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SEDIMENTARY STRUCTURE IN GRAY KAOLINS OF GEORGIA

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Abstract—One Tertiary and two Cretaceous gray kaolin sites in Georgia were examined using X-ray radiography of core sections to determine the processes of formation of the deposits. The Tertiary kaolin was oxidized in the upper 3 m of the deposit and reduced below that point. The two Cretaceous kaolins were reduced from the top of the deposit to an abrupt boundary with oxidized red kaolin below. Radiography of the first Cretaceous core revealed thin laminar bedding in the gray kaolin and in the underlying red kaolin. The laminae continue without interruption across the gray kaolin/red kaolin boundary. The laminae were not visible in the gray kaolin except in radiographs. Sedimentary bedding was not observed visually or radiographically at the Tertiary site nor in sections of the core from the second Cretaceous site where kaolinite was recrystallized to large vermiforms. The original sedimentary structure in the first Cretaceous kaolin was preserved possibly due to the inhibition of kaolinite recrystallization by a higher organic matter content. Recrystallization of kaolinite and iron compounds may have destroyed sedimentary structures in part or all of the other two kaolin cores. It is hypothesized that the first Cretaceous kaolin sampled was deposited as a kaolinite-iron oxide mixture in an environment free of subsequent physical and biological mixing. The same hypothesis may apply to the other two kaolins but recrystallization after deposition has destroyed sedimentary structures.

Key Words—Gray kaolin, Kaolinite, Sedimentary structure, X-ray radiography.

INTRODUCTION

The depositional environment and the post depositional history of most of the Georgia kaolin deposits are unknown due to the lack of visible depositional features in the relatively homogeneous white kaolin deposits. Most authors agree that the kaolin deposits are derived from materials weathered from the Piedmont crystalline rocks and transported to their present location (Austin, 1978; Bates, 1964; Hurst, 1979; Schrader *et al.,* 1983). There is little agreement, however, as to whether the deposits were originally feldspathic sand or kaolinite-rich clay and on the environment of deposition. Austin (1978), in a review of literature and personal observations on the stratigraphy of kaolins, did not report observing sedimentary structure in the commercial deposits but noted crossbedding and cut and fill structures in the surrounding sandy deposits. He observed post-burial bioturbation at the top of some Cretaceous deposits and 1- to 3-mm-diameter tubular forms and brown spots in Tertiary kaolins.

X-ray radiography is a technique in which spatial differences in composition within a sample are measured by the differences in absorption of X-rays as they penetrate the sample (Bouma, 1969). In the years following the application of the technique to the study of sedimentary structure by Hamblin (1962), radiography has become a common characterization tool in sedimentary petrology. However, no reports have been published of the application of radiography to the study of sedimentary structure in kaolins.

Georgia kaolins occur in two chemical environments. Those kaolins which are cream to red in color are presently oxidized. Kaolin deposits in reducing environments are termed gray kaolins. Many of the oxidized kaolins presently mined in the Coastal Plain of the United States may have been reduced at some time in their history but have since oxidized (Hurst, 1979; Schrader *et al.,* 1983).

As a part of a study of gray kaolins, one Tertiary and two Cretaceous kaolin deposits of Georgia were cored and were examined by a variety of techniques. Extensive recrystallization of the sulfides was found in portions of all the gray kaolins sampled (White *et al.,* 1991). In addition, the Tertiary and one of the Cretaceous gray kaolins had undergone recrystallization of the kaolinite (White *et al.,* 1992). This report presents the results of examining the cores by X-ray radiography to search for the presence of sedimentary structure as an indicator of the depositional and post-depositional history.

MATERIALS AND METHODS

Three cores, one of Tertiary and two of Cretaceous age gray kaolins, were obtained in cooperation with J. M. Huber Corp. from proprietary sites in Twiggs and

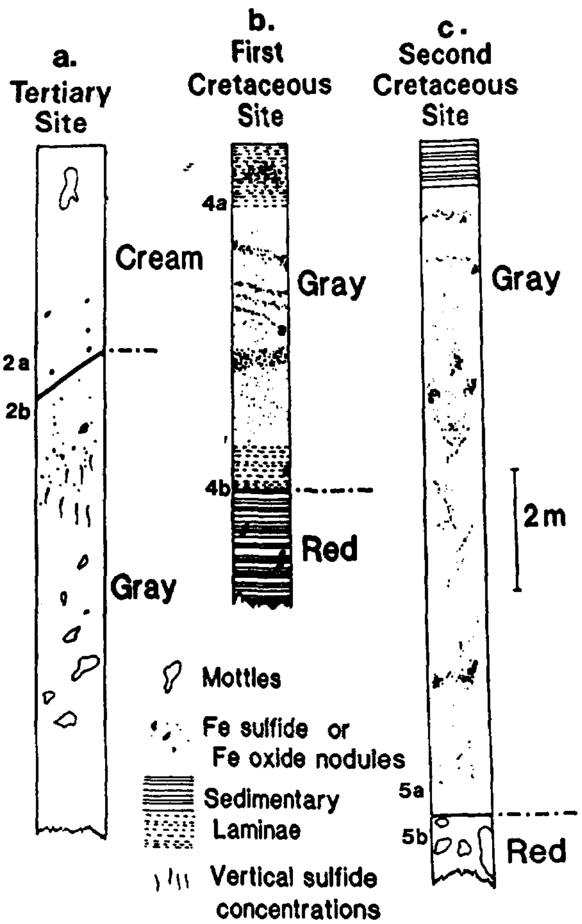

Figure 1. Summary of the visual and radiographic features of the three gray kaolin cores investigated. Some features have been exaggerated to be visible at the scale shown. Sedimentary laminae denoted by dashed lines are visible only by radiography. Laminae denoted by solid lines are visible with the unaided eye. (a) Tertiary site. (b) First Cretaceous site. (c) Second Cretaceous site. Locations for other figures are indicated by numbers and letters beside the core diagrams.

Wilkinson Counties, in the central Georgia kaolin district. The cores were refrigerated as soon as possible after sampling to reduce post-sampling microbial oxidation. Core samples, where physically possible, were split along the core axis with a wire sample cutter into three subsamples to produce a 1-cm-thick central slice along the core axis. Each central core slice was photographed and an X-ray radiograph was taken using a Picker-Andrex X-ray radiography unit with an accelerating voltage of 40 kV and 4 ma for 3.5 minutes. Optimum exposure to X-rays was determined at the outset by experimenting with various exposures. Kodak M2 Industrex X-ray film was placed beneath the clay slice to record structure during X-ray exposure (Bouma, 1969). All radiographs shown are photographic positives, thus the densest areas in the cores are the blackest regions in the prints. Colors of mottles were determined using a Munsell color book (Munsell Color Company, Inc., Baltimore, MD 21218). Colors for the kaolin matrix are not given because all cream and gray kaolins had low chroma matrix colors with values of 7 or above, which made color determination unreliable. Samples were also examined by X-ray diffraction, scanning electron microscopy (SEM), and other physical and chemical techniques (White *et al.*, 1991, 1992).

RESULTS

The Tertiary site was covered with 12 m of overburden. The upper 3 m of the kaolin was cream kaolin with scattered 3- to 5-mm red (10R 4/6) and larger, >5 cm, vertically elongated reddish yellow (7.5YR 6/8) mottles (Figure 1a). The cream kaolin/gray kaolin interface was abrupt and highly angular. Directly below the interface, the gray kaolin was very brittle with common, separate, weakly expressed iron sulfide pisoliths. Visible pyrite was observed within 20 cm of the interface as occasional sulfide nodules. Small vertical, linear regions of localized pyrite concentration about 1 mm across and 4 mm long and weakly indurated <5-mm-diameter pisoliths were visible from the cream kaolin/gray kaolin interface to 2 m below the cream kaolin/gray kaolin interface. Gray mottles similar in size and shape to yellow Fe oxide mottles in the cream kaolin were observed starting about 2 m below the cream kaolin/gray kaolin interface. About 9 m below the top of the kaolin deposit, the gray kaolin became gritty due to increasing sand-size quartz. Therefore, sampling was terminated at this depth.

X-ray radiography established that the Fe-oxide concentrations in the cream kaolin appearing as 3- to 5-mm-diameter reddish mottles were continuous through the core slice (Figure 2a). Radiographs of the gray kaolin from 15 cm below the oxidation-reduction interface and 35 cm below the Fe-oxide concentrations revealed <2-mm-diameter thread-like concentrations of dense material corresponding to the vertical linear regions of pyrite noted visually (Figure 2b). The pisolitic character of the gray kaolin just below the cream kaolin was also visible by radiography but with insufficient contrast to be reproduced photographically. The large gray mottles were not visible by radiography nor was any form of primary sedimentary structure detectable in the Tertiary deposit.

The first Cretaceous kaolin deposit was found beneath 24 m of overburden (Figure 1). The kaolin was gray at the surface with large (>1 cm in the shortest dimension) nodules of marcasite at the interface with the overburden (Figure 1b). The deposit contained visible sulfides throughout. An abrupt boundary with red, hematite-rich kaolin was reached about 4.6 m below the top of the deposit. The red (10R 4/6) kaolin had visible, thin (2 to 10 mm) sedimentary laminae. Large (>1 cm) white and yellow (10YR 8/6) mottles also

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were present with no apparent relationship to the sedimentary features. Coring was terminated after about 2 m of the red kaolin was sampled.

X-ray radiographs of the vertical slices of the first Cretaceous core showed 1- to 3-mm-thick sedimentary laminae in the top portion of the deposit in areas that were visually homogeneous (Figures 3 and 4a). The thin laminae end abruptly 0.85 m below the top of the deposit (Figures 3 and 4a). Below this point, the only radiographic features for the next 3.35 m are occasional regions of sulfide accumulation suggesting sedimentary laminae (e.g., at about 1.07, 1.52, 2.05, 2.07, 2.15, and 2.75 to 2.95 m) superimposed on very faint, thin sedimentary layers (e.g., at about 2.45 and 2.55 to 2.64 m). At a depth of 4.2 m below the top of the deposit, thin laminae like those shown by radiography at the surface of the deposit become visible again in the radiographs. The sedimentary structure was continuous without interruption from 4.2 m through the gray kaolin/red kaolin interface at 4.6 m (Figures 3 and 4b). The laminae were detected only by X-ray radiography above the gray-to-red contact but were visible in the underlying red kaolin.

The second Cretaceous kaolin was below 18.5 m of overburden (Figure 1c). The upper 75 cm of the second Cretaceous core had alternating 2- to 5-mm-thick strong brown (7.5YR 5/6) and pinkish gray (7.5YR 7/2) layers. The deposit then became gray and lacked sedimentary structures for the next 8.75 m where an abrupt boundary with red kaolin was reached. Much of this deposit was very brittle with sulfide nodules of several cm in size common; some regions contained high sulfide contents in the sand-size fraction (White *et al.*, 1991). As at the first Cretaceous site, coring was terminated after about a meter of the red kaolin was sampled. Sedimentary features were evident in the top 75 cm of the deposit, but none were shown by visual or radiographic data below that depth in the gray or red kaolin. Radiographs revealed that the visible mottling pattern present in the red kaolin also was present in the gray kaolin directly above, even though it was not visible to the unaided eye (Figure 5).

DISCUSSION

The Tertiary core did not show sedimentary structures visually or by X-ray radiography. The <2-mm linear concentrations of sulfides and the pisolitic character of the central portion of the deposit were similar to features described by Austin (1978). The portion of the deposit containing pisoliths had the highest sulfide content (White *et al.*, 1991) and kaolinite crystallinity values (White *et al.*, 1992). The pisoliths appeared to represent sulfide and possibly organic matter concentrations rather than kaolinite vermiform formation. No evidence of gibbsite transformation to kaolinite as suggested by Austin (1978) was observed. As shown in a previous report (White *et al.*, 1992), the kaolinite

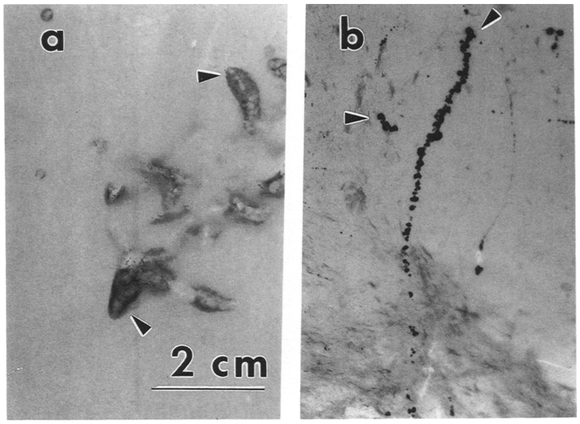

Figure 2. Selected X-ray radiographic features from the Tertiary kaolin deposit. The scale is the same on both radiographs (features noted by arrows). (a) Fe oxide concentrations in the cream kaolin. (b) Sulfide-filled pores in the gray kaolin just below the cream/gray kaolin interface.

in the Tertiary core had undergone appreciable recrystallization into vermiforms. The 3- to 5-mm-diameter mottles observed in the cream kaolin appeared to represent root or worm tubules which had later been filled with kaolinite. The tubules were visible due to preferential precipitation of Fe oxide. The filled tubules in the Tertiary kaolin deposit are not common enough to be conclusive about the depositional environment, but the upwardly fining sequence implies a fluvial depositional environment.

The thin laminae in the radiographs obtained from the first Cretaceous kaolin core were undisturbed by bioturbation (Figures 1b and 3). The lack of bioturbation indicates a depositional environment with a high sedimentation rate that suppressed bioturbation such as in a delta or submarine fan. If the kaolinite had been deposited in a backswamp or other nearshore environment, such as a lagoon, sedimentary structure similar to that of the second Cretaceous site may have been observed. In these environments, however, bioturbation would have been expected to have mixed some parts of the sediments prior to burial except in cases where the bottom waters were too oxygen poor to support infauna. Relicts of bioturbation, such as the filled root tubules observed for a small portion of the Tertiary core would be common features in the radiography results. The presence of sedimentary structure in radiographs from the first Cretaceous site and the visible structure in the first 75 cm of the second Cretaceous core suggest that the kaolinite was deposited in an environment such as a deltaic front, submarine fan, or other environment that would not exhibit bioturbation due to the fast rate of deposition. Multiple origins for the Georgia kaolin deposits have been proposed (see Keller, 1977, and Hurst, 1979, for reviews of Georgia kaolin origins). Our data suggest that the

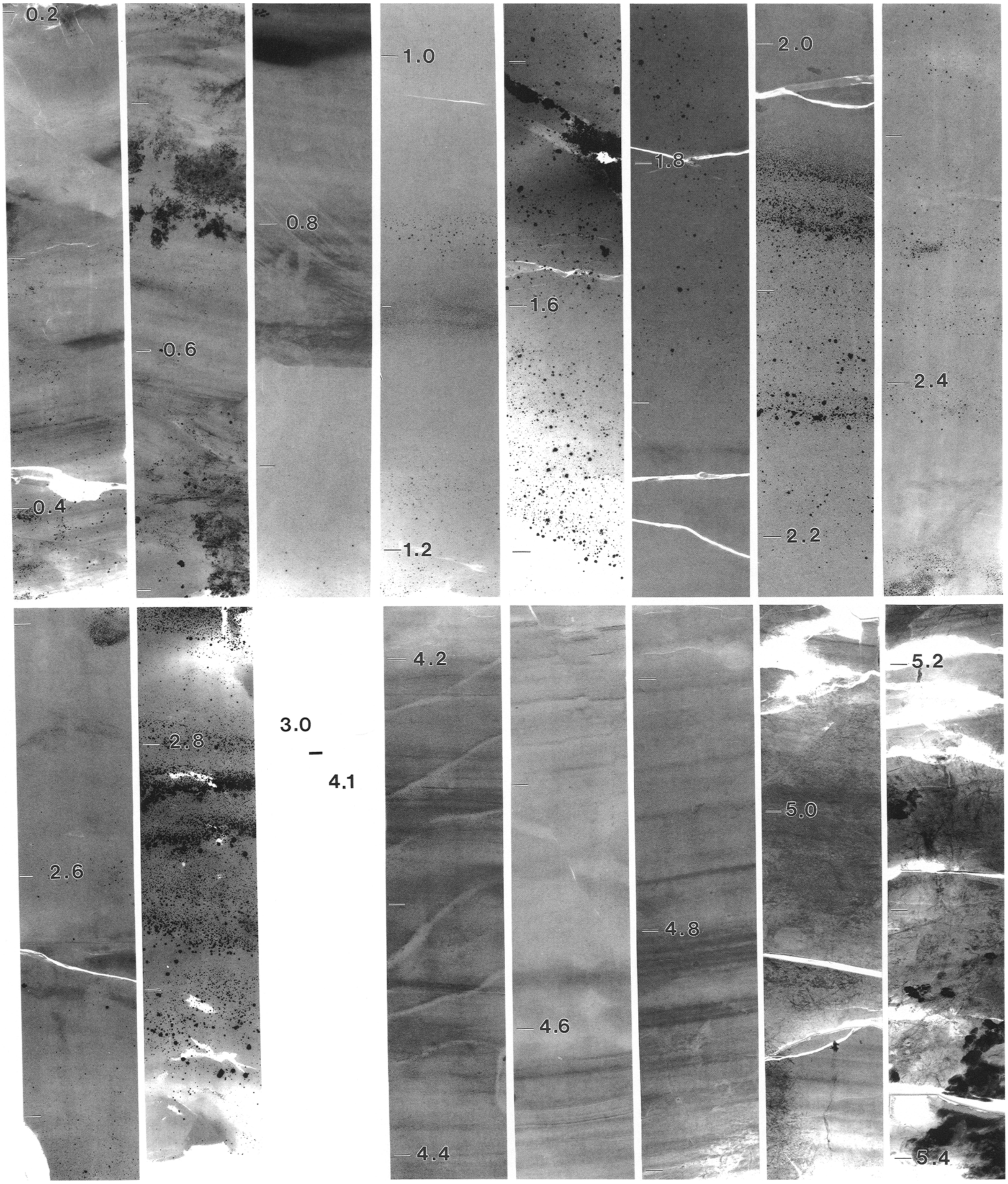

Figure 3. X-ray radiographic survey of the first Cretaceous kaolin core. Depths are in meters. The boundary between the gray and red kaolins is at 4.6 m. The interval from 3.0 to 4.1 m is missing.

Tertiary and Cretaceous kaolins sampled represent two origins. The abrupt disappearance of the sedimentary laminae near the top of the deposit may represent reworking associated with an unconformity. The gradual increase in contrast of the sedimentary features at 4.2 meters below the top of the deposit (Figure 3) implies that the reappearance of structure is not related to an erosional unconformity. The Fe which is a major source of the contrast in the radiographs has been redistributed by sulfide recrystallization. This redistribution re-

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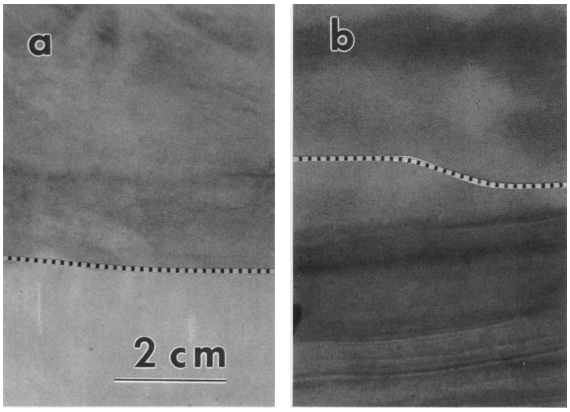

Figure 4. Selected X-ray radiographic features of the first Cretaceous core. The scale is the same for both radiographs. (a) View of the core at 0.85 m showing the abrupt disappearance of sedimentary layering at that point (dotted line). (b) View of the core at 4.6 m showing the continuity of the sedimentary structure above and below the gray kaolin/red kaolin interface (dotted line).

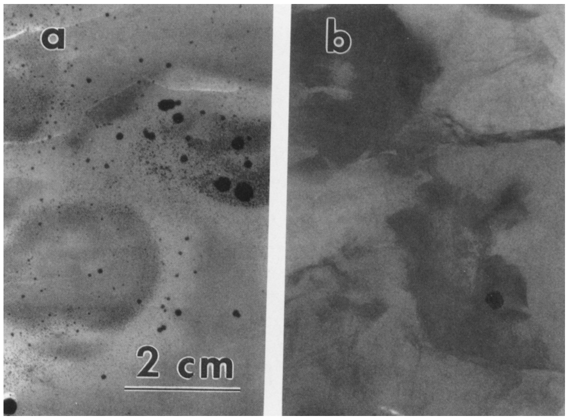

Figure 5. Selected X-ray radiographs from the second Cretaceous kaolin core showing the similarity in structures observed in the gray (a) and underlying red kaolins (b). Scale is the same in both radiographs.

duced the contrast resulting in an inability to detect the sedimentary features. Sulfide recrystallization below this depth was probably inhibited by the redox buffering influence of the large accumulation of ferric iron in the underlying red kaolin and lack of microbially utilizable organic carbon. As a result, the visibility of the sedimentary features is preserved.

The radiographic data showing that the sedimentary layering and mottling patterns are present in the gray Cretaceous kaolin and in the red kaolins at the base of the core strongly suggests that the gray and red kaolins were deposited as a single unit. The continuity of sedimentary features across the reduction-oxidation boundary implies that the gray and red kaolins were chemically similar when deposited.

It is hypothesized that the kaolin was deposited as a kaolin-iron oxide mixture derived from the erosion of the Piedmont region. Many soils presently occurring in the Piedmont region of the Southeastern United States are very rich in kaolinite and iron oxides, and erosion of these soils would yield material similar to that encountered in these cores. Sometime after deposition, reducing conditions were produced by the utilization of the organic matter originally present by sulfur- and iron-reducing bacteria. Reducing conditions caused a release of ferrous Fe from the oxides which combined with available H_2S to form pyrite or marcasite. The Fe released by reducing conditions which was not chemically combined with sulfur diffused to the lower part of the deposit where it was reoxidized by unreduced hematite present. This reoxidation resulted in an enriched region of iron oxides at the base of the deposit. The oxidized, red kaolin sections of the Cretaceous deposits were not reduced because insufficient organic material was present to sustain reducing conditions or due to the diffusion of oxygen-rich groundwater into the deposit from an underlying sandy aquifer. If one assumes that reduction was induced by microbial action on the sulfur present according to the equation (from Berner, 1984)

$$2CH_2O + SO_4^{2-} \rightarrow H_2S + 2HCO_3^-,$$

then two moles of carbon are required to produce one mole of sulfide; therefore, four moles of organic carbon are required to produce one mole of FeS_2. Considering the differences in atomic weight, four moles of organic carbon almost exactly equals the atomic weight of FeS_2, requiring only a few percent organic carbon to mobilize the iron in the deposit.

The absence of depositional layering in sections of the kaolinite from the Tertiary and second Cretaceous sites is at least in part the result of post-depositional recrystallization of the kaolinite in these deposits (White *et al.*, 1992). One reason for the lack of kaolinite recrystallization in the deposit at the first Cretaceous site may be the higher residual organic carbon content of the deposit after sulfide formation and Fe leaching. The organic content of the deposit which has not been recrystallized was higher (average 0.37%) than the 0.10% organic carbon content of the recrystallized kaolin deposits (White *et al.*, 1991). An alternate hypothesis involving bioturbation or pedoturbation may be invoked to explain the lack of sedimentary structure in the gray kaolins but such processes would be expected to leave their own signature upon the deposit.

CONCLUSIONS

Three kaolin cores, one of Tertiary age and two of Cretaceous age, were examined visually and by X-ray radiography for sedimentary structure. No sedimentary structure was evident in the Tertiary core. Sedimentary laminations were found by radiography throughout most of the gray and red kaolin in the first Cretaceous core and visually in the upper 75 cm of the second Cretaceous core. The thin sedimentary layering observed indicates that the Cretaceous kaolin deposits were formed in quiet water environments with minor currents where bioturbation was minimal. It is hypothesized that the kaolin was deposited as a mixture of kaolinite and iron oxide. A postdepositional reducing environment resulted in the removal of the iron oxide. The expression of sedimentary structure was masked by the reduction of the iron oxides to form sulfides and the recrystallization of kaolinite.

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