml. of double-distilled water in a polyethylene container for twenty days, to equilibrate, or at least achieve a steady state, between solution and solid. Our experience has been that about three-days shaking of clay minerals in distilled water brings the solution to constancy. Use of outcrop-wet clay specimens provides a clay-water system that has stood, and reacted, on the outcrop usually for years. The addition of water in the laboratory diluted the solution held within the clay rock and reactivated further dissolution. The actual ratio of solid to water in the laboratory suspension is not significant except that the solid must persist. The clear centrifugate was analyzed (analytical procedure of Keller, Balgord and Reesman 1963), yielding the solubility data shown in Table 3. The accompanying derivations were calculated on an IBM 1620 computer.

Table 3 shows that the equilibrated, or steady-state, suspension of the New Albany Shale yielded 78 and 68 ppm dissolved Si and Al respectively, and a pH of 3.0 (which is higher than pH 1 to 2 found in the water percolating in excess on the outcrop). We interpret the rise in pH to dilution of the acid by water, and also to the reaction with, and the buffering effect of, the illite in the New Albany Shale and the probable endellite forming in it.

The dissolved Si and Al from the samples of both endellites are notably less, but K and Na more, than that from the illitic rocks, and the pH is somewhat higher. From the Richmond Shale, the dissolved Si and Al rose to 93 and 120 ppm respectively. The pH (2.5) in the Richmond Shale suspension, which is lower than that (pH 3.0) in the New Albany is interpreted as due to lack of buffering against the external source of  $H^+$  ions in the Richmond shale because endellite is not formed from it or, alternatively, to conversion to a H-clay that is chemically more stable.

To calculate the apparent standard free energies of formation from the solubility data of the clay minerals, we assume the following:

- (1) The mineral system dissolves in double-distilled water (exposed to the atmosphere) and comes to equilibrium,
- (2) The species of ions in solution are known, and no significant complexing of ions occurs,
- (3) The standard free energies of the solute substances are known,
- (4) If the solid phase is multicomponent, the mineral characterized by the least-negative free energy will be attacked the most, and the solution will be in equilibrium with it. If all components in the system are in equilibrium with each other, the chemical potential of each phase is the same—hence, the liquid represents the equilibrium of the solid phase as a group. Data used in the calculation of the apparent standard free energies of formation are presented in Table 4.

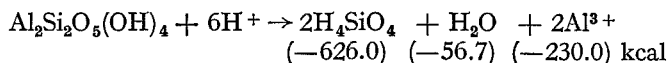
*Calculations for the kaolin formula,  $Al_2Si_2O_5(OH)_4$ , in the shales and clays.* The kaolin ( $2H_2O$ -hydration) formula is used to permit direct comparison

TABLE 4.—FREE ENERGY DATA USED IN CALCULATIONS.

	Kcal/mol	Source
Al <sup>3+</sup>	-115.0	Latimer (1952)
H <sub>4</sub> SiO <sub>4</sub>	-313.00	Modified from Siever (1957)
K <sup>+</sup>	- 67.46	Latimer (1952)
Na <sup>+</sup>	- 62.589	Latimer (1952)
Al(OH) <sup>2+</sup>	-164.9	Raupach (1963)
Al(OH) <sub>2</sub> <sup>1+</sup>	-215.1	Raupach (1963)
Al(OH) <sub>4</sub> <sup>-</sup>	-313.9	Raupach (1963)
H <sub>2</sub> O	- 56.72	Wicks and Block (1963)
OH <sup>-</sup>	- 37.62	Calc. from Wicks and Block

of the endellite by composition with other kaolin minerals; for endellite, *per se*, -113.4 kcal  $F_f^\circ$  for 2H<sub>2</sub>O, would be added.

The reaction of a solid (excess) kaolin-formula mineral with an excess of external H<sup>+</sup> ions may be represented:



Total sum of standard molar free energy of products, as designated,

$$\Sigma F_{f,pro}^\circ = -912.7 \text{ kcal} \quad (1)$$

The constant of equilibrium for this reaction is expressed:

$$K_{eq} = [\text{H}_4\text{SiO}_4]^2 [\text{Al}^{3+}]^2 / [\text{H}^+]^6 \quad (2)$$

Hence,

$$\log K_{eq} = 2 \log [\text{H}_4\text{SiO}_4] + 2 \log [\text{Al}^{3+}] + 6 \text{ pH} \quad (3)$$

$\log K_{eq}$  for porcellanous endellite, sample (c), becomes:

$$\begin{aligned} \log K_{eq(c)} &= (-6.40) + (-7.60) + (22.2) \\ &= 8.2 \end{aligned} \quad (4)$$

The change in standard free energy of a reaction,  $\Delta F_R^\circ$ , is,

$$\Delta F_R^\circ = -1.364 \log K_{eq} \quad (5)$$

The change in standard free energy (between reactants and products) in the dissolution of porcellanous endellite, (c), is found to be:

$$\Delta F_{R(c)}^\circ = -1.364 (8.2) = -11.18 \text{ kcal} \quad (6)$$

Furthermore, in a reaction;

$$\Delta F_R^\circ = \Sigma F_{f,products}^\circ - \Sigma F_{f,reactants}^\circ \quad (7)$$

Then, the apparent standard free energy of formation of the kaolin formula (compound) in the porcellanous endellite, (c), is

$$F^{\circ}_{f,kaol(c)} = -912.7 - (-11.18) = -901.52 \text{ kcal} \quad (8)$$

By similar calculation, the apparent  $F^{\circ}_f$  for the kaolin formula represented in the other clays is found to be:

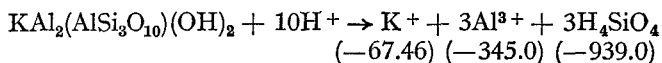
New Albany shale clay	-902.52 kcal
Plastic endellite	-900.36 kcal
Richmond shale clay	-905.85 kcal
Other sources of $F^{\circ}_f$ for clay minerals:	
Kaolinite (calorimetry, Barany and Kelley, 1961)	-903.8 kcal
Halloysite (same reference)	-899.3 kcal
Endellite (dehydration data, N. M. Saum, personal com.)	-902.1 kcal

Using the values obtained from calorimetry by Barany and Kelley (1961) as a standard reference for kaolinite and halloysite, we found that our values obtained by solution are of the same order of magnitude. This gives confidence in our laboratory work, and also in the assumption that equilibrium was reached between the clay and the solution—indeed, if saturation had not been reached, our  $F^{\circ}_f$  would have been a larger number (more negative), not less, than that of kaolinite. The  $F^{\circ}_f$  for the kaolin formula in the new Albany shale, where endellite was provisionally found by X-ray, is less negative than that of kaolinite, but in the Richmond shale where no kaolin-group mineral was recorded, undersaturation, shown by  $F^{\circ}_f$  higher than kaolinite, was measured.

The conclusion, therefore, from these solution data is that the present geochemical systems in the endellite and New Albany shale are producing a kaolin-formula mineral in equilibrium with the solution, and that the sources of the Si and Al are the parent materials being attacked by the excess sulfuric acid.

The next step is to investigate similarly the illite in the clay systems for its relationship to endellite formation.

*Calculations for the muscovite formula, and "ideal" variety of illite.* The departure of illite from ideality will be discussed relative to the ideality after the calculations are presented. The reaction of illite with an external excess of  $H^+$  ions, is shown:



$$\Sigma F^{\circ}_{f,pro} = -1351.46 \text{ kcal} \quad (9)$$

$$K_{eq,ill} = [K^+] [Al^{3+}]^3 [H_4SiO_4]^3 / [H^+]^{10} \quad (10)$$

$$\log K_{eq,ill} = \log [K^+] + 3 \log [Al^{3+}] + 3 \log [H_4SiO_4] + 10 \text{ pH} \quad (11)$$

For New Albany illite, (a):

$$\log K_{eq} = 9.36 \quad (12)$$

$$\Delta F^{\circ}_R = -12.67 \quad (13)$$

$$\text{and } F^{\circ}_f, \text{ill(a)} = -1338.79 \quad (14)$$

For other illites and muscovite, their apparent  $F^{\circ}_f$  are:

Richmond shale	-1344.46 kcal
<2m Fithian (mean)	-1339.95 kcal
Mean taken from a range, 1337.55 to 1342.95, in 6* dissolutions	
<2m Beavers Bend (mean)	-1331.85 kcal
Range, 1330.75 to 1332.85 in 4* dissolutions	
Muscovite (Solution data from Keller, Balgord, and Reesman, 1963)	-1329.35 kcal
Muscovite (calculated from data from K. K. Kelley)	-1330.1 $\pm$ 1.3 kcal

Taking the  $F^{\circ}_f$  determined for muscovite,  $-1330.1 \pm 1.3$  kcal, by Kelley (personal communication, 1964) as standard, our value determined from solubility data,  $-1329.35$  kcal, is reassuring. The value for Beaver Bend illite,  $-1331.85$  kcal, is close to that of muscovite and suggests that Beaver Bend is a relatively pure, micaceous clay as Mankin and Dodd (1963) proposed. Fithian illite fractions are likely to be non-uniform, as shown by our solution experiments and the experience of others.

Illite, a name for a mineral group, whose constituents may originate diversely by at least six processes (Keller, 1964), is variable in chemical composition and in degree of physical disordering in crystals, which may be polymorphic (Levinson, 1955). The binding energy values of physically disordered crystals formed at low temperature are more negative, i.e. more stable, at low temperature than are their more-ordered, high-temperature counterparts (calculations by Maynard Slaughter, personal communication, 1964). A similar energy relationship is shown by our experiments.

The  $F^{\circ}_f$  of the illite in the New Albany shale falls within the low range of Fithian fractions and indicates that the (1) illite, (2) endellite, and (3) solution in this system are in equilibrium. Thus, illite or endellite, being in equilibrium with the same solution, may theoretically be transformed each to the other. Realistically, owing to the excess of  $H^+$  ions from the  $H_2SO_4$ , New Albany illite will tend potentially to be converted into endellite.

*Correlation of apparent free energy data with the geological environment.* Among the several changes in geological environment that might induce clay mineral precipitations from solution, two are uniquely applicable in the Stanford occurrence: (1) reaction by the solution with a susceptible, low-stability variety of illite or residuum as observed here, or (2) a rise in pH

\* These measurements made on one sample of each clay from which a centrifugate was taken; then new distilled water was added, shaken for a given time and centrifuged; and thus repeated. One sample of Beaver Bend illite shaken for 18 months yielded pH 6.5, and the same  $F^{\circ}_f$  as the mean of all four; the 18-month Fithian sample yielded pH 4, and  $-1342.45$  kcal. The Beaver Bend material is purer illite than most Fithian fractions, as has also been observed by X-ray and other measurements.

The effect of change in concentration of  $H^+$  ions in the kaolin-endellite reaction is a 6-power function (see equation), and in the illite reaction a 10-power function. The source of  $H_2SO_4$  in the New Albany shale yields a pH lower than the buffered values of kaolin-formula clays or illite, as observed in the laboratory; but clay mineral precipitation will ensue as these excessively acid solutions react with low-stability clay parent material in the residuum layer or encounter carbonate minerals or solutions, raising the pH.

The noteworthy variability of range in the free energy values in illite minerals has been pointed out in a foregoing section, whereas the free energy values of the kaolin minerals are relatively more constant. We have shown that in a given system one illite of lesser stability may be dissolved to produce endellite, whereas another illite of higher stability may not be transformed. Further application of this relationship is being studied, particularly within the illite-“fire clay” mineral-kaolinite system.

The apparent  $F^\circ_f$  value for mica (illite) in the Richmond shale,  $-1344.46$  kcal, is larger (more negative) than any other illite values, including the highest we have measured for Fithian. The conclusion is that the solution in the Richmond altered zone is undersaturated with respect to endellite and illite of most negative  $F^\circ_f$ —hence, this shale is being altered without deposition of clay minerals taking place now.

*Calculations for residuum samples.* By similar calculations, the dissolved products of the “non-harsh parent residuum” surrounding and enclosing the endellite masses yield apparent  $F^\circ_f$ 's of  $-898.09$  kcal relative to the kaolinite formula, and of  $-1330.67$  kcal for the muscovite formula. Being approximately 3.4 kcal less negative than the calculated value for porcellanous endellite indicates higher solubility (hence, higher susceptibility to alteration) of the parent residuum than that of endellite. Probably allophane (higher solubility) is present—similar to allophane associated with endellite in “indianaite”.

The apparent  $F^\circ_f$ 's of the reddish first-stage, “recent Brassfield residuum” collected at the southern locality are  $-901.92$  kcal and  $-1340.52$  kcal for kaolinite and muscovite formulas respectively. These values are within the typical ranges for endellite and illite and therefore accord with equilibrium relations between those minerals, which is in agreement with thin-section evidence (Plate 3).

## GEOLOGICAL IMPLICATIONS

With respect to the genesis of endellite in the geological environment, it is obvious from the Stanford, Kentucky, occurrence that a clay residue derived from certain limestones is notably more susceptible to reaction with acid solutions than is illite from typical shale. Higher susceptibility may arise because limestone-derived clay has been through one or more cycles of sedimentation; therefore, the clay is likely to: (1) be colloidal or nearly so in particle size, because it has been deposited with nonclastic materials in the sedimentational sorting sequence, (2) be defective in crystallinity because of

depletion of easily leached cations during prior weathering—indeed, yielding possibly an essentially amorphous state to X-ray, (3) be high in surface energy owing to high specific surface that is characterized by a different ionic population and direction of bonding forces (at the surface) than that which exists in the organized interior of the compound, and (4) contain a significant amount of reconstituted and/or authigenic mineral or mineraloid compounds.

## SIMILARITY BETWEEN KENTUCKY AND INDIANA ENDELLITES

Commercial deposits of the clay rock containing endellite and allophane, were mined from Gardner Mine Ridge, Lawrence County, Indiana, from 1874 to 1891. In addition to a series of earlier papers on them which include the introduction of the name "indianaite" by Cox in 1874 (see references in Callaghan, 1948; and Sunderman, 1963), they were mapped, analyzed and well-documented by the last-named writers. White discussed the properties of Lawrence County allophanes in 1953. The clay deposits and associated iron ore are contained in the newly proposed "Spice Valley Member" (Sunderman, 1963) of the Pennsylvanian Mansfield sandstone and conglomerate. The Spice Valley Member rests unconformably on variously the Mississippian Chester, Elwren Formation, Beech Creek Limestone, Glen Dean Limestone, and possibly the shale of the Hardinsburg Formation.

Callaghan (1948), and Sunderman (1963, pp. 5, 85), discuss some eight different postulates of origin of the endellite before presenting their interpretations. Although all of theirs, as well as ours which is outlined below, possess some unique emphasis on times and processes of reaction, they all overlap sufficiently so that the major ideas of each can be "read into" those of the others. Without taking space to compare and contrast the hypotheses, we suggest the following geological events to describe the origin of the Indiana endellite.

1. Sedimentation through the Chester series, and probably through the St. Louis Limestone (reported by Malott, 1946, pp. 96-101 for the nearby Bedford region).

2. Uplift, erosion and pronounced weathering culminating in the development of a residuum overlying the eroded Mississippian formations. The residuum represents an oxidized well-leached residue (the mahogany clay of Callaghan) principally from the Mississippian Limestones. The Beech Creek Limestone, observed in the abandoned Wilson mine near Huron, Indiana, was a notable contributor to this residuum.

3. Deposition of the conglomeratic and sandy parts of the lower Mansfield Formation. Rapid deposition of conglomerate by energetic streams on, and intertonguing with, the plastic underlying "mahogany" residual clay. Occasional differential settling and soft-rock deformation, and intrusion and flowing between the clay and the heavy overlying Mansfield sediments, to

produce apophyses of the clay in the sandstone, and down-sunk boulders of conglomeratic sandstone in the soft clay.

4. Complete deposition of the highly pyritic Mansfield Formation.

5. Further sedimentation, post-Paleozoic uplift, and erosion to yield the present topography. The slightly dipping rocks (about 35 ft per mile, Callaghan, 1948, p. 12) constitute a gently inclined permeable layer down which ground water can move as next described.

6. Beginning probably in Tertiary time, and continuing until today, sulfuric acid solution from the oxidizing pyrite in the Mansfield Formation percolated into the "mahogany-clay" residuum, and reconstituted it into endellite and allophane that are relatively free from iron and concentrated the iron oxide elsewhere. Callaghan noted iron sulfides in the Mansfield Formation in a road cut 2 miles east of Gardner Ridge; here we found seep water from the exposed layers to test pH 1.0. Although the geological ages of the rocks are different, the physical and geochemical conditions are similar at the Stanford, Kentucky, and Lawrence County, Indiana, endellite deposits. We believe the processes of origin of the two deposits are basically the same.

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