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CLAY MINERAL SEGREGATION BY FLOCCULATION IN THE PORTERS CREEK FORMATION

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Abstract—The Porters Creek Formation is mined as an absorbent clay in Illinois, Mississippi, Missouri, and Tennessee. The absorptive properties of the Porters Creek Formation are due to the high content of smectite which constitutes >50% of the minerals present. Analyses of 220 samples of the Porters Creek collected in Illinois, Missouri, and Tennessee indicate that the smectite content is highest on the western side of the Mississippi embayment and that the kaolinite content is highest on the northeastern side. The major influx of detritral clays appears to have entered the embayment from a large river on the northeast side. A major control of the distribution of clay minerals during the time of Porters Creek deposition was differential flocculation of kaolinite, illite, and smectite, as evidenced by the numerous syneresis cracks on bedding planes in the area of greatest kaolinite content. Estimates of the smectite, illite, and kaolinite contents suggest both horizontal and vertical variations among these clay minerals. In certain localities the oxidation of pyrite has created acid conditions, which apparently were conducive to the formation of authigenic halloysite.

Key Words—Flocculation, Illite, Kaolinite, Sedimentation, Smectite.

INTRODUCTION

The marine Porters Creek Formation of Paleocene age in Illinois, Mississippi, Missouri, and Tennessee is an important source of absorbent clays; the clays are used for such purposes as pet litter, agricultural chemicals and fertilizers, and in the clean-up of oil and grease spills. According to Bennett (1976), the higher the smectite content of the clay, the better the absorbent properties. The distribution patterns of the clay minerals in this formation are therefore important in attempting to locate areas of the greatest commercial significance. Various studies have documented the segregation of clay mineral species in marine environments (Edzwald and O'Melia, 1975; Gibbs, 1977). Parham (1966) concluded that landward accumulation of kaolinite relative to illite and smectite commonly takes place during transport of detrital clays from fresh to saline waters, and laboratory studies by Whitehouse and McCarter (1958) showed that kaolinite and illite readily flocculate when they are introduced into saline environments.

From sedimentary structures and paleontological indicators, Pryor and Glass (1961) established environments of deposition of Tertiary sediments in the northern Mississippi embayment. On the basis of interformational comparisons, they found clay mineral distributions to be correlative with these environments: kaolinite was concentrated in fluviatile sediments; kaolinite, illite, and smectite were all present in inner neritic sediments; and smectite dominated the outer neritic clay assemblages. They stated that neither source area nor diagenesis was responsible for these variations, but that the detrital clays were segregated during their original deposition.

The present study was conducted to determine intraformational clay mineral distributions in the Porters Creek Formation in the northern Mississippi embayment, to investigate the diagenetic vs. detrital mechanisms responsible for these distributions, and to ascertain if any of these distributions correspond to environmental changes that have been proposed for the Paleocene epoch.

GEOLOGIC SETTING

The Paleocene Porters Creek Formation consists of smectitic, conchoidally fracturing shales and mudstones and forms part of a large re-entrant of Cretaceous and Tertiary rocks deposited in the Mississippi embayment (Figure 1). The Mississippi embayment is a structural low that formed during the Cretaceous period and continued with increasing subsidence through the Eocene epoch. Crustal extensions and subsidence along the embayment axis have been attributed to the emplacement of Mesozoic intrusives (Kane *et al.*, 1979; Pinckney, 1980). Porters Creek strata represent deposition during stillstand and regression after maximum transgression within the embayment (Pryor and Glass, 1961). A general stratigraphic column of embayment rocks is shown in Figure 2.

PROCEDURES

Sample collection

Two hundred twenty samples of the Porters Creek Formation were collected during the summer of 1980

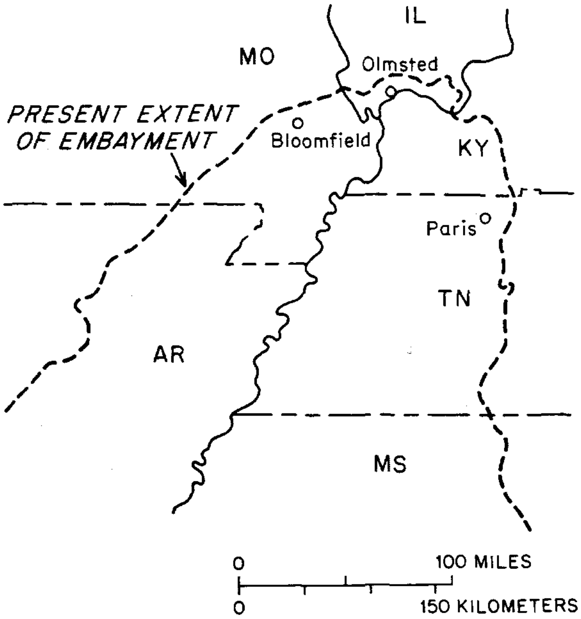

Figure 1. Present extent of the northern Mississippi embayment.

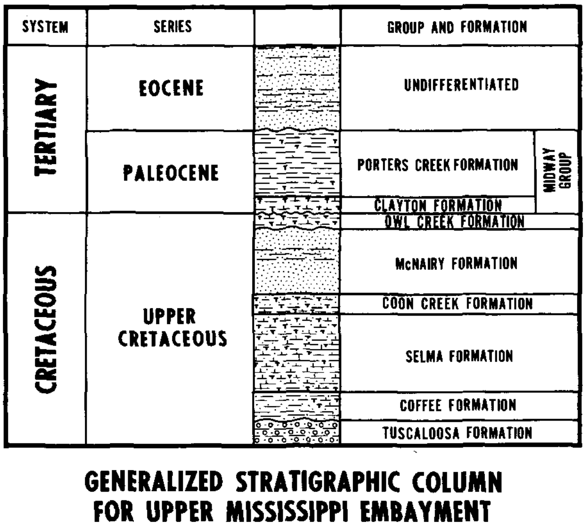

Figure 2. Generalized stratigraphic column for the upper Mississippi embayment (from Pryor and Glass, 1961).

from high walls of open pit mines and drill hole samples. The principal sample localities are shown in Figure 1 at Bloomfield, Missouri; Olmsted, Illinois; and Paris, Tennessee. Highwall samples were obtained by channeling each 4-ft interval (1.23 m) of outcrop vertically and splitting the samples to about 500 g. Drill hole samples were provided by Edward M. Lowe, Inc. Five hundred grams from each 4-ft interval (1.23 m) of drill hole sample was obtained for laboratory examination. All samples, stored in air-tight containers in the field, were still damp when the containers were opened for laboratory analyses.

Sample preparation and analyses

All samples were oven dried at 35°–40°C. Most of each sample was then ground to <4 mesh (4.75 mm), except for some small chunks which were selected for scanning electron microscopy. The minerals in the Porters Creek Formation samples were identified using X-ray powder diffraction (XRD). XRD traces were obtained using CuKα radiation on a Norelco XRG 2500 diffractometer.

The percentages of clay minerals were estimated from XRD traces of <2-μm size fractions. Many samples would not disaggregate by soaking and ultrasonic vibration; hence, 10 g of each of these well indurated samples were wet ground in distilled water in a mortar and pestle at 50% solids for 1.5 min. The sample was then gravity settled to obtain a <2-μm size fraction (Jackson, 1956), centrifuged, and smeared on a glass slide as a thick slurry and dried.

The peak areas of the 5.2°, 8.85°, and 12.42°2θ reflections of glycolated samples were equated to smectite, illite, and kaolinite mineral percentages, respectively, in the ratio of 4:1:1.4 (Johns *et al.,* 1954). This technique gives proportionate ratios of the clay minerals present. For example, if the sample contains smectite, illite and kaolinite, the area under the 001 reflection of the glycolated smectite is measured, as are the areas under the 001 illite and the 001 kaolinite peaks. The area under the smectite peak is divided by 4, and that under the kaolinite peak area by 1.4 to equate the proportions of each clay mineral present in the sample.

Scanning electron microscopy was conducted on ETEC Autoscan and Cambridge Stereoscan instruments, the latter equipped with an Ortec energy-dispersive X-ray spectrometer.

MINERAL COMPOSITION OF THE PORTERS CREEK

The Porters Creek Formation is a smectite-rich mudstone containing detectable amounts of kaolinite, illite, and halloysite, and locally traces of chlorite in the clay fraction. The dominant non-clay minerals are quartz, muscovite, feldspars, and siderite. Locally, fragments of diatoms have been noted in scanning electron micrographs, and trace amounts of opaline silica have been detected on a few XRD traces. Calcite is present in the tests of detrital foraminifera and nannofossils in the basal 20 ft (6.1 m) of the Bloomfield, Missouri, section. The abundances of the non-clay minerals range from 6 to 30%, with quartz being the most abundant, ranging from 4 to 22%. Trace amounts of heavy minerals have also been identified, including goethite, rutile, zircon, tourmaline, magnetite, pyrite, staurolite, kyanite, and sillimanite (Murray and Bennett, 1976).

These clay mineral ranges agree well with those reported by Pryor and Glass (1961). The smectite content of the mixed-layer illite/smectite is >83%, using the technique of Perry and Hower (1970). Because of its small percentage of illite layers, this clay will be referred to as smectite, rather than illite/smectite.

Authigenic mineral constituents

Two mineral constituents in the samples examined from the Porters Creek Formation are believed to be authigenic. These are halloysite and clinoptilolite, the former identified at the Paris, Tennessee, location and the latter at the Bloomfield, Missouri, location. XRD data for samples from Paris, Tennessee, indicated the presence of halloysite(10Å) in the lower portion of the Porters Creek section. Scanning electron micrographs showed spherical, nodular aggregates (Figure 3). Energy-dispersive elemental analyses of these aggregates indicated alumina : silica ratios of ~1:1. Halloysite was identified by changes in the intensity of the kaolinite 001 reflection at 7.12 Å after heating the sample to 180°C, as described by Carroll (1970). Bennett (1976) found that the pH in the Porter Creek strata at Paris, Tennessee, was 4 in the lower portion of the section, in which most of the halloysite was identified. The upper 22 to 25 ft (6.1–7.6 m) is brown, and the lower 30 to 40 ft (9.1–12.2 m) is dark gray to black and contains finely disseminated pyrite. Thus, the upper portion is probably oxidized, and the sulfuric acid that formed by the destruction of pyrite probably dissolved the alumina and silica that precipitated as halloysite aggregates in small open pores in the lower, dark-colored mudstone. Some halloysite but no pyrite was detected in the upper, brown oxidized zone. Sudo and Shimeda (1977) described similar halloysite occurrences in what they call "acid clay" deposits. No halloysite was detected in samples from Olmsted, Illinois, or from Bloomfield, Missouri.

Clinoptilolite was identified locally in amounts of 2–4% in samples from Bloomfield, Missouri. XRD data and thermal stability at 270°C (Mumpton, 1960) were used to identify the zeolite as clinoptilolite. Because zeolites are commonly associated with pyroclastic and other volcanic materials, volcanic debris was specifically looked for in this study, but none was detected. Neither Grim (1933), Pryor and Glass (1961), nor Bennett (1976) reported volcanic material in their studies of the Porters Creek strata. In the Bloomfield, Missouri, section clinoptilolite is most abundant just below the uppermost occurrence of calcareous foraminifera tests in the basal strata. The clinoptilolite formed in voids below the calcareous foram tests, suggesting that enough calcium, alumina, and silica were present in the ground water or the innate mudstone water to precipitate very well crystallized clinoptilolite.

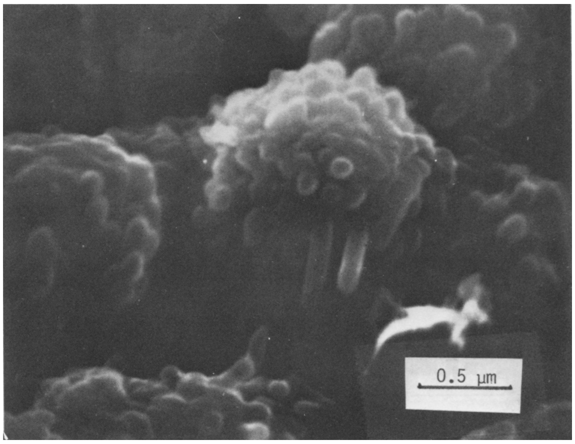

Figure 3. Scanning electron micrograph showing spherical aggregates thought to be halloysite.

Detrital clay mineral composition

XRD estimates of the detrital clay minerals show the dominant clay mineral to be calcium montmorillonite, with subordinate amounts of kaolinite and illite. Figure 4 shows a plot of the percentages of kaolinite vs. depth, as determined from channel samples collected from exposed high walls at Bloomfield, Missouri; Olmsted, Illinois; and Paris, Tennessee. The kaolinite percentage in the Porters Creek Formation at the Paris, Tennessee, location ranges from 40 to 50%, whereas at Olmsted, Illinois, it ranges from 10 to 25% and at Bloomfield, Missouri, between 3 and 20%. At Paris, Tennessee, the kaolinite content is relatively uniform from top to bottom of the section sampled, whereas at both Olmsted, Illinois, and Bloomfield, Missouri, the kaolinite content increases upward in the sampled sections. Drill-hole samples analyzed from Bloomfield, Missouri, and Paris, Tennessee, confirm these observations. The illite content at all three locations is relatively constant (7–10%), whereas the kaolinite and smectite contents have an inverse relationship, i.e., as the kaolinite content increases the smectite content decreases. The presence of halloysite(7Å) is indicated by the shaded area on the lower portion of the Paris, Tennessee, kaolinite-percentage plot. Two drill-hole sample locations and another channel-sample section at Paris, Tennessee, showed a range in the kaolinite content of 33–50%, which indicates considerable lateral variability in the kaolinite content at this location.

CLAY MINERAL DISPERSAL

From electric logs of Cretaceous, Paleocene, and lower Eocene formations in the northern Mississippi embayment and sand-shale isopach maps, Stearns (1957) presented evidence for a deltaic system in the northeastern portion of the area. This deltaic system was well developed in late Cretaceous, Paleocene, and Eocene time.

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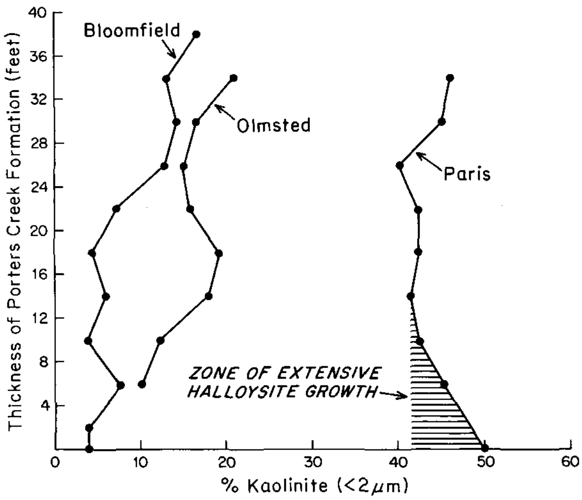

Figure 4. Kaolinite percentages as a function of depth in the Porters Creek Formation.

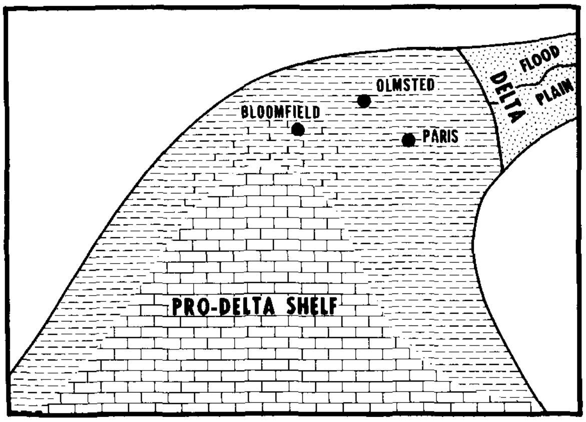

Figure 5. Schematic diagram of embayment environments envisioned immediately after maximum Paleocene transgression (modified from Pryor, 1960).

From dispersal directions in the upper Cretaceous McNairy Formation based on cross bed measurements, Pryor (1960) stated that the dominant dispersal directions were northeast to southwest. Stearns (1957) and Potter and Pryor (1961) also suggested southwestern dispersal directions in the central craton for sedimentary rocks of upper Cretaceous, Paleocene, and Eocene ages.

The Paris, Olmsted, and Bloomfield localities of the Porters Creek Formation, respectively, represent a proximal to distal formational cross section with respect to the clastic dispersal point represented by a delta (Figure 5). The kaolinite percentages shown in Figure 4 support a selective decrease of kaolinite away from a dispersal point near the Paris, Tennessee, locality of a large delta.

A decrease in kaolinite content seaward from dispersal points has been noted by many authors; e.g., Van Andel and Postma (1954) found illite and kaolinite landward of smectite in the Gulf of Paria sediments. Gradual seaward decreases in kaolinite : illite ratios for the North Carolina Pamlico River Estuary were attributed to selective flocculation of kaolinite on contact with increased salinities (Edzwald and O'Melia, 1975). Kaolinite has also been found landward of illite-chlorite-smectite assemblages in the Atlantic Coastal Plain (Grout and Glass, 1960).

Clay deposition by differential flocculation was probably responsible for the decrease in kaolinite content from east near the dispersal point to west in the laterally continuous Porters Creek Formation. The increase in kaolinite content upward from the base in the Olmsted, Illinois, and the Bloomfield, Missouri, Porters Creek sections can be explained by at least two hypotheses. The first is that a prograding delta dispersal point shifted, and more detrital kaolinite was carried west as the embayment filled. Another explanation is that the kaolinite content increased upward due to alteration by downward percolating water. If this second hypothesis were correct, however, the kaolinite content should increase substantially in the top, brown oxidized zone compared with the dark-colored unoxidized mudstone in the lower part of the sections. This is not the case, because as shown on Figure 4 the kaolinite content is relatively constant throughout the Paris section and increases rather gradually upward in both the Olmsted and Bloomfield sections.

An alternative mechanism for the segregation of detrital clay minerals other than selective flocculation is particle size differences of the various clay minerals and, thus, different settling rates. Gibbs (1977) stated that organic and metallic coatings have given Amazon River kaolinite, illite, and smectite the same tendency to flocculate; therefore, sorting of clay minerals was primarily by particle size. This phenomenon resulted in downshelf transport of smectite because of its smaller particle size compared with that of kaolinite and illite.

The particle size of kaolinite and illite is larger than that of smectite in the areas sampled for the present study. A representative particle-size distribution of each of the clay minerals in the clay-size fraction is shown in Figure 6. Illite and kaolinite are both relatively coarse grained, and if particle settling was the primary reason for segregation, these two clays should have concentrated together, which is not the case. Therefore, a mechanism other than particle size must be invoked to explain the clay mineral segregation.

Selective flocculation appears to be the mechanism that best explains the concentration of kaolinite in the Porters Creek Formation near the dispersal area along the northeast portion of the Mississippi embayment relative to illite and smectite, which were apparently carried to the north and west. Syneresis cracks are pres-

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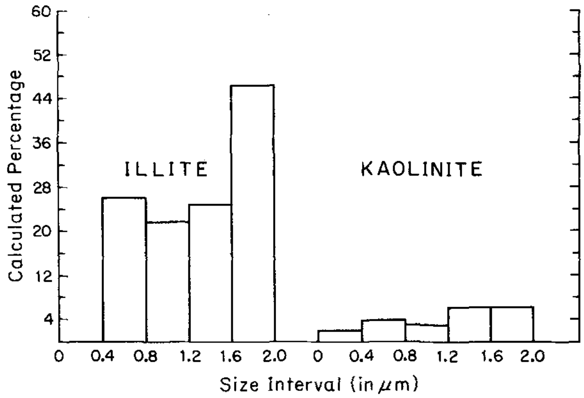

Figure 6. Typical particle size distribution of illite and kaolinite in the Porters Creek Formation in the <2-μm fraction.

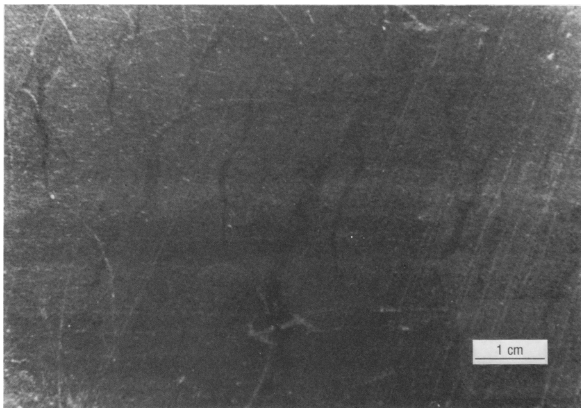

Figure 7. Syneresis cracks in the Porters Creek Formation from a sample collected near Paris, Tennessee.

ent throughout the section at Paris, Tennessee, which supports the hypothesis of kaolinite deposition and concentration by flocculation. Syneresis is a continuation of the flocculation process in which the clays, even after deposition, continue to attract each other by electrochemical mechanisms (Potter *et al.,* 1980). Dewatering of the clay material because of this attraction process forms cracks in the sediment. Such syneresis cracks are usually 0.2–1.0 mm across and filled with material that is compositionally similar to the surrounding claystone (Selley, 1976). Cracks observed in the Porters Creek Formation (Figure 7) ranged from 0.5 to 1.5 mm across; they are ~12 cm in length and 1–16 cm deep. The cracks are perpendicular and oblique to bedding planes and may "V" up or down (Thomas, 1981). The cracks are filled with clay of the same composition as the surrounding material.

SOURCE OF DETRITAL CLAY MINERALS

Pryor and Glass (1961) reported that the source of sediments in the northern Mississippi embayment was chiefly the Blue Ridge and Piedmont Plateau provinces of the southern Appalachians. An eastern source of coarse clastic material was proposed for this region by Grim (1933), Pryor (1960), and Potter and Pryor (1961), but part of the detrital clay minerals, namely smectite, does not fit well into an Appalachian provenance.

Pevear (1972) found that the dominant clay mineral forming in Piedmont soils is kaolinite. Potter *et al.* (1975) observed that relatively no smectite is being derived from Appalachian drainages which presently feed the Gulf of Mexico, but large quantities of smectite appear to be coming from western sources.

In late Cretaceous time, many smectite-rich shales were uplifted on the western plains (McGookey *et al.,* 1972), and erosional products were transported eastward toward the Mississippi embayment. MacNeil (1966) suggested the possibility of a western source for the smectite-rich Porters Creek Formation in the southern portion of the Mississippi embayment. Our data suggest that kaolinite and illite came primarily from an Appalachian source and that smectite came primarily from the western plains, as shown in Figure 8.

Pryor and Glass (1961) showed that at the beginning of Paleocene time a maximum transgression was followed by gradual regression and stillstand. During the regression and stillstand the landward accumulation of sediments deposited in the northeast region of the embayment became subject to erosion. These sediments, presumably containing kaolinite and illite contents similar to or possibly greater than those found in the Paris, Tennessee, section, influenced the clay mineral

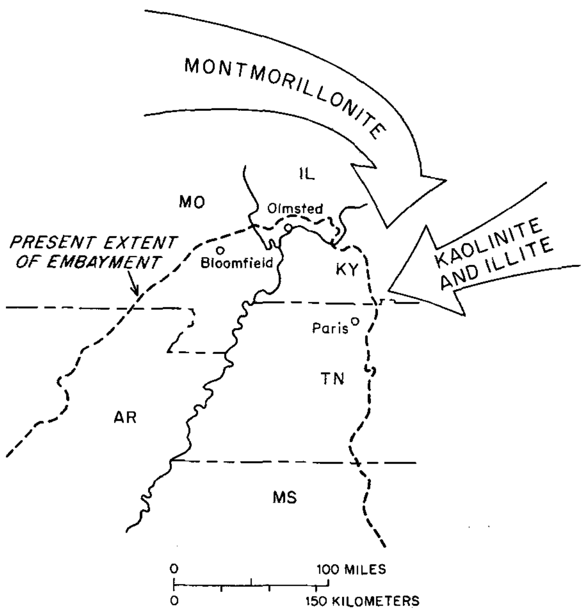

Figure 8. Proposed direction of transportation for the major clay types observed in the northern Mississippi embayment.

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composition being carried into the embayment by increasing the relative percentages of these two clay minerals. This may account for the increasing kaolinite percentages from the base upward, as seen in the Olmsted and Bloomfield sections (Figure 4).

SUMMARY AND CONCLUSIONS

The percentage of kaolinite in the study area increases from west to east and the percentage of smectite increases from east to west. This distribution can best be explained by selective flocculation of kaolinite as it entered the marine Mississippi embayment. Syneresis cracks are abundant in the Paris, Tennessee, area, which supports the hypothesis of deposition by selective flocculation.

The increase in kaolinite content from the base upward in the Porters Creek sections at Bloomfield, Missouri, and Olmsted, Illinois, is best explained by erosion of kaolinite-rich sediments deposited during maximum transgression of the inland sea in early Paleocene time. This erosion apparently took place as the sea regressed and at stillstand during middle and late Paleocene time.

Authigenic halloysite and clinoptilolite formed post-depositionally locally as a result of special alteration conditions.

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