To the Graduate Council:

I am submitting herewith a thesis written by Harold L. Webb entitled "Do Tertiary Kaolins Represent Reworked Cretaceous Kaolins?". I have examined the final copy of this thesis for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Master of Science, with a major in Geology.

Otto C. Kopp, Major Professor

We have read this thesis and

recommend its acceptance:

Accepted for the Council:

Associate Vice Chancellor
and Dean of The Graduate School

DO TERTIARY KAOLINS REPRESENT REWORKED CRETACEOUS KAOLINS?

A Thesis

Presented

for the

Master of Science

Degree

The University of Tennessee, Knoxville

Harold L. Webb

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ABSTRACT

Samples from Tertiary and Cretaceous clay deposits were collected from three areas of concentrated mining activity in east-central Georgia. Clay lenses occur at the top of the Tertiary Huber Formation ending a fining upward cycle and are separated from overlying sediments by a sharply defined unconformity. Clay lenses at the top of Cretaceous (?) sediments are also separated by a sharply defined unconformity, overlain by coarse, cross-bedded sand deposits ranging from 5-10 meters thick, which comprise the lower Huber Formation. Along the northern edge of the field area, the Huber Formation onlaps the Piedmont in some areas, whereas the Cretaceous sediments are absent.

Preliminary investigations of samples from the Tertiary Huber Formation yield XRD crystallinity indices ranging from 0.18-0.48, indicating the presence of poorly-crystallized kaolinite. Well-crystallized kaolinite from Cretaceous clay lenses yield crystallinity indices ranging from 0.55-1.43.

Scanning electron micrographs of Tertiary samples exhibit subhedral to anhedral, mostly submicrometer (around 74% <0.5 micrometer) clay agglomerates and individual particles. Photomicrographs of Cretaceous samples reveal euhedral, psuedohexagonal kaolinite plates and vermicular stacks of kaolinite. The differences in internal structural order between Cretaceous and Tertiary kaolin samples taken in consideration along with the differences in particle size distribution and morphology indicate that the Tertiary kaolins do not represent reworked Cretaceous kaolins.

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CHAPTER I

Introduction

Commercial deposits of white kaolin clay occur along the northern margin of the Georgia Coastal Plain (Figure 1), with associated sporadic occurrences of low grade bauxite (Austin, 1972). The Inner Coastal Plain bauxite and kaolin deposits, from South Carolina to Arkansas, supply about 10% of the bauxite and essentially all of the kaolin used in the United States.

Kaolin clay produced in Georgia was valued at approximately $934 million in 1991. Georgia is by far the leading producer of kaolin in the United States with nearly 8 million metric tons being produced in 1991 (U.S. Bureau of Mines 1991). The kaolin reserves of Georgia are estimated be 5 to 10 billion tons. Kaolin has a long history of use in ceramics, pottery, fine chinaware and stoneware. The paper industry now consumes most of the kaolin production. The benefits of utilizing kaolin in the manufacture of paper are to reduce cost by substituting the clay for more expensive pulp and to improve the physical characteristics of the paper. By covering the rough surface of the cellulose fiber with platelets of kaolin the surface is transformed into a smooth, bright, ink-receptive surface. Kaolin has many other industrial uses because it is white, chemically inert over a wide range of pH's, soft and nonabrasive, and has low conductivity of heat and electricity. In addition, it is less expensive than most of the materials with which it competes (Buie *et al.*, 1979).

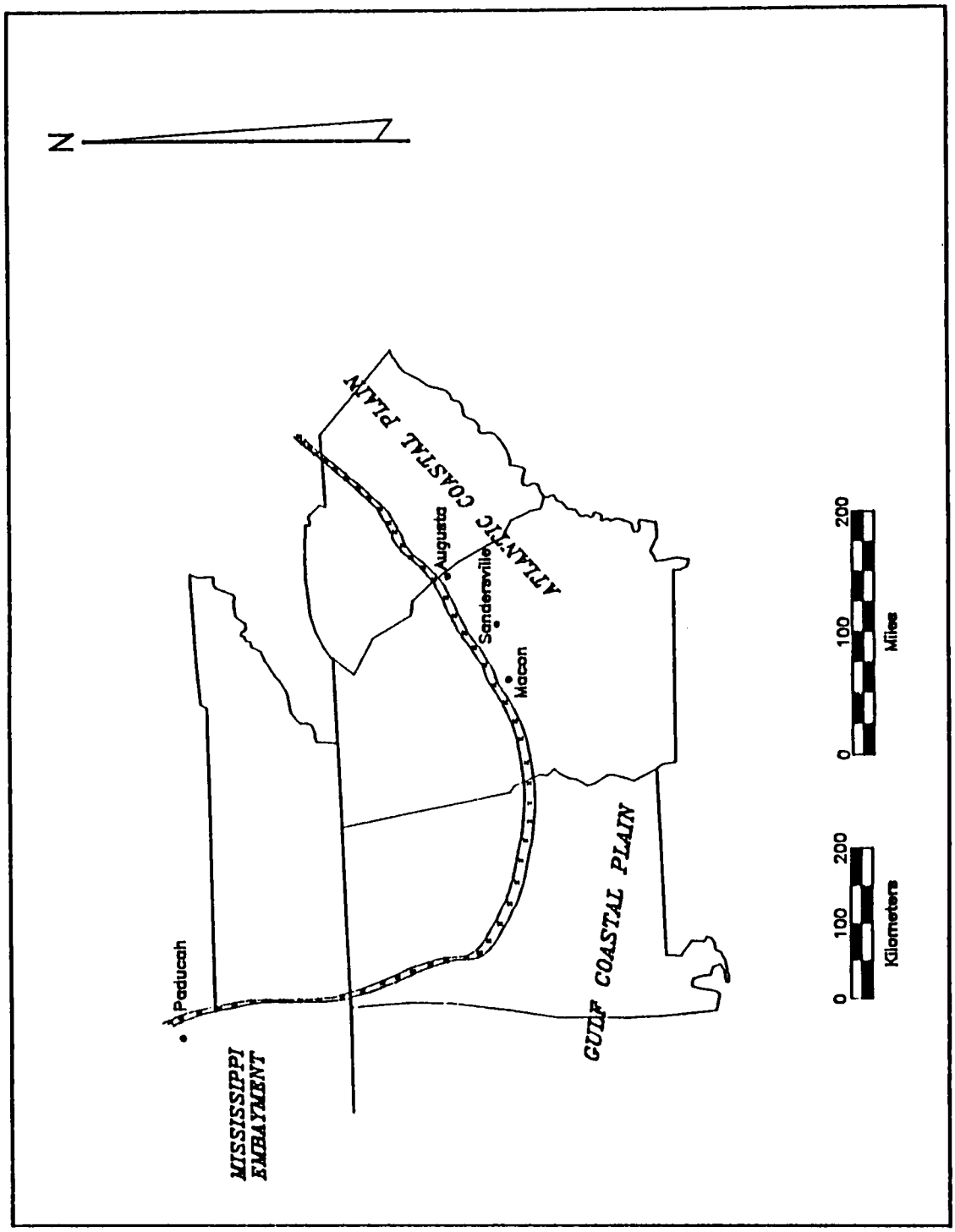

Figure 1. Map of Coastal Plain. Pattern represents approximate location of "fallline". Kaolin outcrop belt is located between Macon and Augusta, Georgia.

Purpose of the Study

The purpose of this study was to determine whether Tertiary kaolin deposits represent reworked Cretaceous kaolin. Certain general characteristics (Table 1) have been used by previous workers to distinguish between Cretaceous and Tertiary kaolin deposits. In hand specimen, Tertiary clay deposits typically have a rough, hackly fracture. The clay commonly has a faint apple-green (Munsell 10Y 8.5/2.5) tint on fresh surfaces which soon oxidizes and become pink (Munsell 5RP 8/2). Occurrences of the Tertiary clay deposits are commonly more laterally extensive than the Cretaceous deposits. In general, the Tertiary clay deposits have a smaller particle-size, higher TiO_2 and Fe_2O_3 contents, and a disordered structure as determined by X-ray diffraction. On the other hand, the Cretaceous kaolin deposits have more ordered crystalline structures, coarser particle-size, and lower Fe_2O_3 and TiO_2 contents. In hand specimen, Cretaceous kaolins have a distinctive conchoidal fracture. Fresh surfaces of Cretaceous kaolin change from cream (Munsell 10YR 9.25/1.5) to tan (Munsell 10YR 8/2) in color upon exposure to the atmosphere. During field observation, the presence of conchoidal fracture combined with relative stratigraphic position is most commonly used to identify Cretaceous kaolin. One feature which distinguishes the soft Cretaceous kaolin deposits from the hard Tertiary kaolin deposits is the presence of large vermiforms (or stacks of kaolin plates) visible in SEM photomicrographs in the Cretaceous kaolins.

TABLE 1 - Comparison of soft and hard kaolin deposits in East Central Georgia

General Characteristics	Soft kaolin (typically Cretaceous)	Hard kaolin (typically Tertiary)
Particle Size	Coarse to intermediate <65% <2 micrometers	Fine to intermediate >80% <2 micrometers
Particle Morphology	Vermicular crystals, large books	Mostly submicrometer crystals, books absent
Bates-Hinckley Crystallinity Index	0.6-1.4	0.2-0.5
Fe_2O_3 content	Lower,0.2-0.4 wt.%	Higher,1.0-2.0 wt.%
TiO_2 content	Lower,1.0- 2.0 wt.%	Higher,2.0-3.0 wt.%
Aluminum content	Higher,approx. 37.5%	Lower,approx. 36.5%
Cation content	Lower,K, Ca, Mg, Na	Higher, K, Ca, Mg, Na
Stratigraphy	Lower Oconee Group Buffalo Creek Fm.	Upper Oconee Group Huber Formation

After Hurst and Pickering (1979)

Geologic Setting

The east central Georgia kaolin district extends across the boundary between, and includes parts of the Piedmont and Atlantic Coastal Plain physiographic provinces. The stratigraphy generally consists of a basement of Paleozoic crystalline rocks with overlying Cretaceous and Tertiary sediments and a thin cover of Quaternary alluvium. The distribution of Cretaceous and Tertiary strata mark the ancient Mesozoic and Cenozoic coastlines.

Structure

Complexly folded and faulted Paleozoic igneous and metamorphic rocks which are uncomformably overlain by gently dipping Coastal Plain strata comprise the dominant structural features. The dip of the Coastal Plain sediments is seaward toward the Atlantic Embayment of Georgia, with slopes of ~4.7m/km for Cretaceous strata and ~2.7m/km for Tertiary strata (Buie *et al.*, 1979). The sedimentary rocks commonly display joints, and some small-scale faulting has been reported in both Cretaceous and Tertiary rocks (Hurst *et al.*, 1979).

Crystalline Rocks

The rocks underlying the Cretaceous strata of the Coastal Plain have been sampled in exploratory wells and were found to consist of various metamorphic, igneous, and metavolcanic rocks which are approximately 380 m.y. in age corresponding to the last episode of metamorphism in the region. The youngest rocks exposed are granitic intrusives dated at around 270 m.y. Along the northern edge of the field area complexly folded Paleozoic igneous, metamorphic, and metavolcanic rocks are exposed in the Piedmont physiographic province. These rocks include a variety of schists, gneisses, granites, diorites, and rhyolites. A nonconformity separates the Paleozoic basement of the Coastal Plain from the overlying Upper Cretaceous and younger rocks. Further down dip Cretaceous sediments are underlain

by Triassic continental basalts and red beds (Hurst *et al.*, 1979). Contour maps of the upper surface of the basement show a well-developed drainage network of southward-flowing streams. The basement dips to the southeast at approximately 11m/km near Huber, Georgia (Long *et al.*, 1986).

Cretaceous Strata

The Cretaceous strata of the Inner Coastal Plain form a wedge-shaped unit that consists largely of siliciclastic sediment deposited in fluvial delta-front to marginal-marine and shelf environments (Hurst *et al.*, 1979). In central Georgia, Upper Cretaceous rocks consist of white to buff, cross-bedded, irregular and channel-fill deposits of medium- to very coarse-grained, subrounded to angular quartz sand, kaolinitic sand, thinly laminated kaolin clay, and massive kaolin clay lenses (Buie *et al.*, 1979). Exposures of Cretaceous strata are limited to deeper stream valleys and kaolin mining operations. The most extensive natural exposure is in the valley of the Ocmulgee River (Buie *et al.*, 1979). West of the Ocmulgee River, the Tuscaloosa Formation is the oldest of the Cretaceous stratigraphic units, which are divided into six formations of Upper Cretaceous age.

In the Upper Cretaceous sediments of western Georgia and eastern Alabama, three major transgressions have been recognized (Reinhardt, 1979). Although they have been called Tuscaloosa (Cooke, 1943) and Middendorf (Scudato and Bond, 1972), all strata containing kaolin beneath the Tertiary Huber Formation, which lies east of the Ocmulgee River, have more recently been referred to as "Cretaceous Undifferentiated". Most recently, (Figure 2) the provisional name "Buffalo Creek Formation" has been given to the typical kaolin-bearing strata of the Upper Cretaceous (Webb *et al.*, 1988). The top of the Cretaceous is marked by an undulating unconformity and is overlain in eastern and central Georgia by Paleocene through Middle Eocene sediments (Hurst *et al.*, 1979). Tertiary formations overlie

the Upper Cretaceous series except near the "fall line", where erosion has stripped them away and in some instances has also removed part of the Cretaceous section. A schematic representation of the relationships between the various erosional surfaces is shown in Figure 3. The unconformity on the crystalline rocks is illustrated as dipping more steeply than those at the top of Cretaceous or Eocene sediments. The nature of the lens-like shape and occurrence of the Cretaceous kaolin deposits is shown schematically. The undulating unconformity marking the top of the Cretaceous sediments can also be seen as well as the overlying Paleocene through Middle Eocene sediments. Tertiary Huber Formation kaolin deposits are shown separated from the overlying sediments by an unconformity, and dipping less steeply than the underlying Cretaceous sediments. Commercially valuable deposits of kaolin typically occur in the upper portions of the Cretaceous beds. Most of the larger and more economically important deposits of Tertiary kaolin deposits are found within a narrow interval at the top of the Huber Formation (Long *et al.*, 1986).

Tertiary Strata (Paleocene to Middle Eocene),

Paleocene through Middle Eocene sediments, consisting mainly of sand, kaolinitic sand, and kaolin, which were named the Huber Formation by Buie (1978), unconformably overly Cretaceous strata in Central Georgia. The basal portion of the Huber Formation typically consists of a clay-clast conglomerate formed by the erosion and redeposition of rounded kaolin clay clasts. These units are similar to the underlying beds and display a wedge-shaped geometry that pinches out updip and increases in thickness downdip.

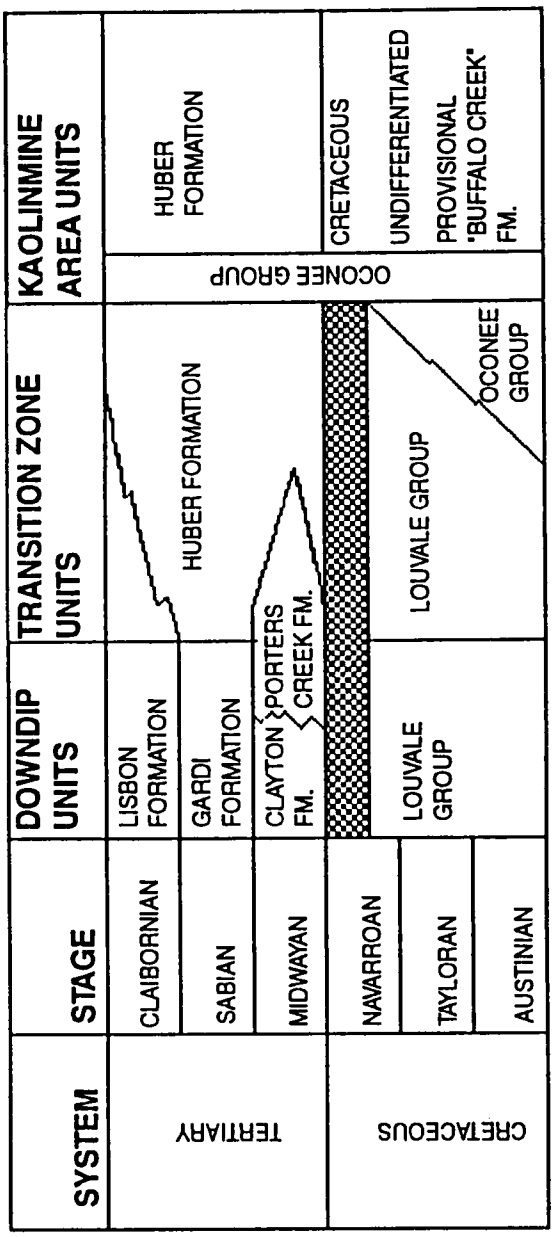

Figure 2. Stratigraphic correlation chart. Modified from Huddlestun (1981).

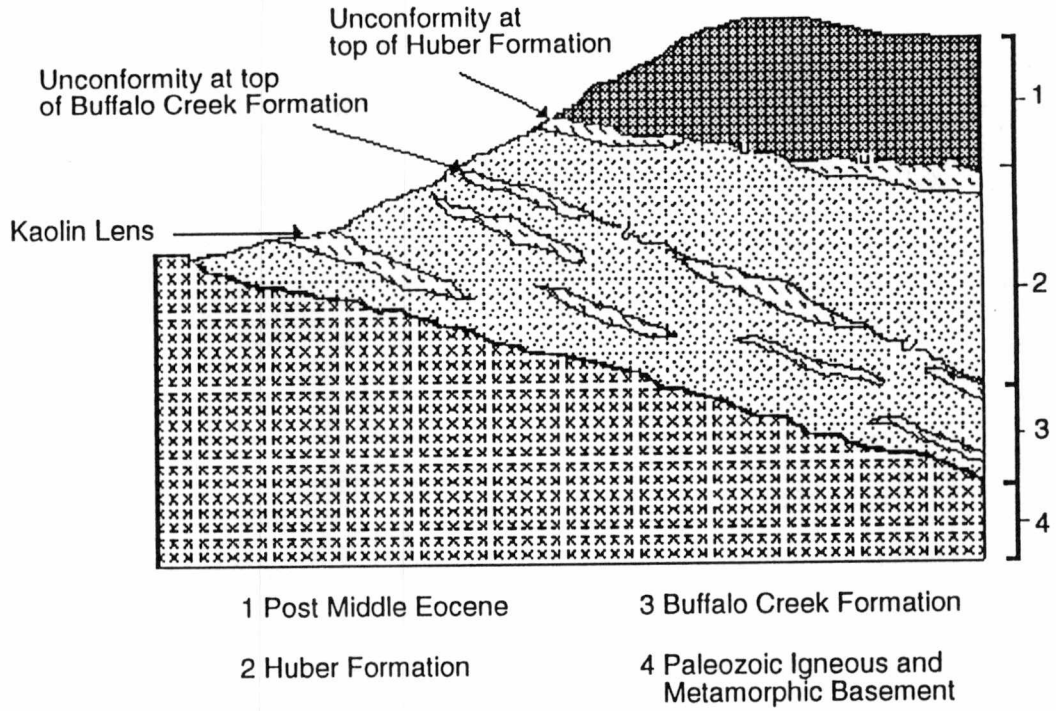

Figure 3. Schematic cross-section. Because of vertical exaggeration dips of stratigraphic units are exaggerated. 1) Post Middle Eocene; 2) Huber Formation; 3) Cretaceous; 4) Paleozoic basement.

The top of the Huber Formation contains abundant burrows produced by tidal-flat organisms. Typical burrows include *Planolites*, (tubular feeding-dwelling structures of sediment-ingesting vermiform animals), and *Thalassinoides*, (feeding-dwelling structures formed by various burrowing crustaceans). Recently, *Diplocraterion* burrows were discovered in kaolin lenses within the Huber Formation (Sprague et al., 1989). Sedimentary structures include abundant channel-fill deposits and extensive cross-bedding. These combined features have been interpreted to be indicative of a littoral environment (Pickering and Hurst, 1989). Greater diversity and thicknesses are typical of sediments belonging to the same time interval in western Georgia and eastern Alabama, with five distinguishable marine transgressions (Hurst *et al.*, 1979; Buie *et al.*, 1979).

Upper Eocene Strata

An uncomformity separates Middle and Upper Eocene strata. Pectin, echinoids, oysters, shark's teeth, marine diatoms, foraminifera, coccoliths, ostracods, and glauconite are present in the Upper Eocene strata indicating littoral and neritic marine conditions, with open-marine conditions predominating (Hurst *et al.*, 1979; Buie *et al.*, 1979). A detailed description of the individual units which comprise the Upper Eocene is given by Huddlestun (1981). General stratigraphic relations are shown in Figure 2 (p.8).

CHAPTER II

Literature Review

Genesis and Deposition

In 1898, George E. Ladd published the first detailed description of the kaolin deposits of the southeast. Since this early work, extensive research on the origin, stratigraphy, chemical and physical properties, as well as commercial applications of these kaolin deposits has been undertaken. As the kaolin industry has grown, investigation into the properties, utilization, exploration, processing, and origin of the clays has increasesd; however, there are many unanswered questions among those who have studied the famous deposits. "Strange as it may seem, the kaolin deposits in the extensive belt in Georgia and South Carolina, which have been studied by many geologists and mineralogists and which lead the world as a source of commercial kaolin, are among the kaolins whose origins are least understood" (Patterson and Buie, 1974). For the most part the literature centers around deposits of economic value. A great deal of information has been gathered due to the increased demand for kaolin, but much of it is unpublished because of its proprietary nature.

Comprehensive studies of the region followed the work of Ladd (1898). Veatch (1909) concluded that the most important clay-bearing stratigraphic unit in Georgia was the Tuscaloosa Formation, which is the lowermost member of the Cretaceous system. Veatch speculated on the origin of the deposits and suggested that the clay-bearing strata in the Tuscaloosa Formation were derived from disintegrated and decomposed aluminous minerals of Piedmont rocks. He suggested that a weathering mantle developed on the Piedmont between the Cambrian and Cretaceous, then was eroded and transported as highly kaolinitic sand during uplift at the beginning of the Cretaceous. He proposed that the highly kaolinitic sand was deposited in shallow water and that the clay was deposited in deeper water with

topographic lows in a deltaic environment. The extremely pure deposits of kaolin clay seen today were considered to be the product of sedimentary particle-size sorting, which occurred after primary deposition.

Neumann (1927) suggested that the massive bedding and lack of well-preserved plant remains were indicative of deposition of the kaolin in an open-marine environment. Neumann also made a few suggestions as to the paleoclimatic conditions which were in effect during the kaolin formation. He believed that the weathering of the Piedmont rocks occurred in a mild, humid, frost-free environment with abundant vegetation. This weathering environment led to the production of argillaceous soils which were then eroded and transported seaward in response to uplift of the Piedmont during the Cretaceous.

Smith (1929) agreed with Neumann's suggestion of seawater deposition of sedimentary kaolins which were produced by the weathering of the crystalline and metamorphic rocks in the Piedmont. He also concluded that the basal Cretaceous sediments in Georgia were Upper Cretaceous in age and correlated them with the Middendorf Formation of eastern South Carolina. Cooke (1943) assigned the basal Cretaceous sediments to the Upper Cretaceous as part of the Tuscaloosa Formation.

Kesler (1963) suggested that kaolinization took place after deposition of feldspathic sands along the coast. This was a major departure from the previous interpretations of Veatch, Newmann, Smith, and Cooke that kaolinization took place in situ on the crystalline rocks of the Piedmont. Kesler reported that there was no basis for subdividing the Upper Cretaceous and that the kaolin lenses had no preferred stratigraphic position. He concluded that the kaolin deposits were the result of the alteration of feldspathic sand deposited as deltaic sediments above sea level. Reworking of the delta-front sediments separated the kaolin from the coarser sediments, resulting in the accumulation of kaolin in ponds at points of lower

elevation. Later workers such as Jonas (1964), and Austin (1972;1978) agreed that kaolinization must have taken place after deposition.

Differences Between "Hard" and "Soft" Kaolin Deposits

It was recognized quite early that substantial differences existed between kaolins from different deposits. Kaolin deposits were originally classified according to physical characteristics determined in hand specimen rather than on the basis of chemical composition or degree of crystal order. Stull and Boles (1926) divided the kaolin deposits into soft, semi-hard, hard, flint, and bauxitic. Hinckley (1965) did an extensive chemical and mineralogical study of Georgia kaolin deposits and by statistical evaluation was able to distinguish between hard and soft kaolins on the basis of their crystallinity, and Al_2O_3 and Fe_2O_3 contents. The hard kaolin had higher Fe_2O_3 contents, lower Al_2O_3 contents, and poorer crystallinity than the soft kaolins. This work, combined with other studies, which determined that hard kaolins have a smaller particle size than soft kaolins, reinforced the concept of a significant distinction between hard and soft kaolin. Other kaolin categories defined in earlier studies lost their significance after this point (Bates 1964). Buie's (1967) summary of the differences between hard and soft kaolins reflected the establishment of two types of kaolin.

In 1964, Bates reviewed the literature concerning the geology, mineralogy, and chemistry of the kaolins. He discussed the variability within the lenses of kaolin and the differences between samples, layers, pits, and the hard and soft clay types. Some of the evidence supported a marine origin, whereas other data supported a fresh-water origin. Alternative theories included the suggestion by Buie (1964) that the kaolins were derived from montmorillonite, which in turn was an alteration product of volcanic ash.

After discovering imprints and molds of Tertiary fossils in the upper portion of a kaolin lens, Buie and Fountain (1967) established the fact that some kaolin deposits were late

Cretaceous in age whereas others were Early Tertiary. On the basis of this single occurrence Buie and Fountain (1967) concluded that the Tertiary kaolin deposits were generally considered to be "hard" and the Cretaceous kaolin deposits "soft". Casts or molds of fossils were found in the upper portion of the Huber in one mine during the present study, but only as burrow fill which obviously postdated the age of the kaolin.

Several theories have been proposed to explain the differences between hard and soft kaolins. The following theories (taken mainly from Dombrowski, 1990), include: post-depositional alteration (Stull and Boles, 1926); differential flocculation and laterization of the hard kaolin (Smith, 1929); differences in depositional environment (Kesler, 1963, Hurst *et al.*, 1979); and reworking by selective winnowing of the soft kaolin and deposition of the winnowed material in saline water (Murray, 1976). Hinckley (1965) suggested that face-to-face flocculation of kaolin particles in a marine environment would result in the properties that distinguish a "hard" kaolin from the less dense "soft" clay, which may have settled in fresh water resulting in edge-to-face particle orientation.

Reworking

Austin (1972, 1978) suggested that Tertiary kaolin deposits originated through reworking of the Cretaceous sediments just before the early Tertiary marine transgression, thus producing the erosional unconformity on the Tertiary kaolin deposits and resulting in the deposition of the overlying Jackson Age sediments. The presence of numerous cut-and-fill structures, which contain clay pebbles and intraformational conglomerates, support the suggestion that extensive reworking did take place subsequent to the deposition of the Cretaceous sediments. Murray (1976) agreed with Austin that most Tertiary clay deposits originated by reworking of Cretaceous sediments.

Dombrowski and Murray (1984) examined the thorium content of several Tertiary and

Cretaceous clays, as well as a sample of the Sparta granite and its associated saprolite. The results of their finding were that the granite and saprolite had higher thorium values than the average of the soft kaolin deposits. Their studies show a 20-25 percent decrease in the average thorium values for the soft kaolin (17.6 ppm) over the saprolite and granite (20-21.5 ppm). The reason suggested for the lower concentrations in of the soft kaolin was that the thorium was depleted by exposure to vadose water during soil formation. The Tertiary samples showed a further decrease in the amount of thorium (12.1 ppm) that was attributed to further exposure of the soft kaolins to vadose water during reworking and redeposition. These values were said to support the hypothesis that the kaolins was formed by weathering, and that reworking and redeposition of Cretaceous kaolin resulted in Tertiary kaolin deposits which have lower thorium concentrations.

Mineralogy, Chemistry, and Morphology

The term clay has several different definitions. Sedimentologically, the term clay refers to any sedimentary particle (regardless of composition) smaller than 2 micrometers. To an engineer, the term clay refers to any sediment that is plastic when wet and indurated when dry. From a clay mineralogists' point of view, the term clay refers to several hydrous aluminosilicates in which iron and magnesium substitute for aluminum to varying degrees. Alkalis and alkaline earths can also be constituents. Hydrogen is contained within the structure as hydroxyl and as water. Water can also be sorbed to the mineral surface. A wide range of possible chemical compositions resulting from substitution exists in clay minerals. Most clays are layer silicates (or phyllosilicates) which have been subdivided into a number of groups based on their structure and chemical composition.

At the present time, several kaolin group species are recognized including: kaolinite, nacrite, dickite, halloysite, chamosite, and cronstedite. Kaolinite [$Al_4(OH)_8Si_4O_{10}$] comprises

a single layer with one octahedral sheet and one tetrahedral sheet, which combined are approximately seven angstroms thick. The ideal composition for kaolinite is: 46.54% SiO_2; 39.50%Al_2O_3; 13.96% H_2O. As pointed out by Bates (1964) in his review of the work on sedimentary kaolins in the southeastern U.S., the term kaolin, rather than kaolinite is preferable "...not only in recognition of former practice, but also because it points to the fact that the clays to be discussed are not monomineralic".

A study of the geology and mineralogy of kaolin was conducted by Veatch (1909) and includes a discussion of the mineralogy of associated sediments and chemical analyses of the clay. Chemical analyses of kaolin clays were also performed by Smith (1929). Subdivision of the clays on the basis of hardness and texture was done by Stull and Bole (1926). The whiteness of the deposits was discussed by Newmann (1927). Ries (1903;1922;1927) compared the coastal plain clay deposits of Georgia and South Carolina with other clay deposits in these and other states in terms of geology, mineralogy, and commercial application. X-ray diffraction was utilized to enhance the understanding of the genesis and characterization of kaolin minerals by Ross and Kerr (1930), a technique which has been used extensively in subsequent studies. Klinefelter *et al.*, (1943) evaluated a suite of samples by various mineralogical, chemical and physical techniques providing important information about the differences between soft and hard clay. In the same year, similar work on the differences between hard and soft clays was done by Mitchell and Henry (1943).

Relationships between kaolinite crystallinity, chemical composition, and physical properties were investigated by Murray and Lyons (1956;1960). Their studies indicated that surface area, ion exchange capacity, and amount of Fe_2O_3 and TiO_2 all increase with decreasing crystallinity. They were also among the first to recognize the presence of stacks (or books) of kaolin almost exclusively in well-crystallized kaolin deposits. Bundy *et al.*,

(1956) studied the relationships between physical and chemical properties of kaolinite minerals using XRD and SEM, as well as a variety of physical test procedures, including water-sorption, surface area, sediment volume, and Hercules and Brookfield viscosities. Correlation between rheological properties and mineralogical impurities, surface area, and particle packing were reported.

Mineralogical and chemical variations were evaluated by Hinckley (1965) in terms of 22 chemical and mineralogical properties using 343 samples representative of soft and hard kaolins. Hinckley was able to distinguish between hard and soft kaolins on the basis of kaolinite crystallinity values. Hard kaolins had consistently lower crystallinity values and higher Fe_2O_3 contents, whereas soft kaolins had consistently higher crystallinity values and lower Fe_2O_3 contents.

A substantial number of SEM analyses were performed on a variety of kaolin deposits from all over the world, including the kaolin deposits from Georgia by Keller (1977; 1982). He examined the three general types of kaolin recognized in the industry: soft, hard, and flint, as well as kaolinite from a granite saprolite in the Georgia Piedmont, which is considered to represent possible source material. In the east central Georgia kaolin district, soft kaolin deposits are typically referred to as Cretaceous in age, whereas hard kaolin deposits are believed to be Tertiary in age. A "rockhard" kaolin that breaks with conchoidal fracture has been described from several localities and is termed "flint" kaolin. According to Hurst *et al.*, (1979) flint kaolin occupies only one stratigraphic position, at the top of the Huber (Tertiary) Formation. The properties of the flint kaolin are attributed to higher than normal silica contents Hurst *et al.*,(1979).

Murray and Janssen (1984) investigated the use of oxygen isotopes as indicators of kaolin genesis. They reported very low delta ^{18}O values (5.52 to 6.70) relative to Standard

Mean Ocean Water for large vermicular books separated from four Georgia kaolin deposits compared to the fine particle-size kaolin plates from those deposits. This was interpreted to suggest that the books of kaolin were altered feldspar grains, based on a comparison between the delta ^{18}O of kaolinite books in sedimentary deposits and kaolinite books from residual kaolin formed by surficial weathering of a granite (delta $^{18}O = 6.43$). These values were also compared to delta ^{18}O values of feldspar grains picked from the Sparta granite for which delta ^{18}O determined was 5.99. They reasoned that the transformation of feldspar to large books in the sedimentary kaolins and the residual kaolin involved very little contribution from meteoric water so that the delta ^{18}O of the large books reflects that of the feldspar. Murray and Jansen (1984) also found little difference between the isotopic signatures of the Cretaceous and Tertiary kaolin deposits. This was expected if the Tertiary kaolins represent reworked Cretaceous kaolins.

The fact that the large vermiforms and books found in the Sparta saprolite have the same isotopic compostions as the feldspar is interesting because the feldspar is thought to have been altered to kaolinite by surficial weathering. Surficial weathering almost certainly involved meteoric water because there is no reported evidence of hydrothermal alteration.

Clay Genesis

Clays minerals occur in a wide variety of soft and hard sedimentary rocks as detrital and diagenetic constituents. Clays are very fine-grained minerals with large surface areas, and tend to be highly reactive. It is generally accepted that the kaolin clay deposits of central Georgia first originated through the weathering of igneous and metamorphic rocks of the Piedmont.

There is evidence of both chemical and physical weathering in the kaolin source area (Keller, 1977; Hurst *et al.*, 1989). Chemical weathering is the dominant influence on the

formation of the tremendous quantities of kaolinite found in the kaolin district today. Hydrolysis is the type of chemical weathering taking place, and occurs by the progressive leaching of ions from the different minerals of the parent material (Chamley, 1989).

In the case of the weathering of potassium feldspar the reaction can be written:

$2KAlSi_3O_8 + 9H_2O + 2H^+ \rightarrow Al_2Si_2O_5(OH)_4 + 4H_4SiO_4 + 2K^+$.

The weathering of potassium feldspar (Henderson, 1986) is thought to follow the reaction steps listed below:

1) feldspar hydrolysis by exchange at the mineral surface of H+ for K+;

2) development of kaolinite.

Bioturbation

The presence of trace fossils has been mentioned in the literature for many years, however only recently have they been described in detail. Shroder (1982) investigated the different trace fossils that are present in the "massive muds" at the top of the Huber Formation. Some of the ichnofossils recognized were: *Thallasinoides*, *Ophiomorpha*, and *Planolites*. Based on his findings Shroder (1982) proposed that the kaolin deposits of the Upper Huber Formation were deposited as argillaceous sediments which were subareally exposed forming a hardened paleosol and that most of the bioturbation post-dated deposition and pre-dated or coincided with marine inundation. He described the kaolin deposits as "...massive sparsely fossiliferous muds which were deposited in a low energy area with restricted circulation".

CHAPTER III

Study Areas, Field Methods and Sample Preparation

Three areas of concentrated mining activity were this subject of investigation: the Sandersville area, consisting of mines in Washington county; the Dry Branch area, consisting of mines in Twiggs and Wilkinson counties; and the Wrens area, consisting of mines in McDuffie, Jefferson and Warren counties. Permission to access most of the mines came from Georgia Kaolin Company, Incorporated, with some additional access being provided by ECC America. Samples were collected in each of the three areas from open-pit exposures. The exposures afforded by mining yielded a suite of samples that approximated a strike section and ranged across the dip, providing a fairly broad coverage of the kaolin district in central Georgia. A map of the sampling locations is shown in Figure 4. A list of sample locations and elevations is shown in Appendix 3.

Field Methods

In every case, samples were collected from areas of current or recently active mining. All samples were collected from relatively fresh surfaces from pit walls, depending on the length of time since the last active mining took place. An axe was used to cut the samples from the highwall in order to produce a fresh, unweathered surface. The samples were then placed in plastic bags which were secured with wire to reduce dessication. Sampling mine exposures was the most convenient and economical method of obtaining information on the hard Tertiary and soft Cretaceous kaolins of the central Georgia area. A list of sample numbers and inferred ages (ages inferred on the basis of physical properties) is presented in Table 2.

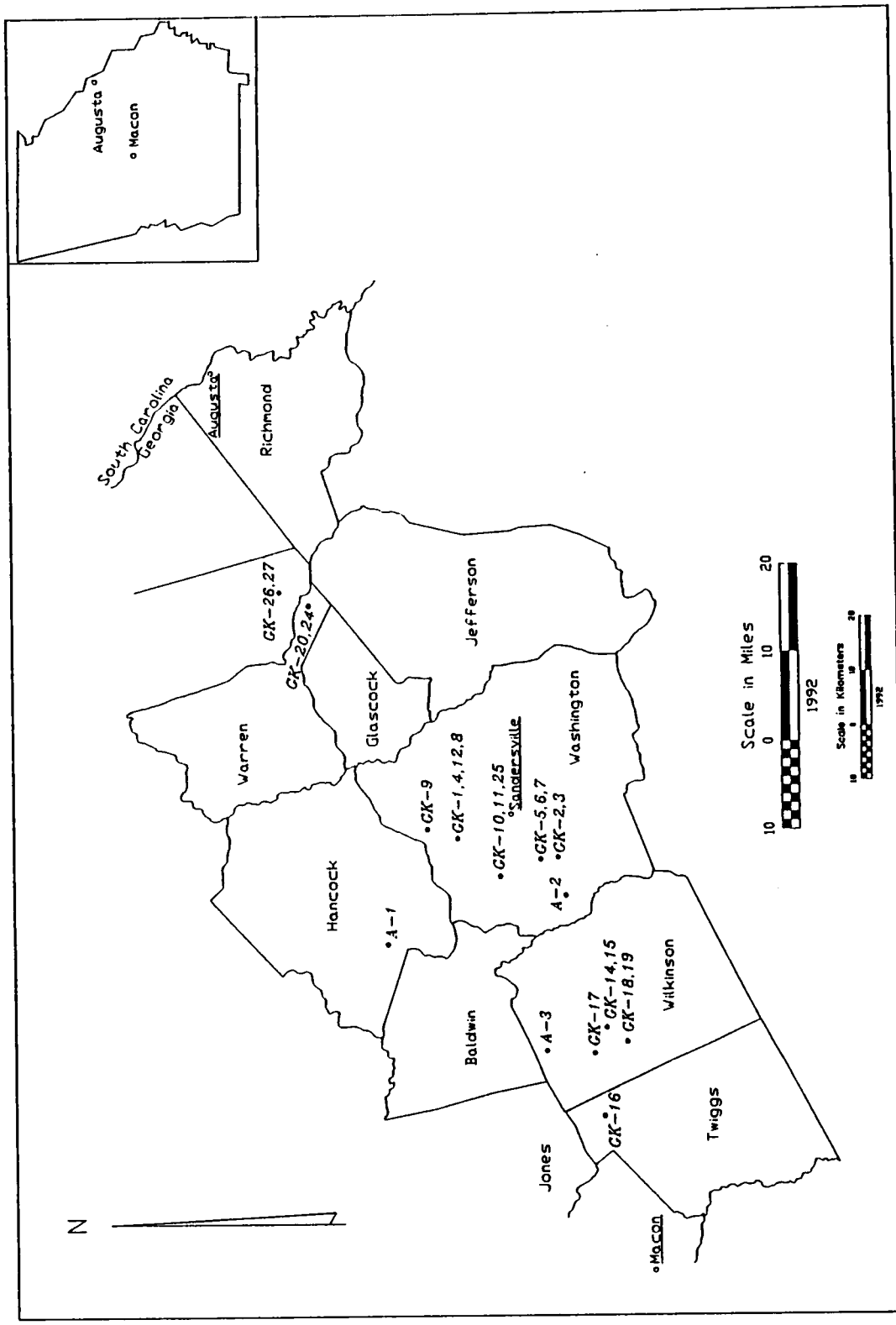

Figure 4. Map of sampling areas.

Table 2 - Sample Numbers and Inferred Ages of Kaolin Deposits

Sample #	Age	Sample #	Age
GK-1	T	GK-15	T
GK-2	K	GK-16	K
GK-3	T	GK-17	T
GK-4	T	GK-18	K
GK-5	K	GK-19	T
GK-6	K	GK-20	T
GK-7	T	GK-24	T
GK-9	T	GK-25	K
GK-10	T	GK-26	T
GK-11	K	GK-27	T
GK-12	K	A-1	K
GK-13	T	A-2	K
GK-14	T	A-3	T

K = Cretaceous
T = Tertiary

The method of sample collection was one of convenience and economy. The clay was collected using a grab sampling method which is not a probabalistic sampling method. A probabalistic sampling protocol is one in which each portion of a given lot to be sampled is given an equal chance of being selected and anything not part of the given lot a zero chance of being selected during sample collection. Core drilling is the only method of obtaining a probabalistic sample from a kaolin deposit, but it was not feasible for this study. The conclusions reached in this investigation must be considered in light of this knowledge, since the only portion of the kaolin deposit accessible was that which was exposed for mining at the time the samples were collected.

Sample Preparation

Preparation of samples involved size reduction and mixing. This was accomplished with a hammer mill. A 4 kg sample was taken for commercial lab testing. Later each sample was quartered and split into 1 kg samples. From these 1 kg splits, a 12 gram sample was obtained for X-ray fluorescence and X-ray diffraction analyses. Another sample of approximately 200 grams was sent to Georgia Kaolin's research laboratory in Springfield, New Jersey for determination of crystallinity index and SEM evaluation.

CHAPTER IV

X-ray Diffraction

X-ray diffraction is especially useful in the study and identification of fine-grained minerals such as clays because morphological and optical data are commonly difficult to obtain and more difficult to interpret.

Instrumentation

A Diano XRD 6, X-ray diffractometer was used during this study. Operating conditions were 45 Kv and 20 Ma with a scan rate of 2 degrees/min. The system utilized a graphite monochromator to obtain Cu K-alpha radiation (lamda = 1.5406 angstroms).

Sample Preparation

From the original 1 kg splits, 200 gm were sent to Dr. Jack Harrison at Georgia Kaolin's research laboratory in New Jersey. Bulk samples were pulverized with a mortar and pestle and then passed thru a 200 mesh screen to break up any lumps that may have formed during pulverization. This material was loaded into a side-packed sample-holder to produce a relatively randomly oriented powder. The procedure and the sample holder used were very similar to those used by the National Institute of Standards and Technology (Harrison, personal communication, 1988).

Results and Discussion

A summary of the minerals found in each sample using X-ray diffraction is given in Table 3. Every sample was found to contain kaolinite. Quartz and muscovite were present in detectable amounts in numerous samples. Only one sample (GK-16) was found to contain a detectable amount of a smectite. Other minerals such as anatase, rutile, hematite, and pyrite have been reported to occur in kaolin deposits, but generally only in small amounts. The presence or absence of these minerals was not confirmed with XRD in this study. Trace

Table 3 - Mineralogy

Sample #	Kaolinite	Quartz	Muscovite	Smectite
GK-1	X		X	
GK-2	X			
GK-3	X	X		
GK-4	X			
GK-5	X			
GK-6	X		X	
GK-7	X	X	X	
GK-9	X	X		
GK-10	X	X	X	
GK-11	X	X		
GK-12	X			
GK-13	X	X	X	
GK-14	X			
GK-15	X	X	X	
GK-16	X		X	X
GK-17	X	X		
GK-18	X			
GK-19	X	X		
GK-20	X		X	
GK-24	X		X	
GK-25	X		X	
GK-26	X	X	X	
GK-27	X	X	X	
A-1	X		X	
A-2	X		X	
A-3	X	X		

amounts of other minerals may occur in the analyzed samples, but in amounts too small to identify with the methods available.

Clay Fraction

A 100 gm portion of each sample was disaggregated in a Waring blender with 400ml of water at 20% solids using 0.3 gm of Calgon as a dispersant. The slurry was then poured into a sedimentation tube and allowed to settle for 1 hour. After sedimenting for 1 hour, 2 ml of liquid were taken from 1 cm below the surface with a pipette to recover the 2 micrometer fraction based on Stokes' Law (Harrison, personal communication, 1988). The 2 ml pipette sample was then placed on a 1X3" glass slide and allowed to air dry for later XRD examination. The sample was X-rayed under the same operating conditions as that of the bulk sample. After an initial X-ray pattern was obtained the sample was glycolated by placing the slide in a desiccator and exposing it to ethylene glycol vapor overnight. The glycolated sample was also X-rayed. The sample was then heated at 450° C for 1 hour to collapse any expandable material and reexamined with XRD. The persistence of the kaolinite peak even after having been subjected to that temperature confirmed the presence of kaolinite.

Crystallinity Indices

The term crystallinity in the context of this study refers to the relative degree of order in the sample. Hinckley (1963) devised the method used in this study. Hinckley was able to distinguish between hard and soft kaolin deposits on the basis of a crystallinity index. It is a measure of the degree of ordering in the a,b plane (also known as b-axis ordering). According to Hinckley (1963), "...as crystal perfection improves, principally because of less random shifts of n $b_o/3$ along b, the resolution of 110 and 111 peaks is improved. The better resolution of the 110 causes the trough between it and the 020 to deepen resulting in an increase in the measured height of the 110 and the 111". The Hinckley

crystallinity index is a convenient, semi-quantitative measurement which assigns a numerical value to the degree of structural order.

A calculation of the crystallinity index was performed for each sample. The same X-ray diffractometer was used with operation conditions of 45 kv and 20 ma with a scan rate of 0.4 degrees per minute. The instrument was set for a linear recorder response. In order to determine the crystallinity index of the sample, a ratio of the peak heights was determined (see Figure 5). A line is drawn from the trough between the 020 and 110 peaks to the background just beyond the 111 peak. The heights of the 110 and 111 peaks are measured above the inserted line. The numerator is the sum of the heights of the 110 and 111 peaks above the background. The denominator of the fraction is the total height of the 110 reflection above background. The crystallinity index is calculated by dividing the resulting fraction.

Results and Discussion

The crystallinity indices of the samples tested ranged from 0.18-1.43. The samples could be divided into two main groups (see Table 4). The first group consists of samples with crystallinity index below 0.5, and the second consists of samples with a crystallinity above 0.5. The samples with low calculated crystallinity indicies ranged from 0.18 to 0.41. The similarity of the X-ray traces and the low range of values suggests that the conditions which produced the poorly crystalline kaolins were similar and quite consistent. In every case the kaolin samples that displayed a rough hackly fracture have crystallinity values < 0.5. There appears to be a definite relationship between physical texture in hand specimen and the degree of internal structural order. In all cases the better ordered kaolins displayed conchoidal fracture.

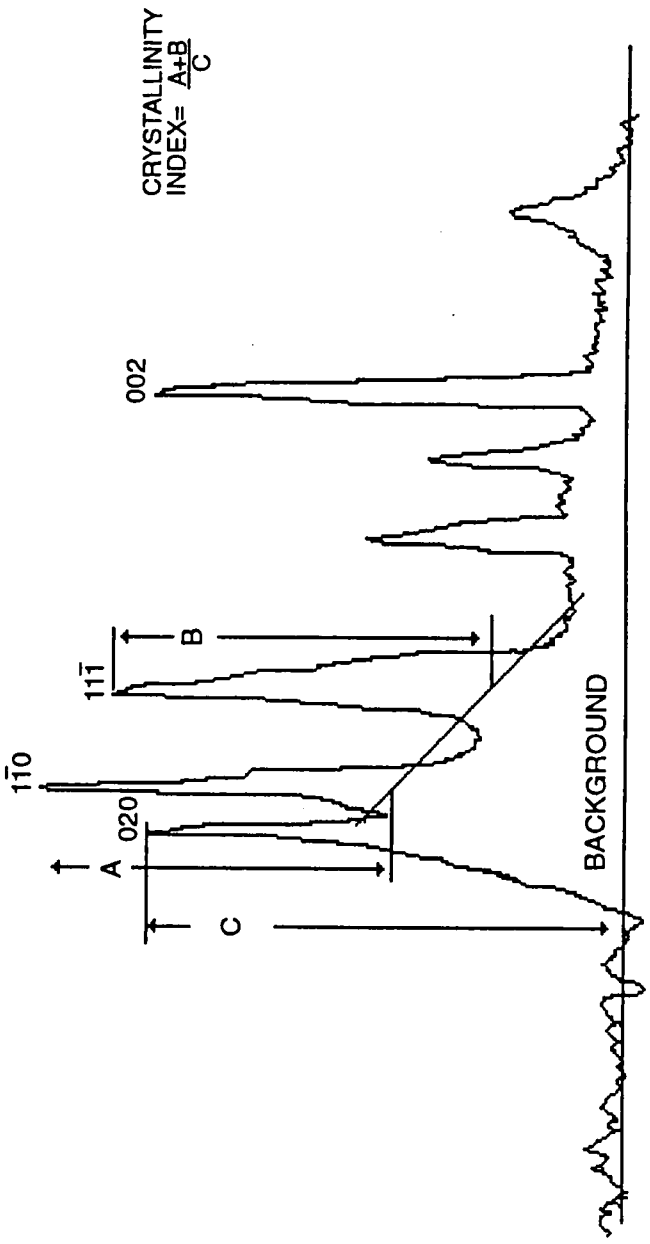

Figure 5. Crystallinity Index Calculation.

Table 4 - Crystallinity Indices for Central Georgia Kaolin Samples

HARD TERTIARY SAMPLES		SOFT CRETACEOUS SAMPLES	
GK-1	0.31	GK-2	0.75
GK-3	0.18	GK-5	0.83
GK-4	0.32	GK-6	1.43
GK-7	0.26	GK-11	0.71
GK-9	0.33	GK-12	0.72
GK-10	0.34	GK-16	0.55
GK-13	0.48	GK-18	1.17
GK-14	0.40	GK-25	0.55
GK-15	0.38	A-1	0.58
GK-17	0.26	A-2	0.57
GK-19	0.21		
GK-20	0.40		
GK-23	0.37		
GK-24	0.41		
GK-26	0.33		
GK-27	0.29		
A-3	0.35		

As with the poorly ordered kaolins, there was a relationship between physical texture in hand specimen and the degree of internal structural order. Figures 6 and 7 illustrate X-ray diffraction patterns which are characteristic of the range of intensities caused by variation in internal structural order of the samples in this study. Figure 6 is a trace of the pattern for the sample with the highest calculated crystallinity index (sample GK-6).

The diffractograms of the other well-crystallized kaolins also displayed sharp well-defined peaks, although not as pronounced. Figure 7 is a trace of the diffractogram for the sample with the lowest calculated crystallinity index (sample GK-3). Other samples with low crystallinity values displayed similar patterns with few well-defined peaks. Numerous studies have been conducted on the crystallinity or degree of order of kaolinite. See for example, Murray and Lyons (1960); Hinckley (1963); Plancon and Tschoubar (1977); Mestdagh (1980); Hassanipak and Esslinger (1985); Brindley *et al.*, (1986), and others. Hinckley was the first to recognize that hard kaolins could be distinguished from soft kaolins on the basis of their crystallinity. The results of Hassanipak and Esslinger (1985) suggested that the Georgia kaolin deposits can be divided into two groups based on the Hinckley C.I. The kaolin samples with a C.I. of >0.74 are termed "soft" and the kaolin samples with a C.I. of <0.74 are termed "hard". The present study confirmed the relationship between physical characteristics of the kaolin in the field and the degree of structural order as indicated by crystallinity index; however, in this study the "hard" kaolins had crystallinity values <0.5 rather than 0.74 as in Hassanipak and Esslinger's study (1985). This could be the result of differences in the diffractometer used, methods of sample preparation or samples.

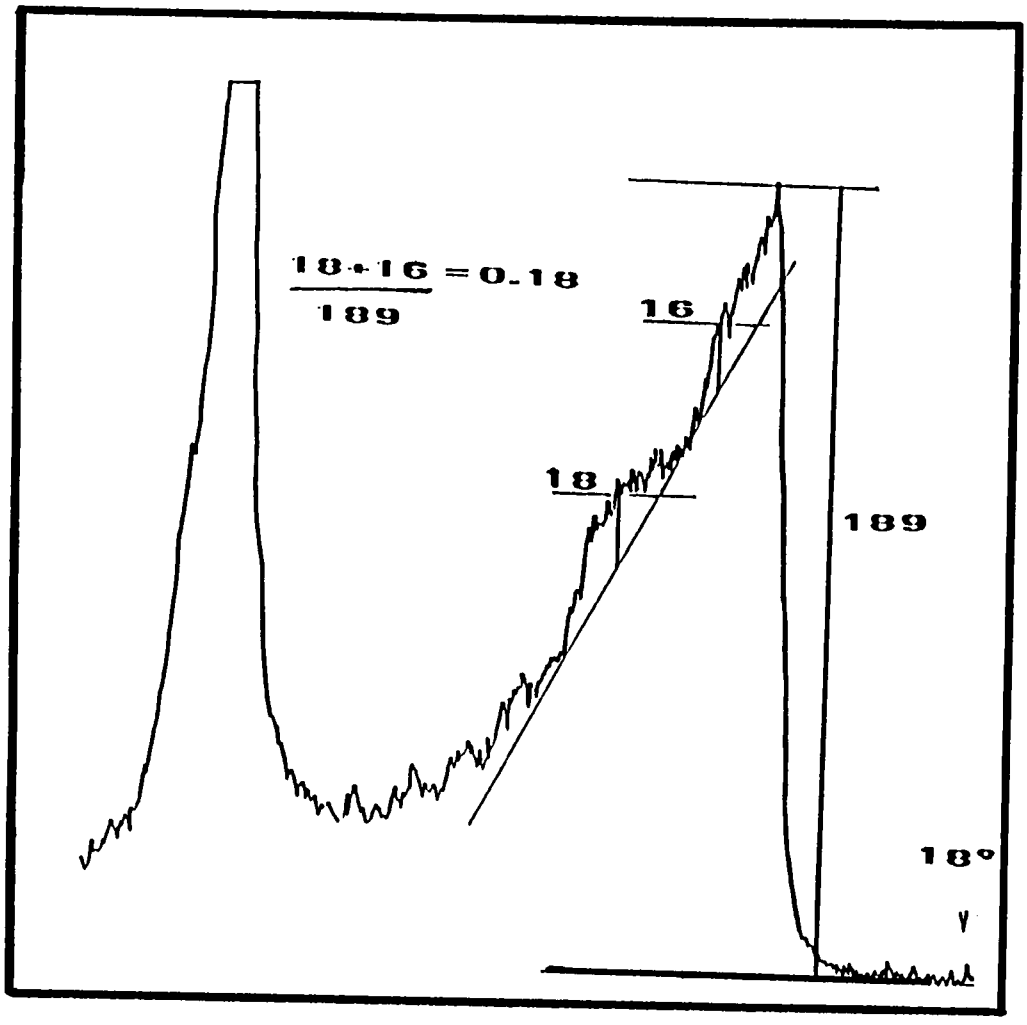

Figure 6. X-Ray Pattern for GK-6.

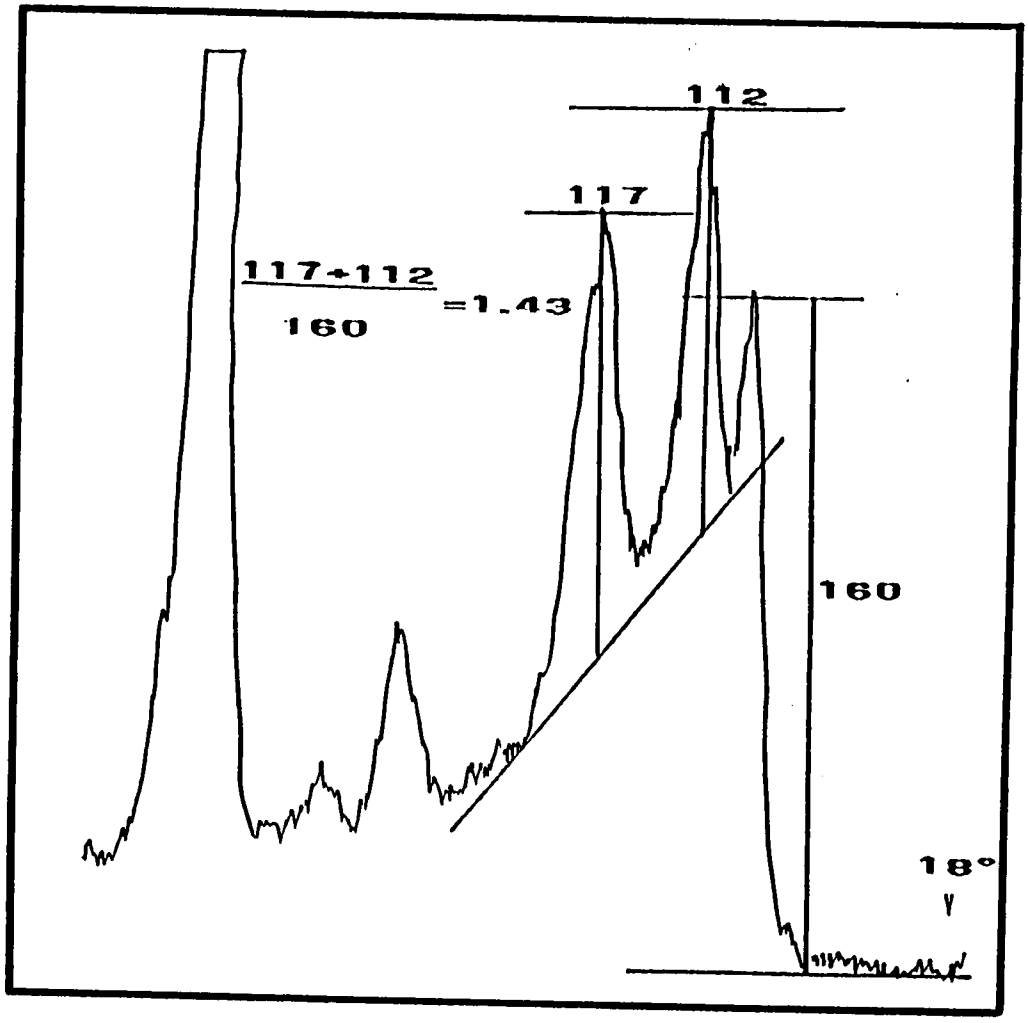

Figure 7. X-Ray Pattern for GK-3.

Several reasons have been suggested to explain the differences in structural order. Austin's (1972) suggested that the Eocene kaolin deposits represent reworked Cretaceous kaolin deposits and implied that the structural order of the clays can be degraded during reworking and redeposition, or that the finest fractions of Cretaceous kaolins are poorly ordered.

Hassanipak and Esslinger (1985) determined the crystallinity of several Cretaceous "soft" kaolin and several Tertiary "hard" kaolin samples. They reasoned that if the Tertiary kaolin represented reworked Cretaceous kaolin, the crystallinity index of a given particle size of Tertiary kaolin might be expected to have the same crystallinity index as the corresponding crystallite size in the Cretaceous kaolin, i.e., the < 1 micrometer fraction of a Tertiary kaolin might be expected to have the same crystallinity index as the < 1 micrometer fraction of a Cretaceous kaolin. It is very important to note that their results showed that all of the size fractions of the Cretaceous kaolin samples exhibited higher crystallinity indicies than the corresponding size fractions of the Tertiary kaolin samples. This strongly suggests that Tertiary kaolin deposits are <u>not</u> the concentrated fine fraction of a Cretaceous kaolin deposits that had been subjected to winnowing during erosion and redeposition.

Crystallite thickness has also been suggested as a possible reason for the differences in structural order based on relative peak heights. If this were true, the finer particle size in Eocene kaolin deposits (having thinner crystallites with fewer repeats of the unit cell) could explain their structural disorder (Hurst, pers. comm., 1988). Discussions with Harrison (pers. comm., 1988) suggested that particle thickness did not play a role in observed structural order. Harrison stated that the average particle size of even the finest fractions of Eocene clays was 500 angstroms, or about 70 unit cells thick. A thickness of only 10 unit cells is required for acceptable X-ray diffraction; therefore, crystallite thickness is probably

not a controlling factor in the apparent structural order in kaolin.

Dombrowski *et al.*, (1989) determined the concentrations of the trace elements La, Th and Sc in kaolin samples and suggested that the difference between the poorly crystallized hard kaolins of east Georgia and South Carolina and the soft kaolin of central Georgia lies primarily in differences in parent rocks, rather than in transport mechanism or post-depositional diagenesis. The question of provenance for clay minerals is a difficult one, and XRD has been used to help determine the source materials. Bristow (1968) used the differences in the degree of ordering of the kaolinite lattice, as measured by XRD, to determine the provenance of the Tertiary kaolinitic sediments of North Devon, England. The clay in these areas was thought to have originated from the erosion of hydrothermally kaolinized granite in the Dartmoor area. The argillaceous materials in the sediments of North Devon was found to consist primarily of fine-grained kaolinite. The kaolinite produced hydrothermally from granite occurs as relatively large crystals compared to the kaolinite of North Devon and has a well-ordered lattice. Bristow (1968) concluded that erosion and transportation would not affect the lattice of the well-ordered kaolinite in a retrograde manner and suggested that the disordered kaolinite was derived from a different source.

There is a significant correlation between the degree of order (crystallinity index) and the iron content of kaolinite (Mestdagh, 1980). Brindley *et al.*, (1986) examined a suite of Georgia kaolin samples ranging from well-ordered to poorly ordered samples and concluded that kaolinite from different localities possessed different degrees of structural disorder and characteristic ranges of iron concentration. High iron contents correlated strongly with a low degree of order.

Samples with higher percentages of <2 micrometer particles consistently display higher iron contents and are less ordered. The differences in the iron contents of the well-ordered and poorly-ordered kaolin can be seen clearly in Figure 8. Differences in iron contents suggest two distinct populations. Figure 9 illustrates the correlation of degree of structural order with iron content.

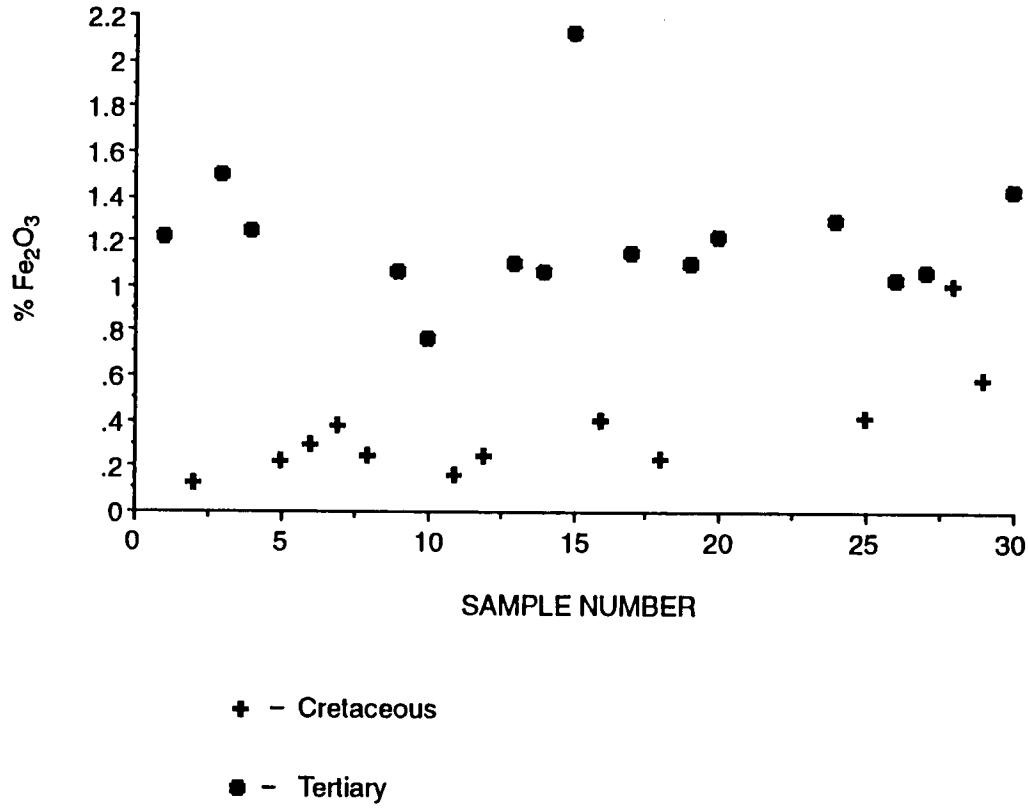

Figure 8. Scatterplot of concentration of Fe_2O_3 vs. sample numbers.

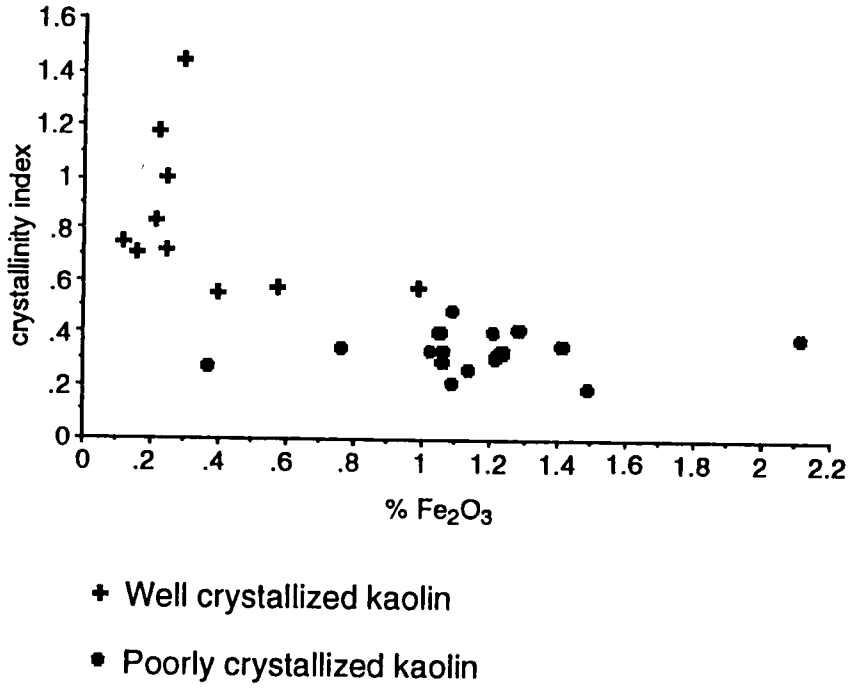

Figure 9. Scatterplot of concentration of Fe_2O_3 vs. crystallinity index.

CHAPTER V

Scanning Electron Microscopy

The extremely small size of individual clay particles has made the use of SEM of significant value to clay mineralogists, especially in the study of textural features such as particle size, shape, and grain to grain arrangement. The morphological characteristics of kaolinite have a considerable effect on their uses in industry and may yield important information concerning both the mineralogy and genesis of these materials. The image produced by SEM is made directly from the surface of the specimen with excellent resolution and depth of field. All of the micrographs shown here were taken on a JEOL JSM 35C using an electron energy of 25 kv.

Specimen Preparation

Each sample was blunged (or slurried) at 20% solids in a Waring blender (except fracture block specimens) using a small amount of Calgon as a dispersant. Most of the slurry was sedimented and used for X-ray diffraction studies. A pipette was used to collect a small amount for an SEM specimen. The slurry was diluted to 0.1% solids. A few drops of dilute slurry were placed on a portion of a glass coverslip that was attached to a sample holder, and the specimen was allowed to air-dry.

A vacuum evaporation sputter coater was used to apply a gold-palladium coating approximately 100 Angstroms thick to enhance conductivity. The coating also helps to prevent local charge build up on the specimen.

Results and Discussion

Single crystals, intergrowths, and aggregates of kaolin were observed in this study. Examples of the basic forms of kaolin photographed are schematically shown in Figure 10. Scanning electron micrographs of samples collected during this study illustrate the same

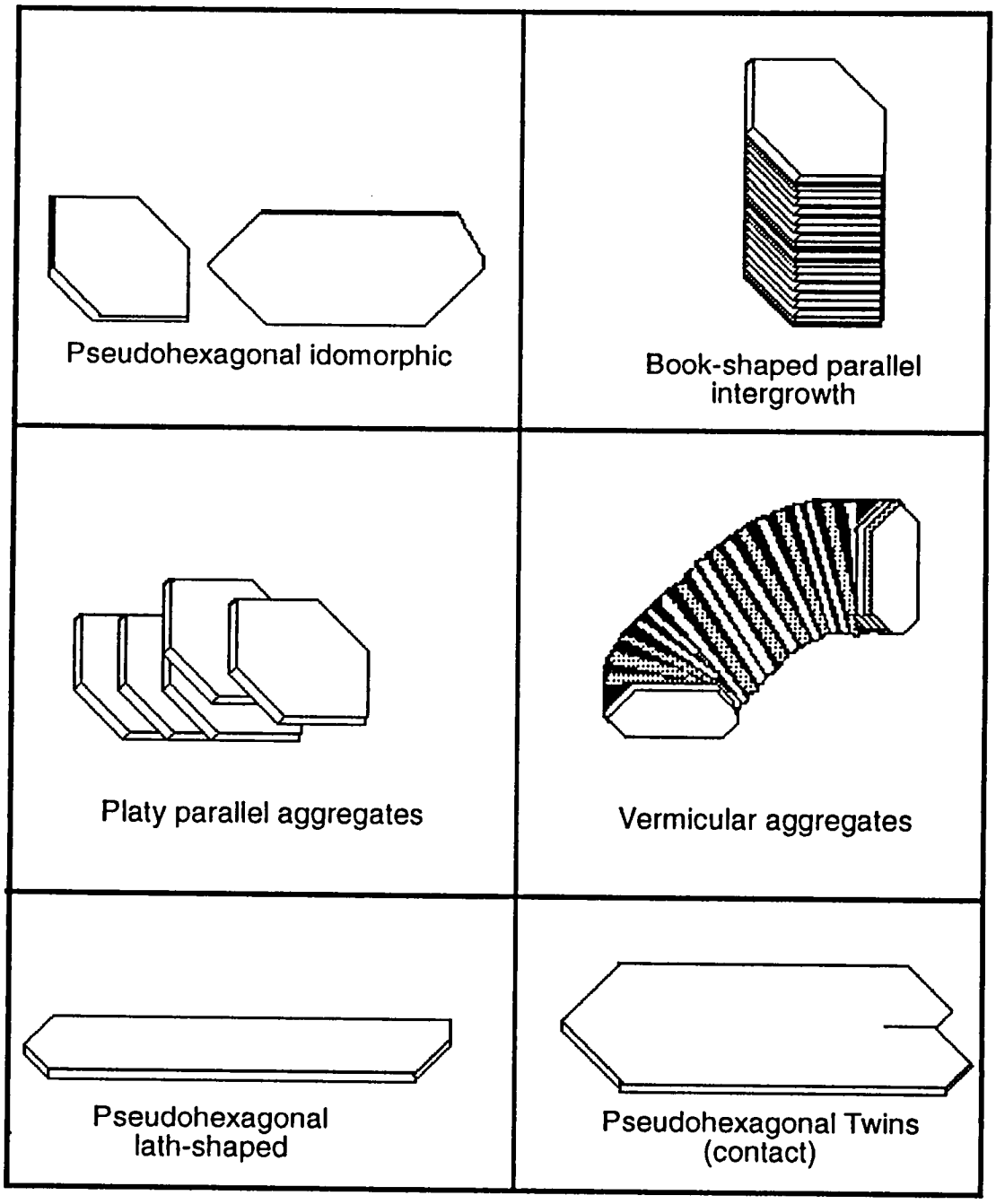

Figure 10. Basic kaolin forms.

relationships between hand specimen gross physical properties and micro-texture reported by Keller (1977). In fracture block specimens soft kaolin (which fractures conchoidally) typically displays a bi-modal size distribution of crystals consisting of a matrix of small crystals surrounding, and on the surface of, larger book-shaped and vermiform parallel intergrowths. In contrast, fracture block specimens of hard kaolin display noticeably smaller plates, often singly, and as overlapping plates in face-to-face contact.

An Eocene sample (GK-9) and a Cretaceous sample (GK-6) are illustrated below at 1,000X and 6,000X. By using the same magnifications direct comparison of the surface textures of the fracture blocks was made possible. The Cretaceous kaolin at 1,000X (Figure 11) was relatively open, resembling a "house of cards" arrangement with particles in contact at many different angles along various surfaces. Parallel intergrowths of kaolin in the form of books and vermiforms are evident and appear to dominate the texture of the sample. By comparison, the Eocene kaolin (Figure 12) exhibited a much more compact structure with few voids. Even at 1,000X it is difficult to resolve the individual platelets of the Eocene sample tight particle packing is evident with little open space. Clay particles are in contact face-to-face, and the texture resembles shingles on the roof of a house. At 6,000X the Cretaceous kaolin (Figure 13) is dominated by a large vermiform on the left-hand side of the photo. The face-to-face orientation of platelets can be seen in the vermiform. Other platelets exhibit face-to-edge orientations. The face-to-face orientations contribute to an open structure and lower bulk density. By comparison, the Eocene kaolin at 6,000X (Figure 14) showed much smaller platelets, no books or vermiforms and a lack of large voids. Notice the "shingled" arrangement of the clay particles. In addition to fracture blocks, photomicrographs were taken of dispersed material which had been sedimented onto glass slides. This technique is widely used in the kaolin industry to examine the morphology of the clay particles in more

Figure 11. Fracture block photo of sample GK-6 a Cretaceous kaolin. Magnification 1000x. Scale bar = 10 micrometers.

Figure 12. Fracture block photo of sample GK-9 a Tertiary kaolin. Magnification 1000x. Scale bar = 10 micrometers.

Figure 13. Fracture block photo of sample GK-6 a Cretaceous kaolin. Magnification 6000X. Scale bar = 1.0 micrometer.

Figure 14. Fracture block photo of GK-9 a Tertiary sample. Magnification 6000X. Scale bar = 1.0 micrometer.

detail. As with the fracture block, samples were examined at the same magnifications to allow direct comparison of size and morphology of individual platelets, intergrowths, and aggregates.

The clay minerals which were identified as well-crystallized by calculating their crystallinity indices from XRD were distinctive when examined with SEM. The coarse kaolin samples tended to be composed of blocky, equant crystallites. These crystals had well-defined, straight edges, commonly with angular indentations suggesting that reentrants developed during twinning. In most 1,000X photos, the larger stacks or books were quite noticeable, consisting of many plates stacked parallel to the c-axis. This stacking did not produce smooth sides, but rather irregular, stepped sides with notches. Some of the books were curved, perhaps due to the presence of more layers on one side than the other or possibly to a difference in thickness of the kaolinite plates from one side of the stack to the other.

The fine kaolin samples tended to consist of aggregates and agglomerates composed of many crystallites. The crystallites in these samples tended to be thinner and commonly had edges that were not well defined. Some of the platelets had a ragged appearance at their edges, whereas others appeared more rounded. The most striking difference between the fine and the coarse particle size clay was the absence of books or stacks in the fine clay.

Soft Cretaceous Kaolins

Sedimented slurry samples of soft kaolin consistently revealed the presence of distinct, well-defined, psuedohexagonal idiomorphic crystals. Twins were also very common. In all micrographs, the particle size of the crystals was greater in the soft kaolins than of the hard kaolins. Sedigraph analyses (see discussion in Chapter VI) confirmed the observations that the crystals in the soft kaolin were coarser grained.

The micro-texture of the soft kaolin has been attributed to a number of factors. It has been suggested that the texture was inherited from the residual kaolin which formed on the igneous and metamorphic rocks of the Georgia Piedmont (Veatch, 1909; Neuman, 1927; Smith, 1929; Murray, 1976). Hinckley (1961) suggested that deposition of the soft, coarse kaolin took place in fresh water, resulting in face-to-edge flocculation with a greater permeability, thus allowing the movement of solutions promoting crystal growth, recrystallization, and oxidation.

Other authors have proposed that the soft kaolins were formed after deposition by intense leaching of arkosic sediments (Kesler, 1951,1956; Jonas, 1959; Austin 1978; Hurst, 1979). These authors suggested that the large vermiforms of kaolin, which are readily cleavable and up to 50 micrometers long, could not possibly represent transported particles. The leaching of the arkosic sediments would also involve mass reduction, which could account for the open, porous micro-texture of the Cretaceous kaolins. A considerable amount of porosity may result from the open, loosely packed arrangement of the crystals. Henning (1986) attributed the presence of pores in residual kaolins containing large vermiform aggregates to mass losses by weathering, suggesting that the porous texture of the Cretaceous kaolin indicates redistribution of material due to diagenetic and/or weathering processes.

Keller (1977) documented the presence of kaolin vermiforms in samples collected from a clay slurry that had been subjected to considerable mechanical agitation in the presence of a chemical dispersant in a commercial clay blunger. This attests to the durability of book-shaped stacks of kaolin. The number of impacts sustained during erosion and transportation would probably be less than the number sustained in commercial processing. Although this is an interesting testament to the durability of kaolin stacks, it does not provide an unequivocal answer to the question of whether these stacks were formed during weathering (and later

transported) or during diagenesis after deposition.

Large books, stacks, and vermiforms are common in residual or primary kaolin deposits. Books and stacks might have been transported, but the likelihood of the vermiforms having been transported is probably low due to their curved, elongated, and fragile nature. The presence of vermiforms in sedimentary kaolin deposits can best be explained by formation during diagenesis.

Hard Tertiary Kaolins

In general, hard kaolin deposits are more compact and have very little open space visible in micrographs of fracture surfaces. The micro-texture of hard kaolin has been described as a face-to-face orientation of tightly packed particles. Hinckley (1961) suggested that the influx of clay sediments into saline water would result in face-to-face flocculation and allow entrapment of iron oxides along with the clays. This type of deposition and particle arrangement might also have served to reduce the permeability, and therefore, retard recrystallization and oxidation of the organics and the iron. This could explain the higher bulk density, more compact nature, and general greater concentration of iron oxide in the hard kaolin deposits.

The texture of the Tertiary kaolin deposits appears to be governed by the effects of sedimentation and possibly even by bioturbation. The parallel arrangement of the clay particles and tight packing are indicative of sedimentary deposition (Henning, 1986).

CHAPTER VI

Particle Size Distribution

The particle size distributions of several samples were determined with an instrument (Sedigraph 5000) that calculates the equivalent spherical diameter of the clay particles based on Stokes' Law. The equipment and testing were provided by ECC America Inc.

Sample Preparation and Analysis

A clay slurry was dispersed with polyacrylate and ammonia at 60% solids and mixed in a Waring blender set on high for 3 minutes. The resulting fully dispersed slurry was loaded in the cell for the sedigraph.

Because kaolinite has a plate-like shape (not spherical), it does not behave exactly according to Stokes' Law. Therefore, using a Sedigraph to determine particle size distribution is imprecise, but it does allow comparison of the overall particle size distribution of different clays. Also, the sample preparation method used may alter the size distribution of the clay particles to some extent.

Most of the samples were analyzed with the Sedigraph to determine their particle size distribution (psd). The curves provide a graphical representation of the overall distribution in grain size. The y-axis is scaled in percent, and the x-axis is scaled in micrometers.

Results and Discussion

The results indicated that the samples represented two different populations of particle size distributions, one which averages 34% >2 micrometer and a second which averages 8% >2 micrometer particles.

Comparing the overall psd between the two populations to the inferred ages of the material samples revealed that the hard (Eocene) kaolins were consistently finer grained, with higher percentages of material in the 1-0.5, and <0.5 micrometer ranges, than the soft (Cretaceous)

kaolin deposits. Tables 5 and 6 show the average percentages of material in the different size fractions for Tertiary and Cretaceous samples, respectively. Tertiary kaolin samples have higher percentages of material in the 1-0.5, and <0.5 micrometer fractions. On the other hand the Cretaceous kaolin samples have much lower percentages of 1-0.5 and <0.5 micrometer material. The data clearly showed that the Cretaceous kaolin had considerably less material in the <0.5 micrometer range that the Tertiary clays.

By way of comparison, Henning (1986) studied three genetic types of kaolinite-bearing sediments including: 1) Kaolin deposits formed by weathering - primary kaolins; 2) Kaolinitic clays formed by redeposition of primary kaolin - secondary kaolin deposits; and 3) Joint-fillings and kaolinite-bearing sandstone-diagenetic kaolin. Significant differences were found in the particle-size distributions of the different sediments. The distributions for the various genetic types of kaolinite were:

Primary kaolin- 30-40% in the 0.4-0.8 micrometer range and the remainder distributed among the other grain fractions.

Secondary kaolin- a maximum of 70% in the <0.4 micrometer fraction with the <2 micrometer range having high percentages.

Diagenetic kaolin- 15-20% in the 1.2-1.6 micrometer range with the remaining size fractions having small percentages.

Based on Henning's work, diagenetic kaolin deposits appear to be the coarsest of the three types.

Table 5 - Average Particle Sizes of Tertiary Samples

Sample #	% > 2μm	% 2 - 1μm	%1 - 0.5μm	% < 0.5μm
GK-1	5	5	10	80
GK-3	5	4	7	84
GK-4	4	4	9	83
GK-7	13	7	10	70
GK-9	4	7	10	79
GK-10	19	16	6	59
GK-13	16	9	11	64
GK-14	2	6	10	82
GK-17	9	8	12	71
GK-19	15	9	14	62
GK-20	4	4	10	82
GK-24	8	8	12	72
GK-26	0	4	28	68
GK-27	5	6	11	78
A-3	9	7	12	72
Averages =	8	7	11	74

Table 6 - Average Particle Sizes of Cretaceous Samples

Sample #	% > 2μm	% 2 - 1μm	%1 - 0.5μm	% < 0.5μm
GK-2	36	18	24	22
GK-5	36	14	20	30
GK-11	18	26	8	48
GK-12	28	18	14	40
GK-16	36	16	12	36
GK-25	44	15	15	26
A-1	32	13	14	41
A-2	45	15	11	29
Averages =	34	17	15	34

The Eocene kaolin deposits of Georgia (averaging 74% < 0.5 micrometers) closely resemble what Henning describes as secondary kaolin (70% < 0.4 micrometers). The Cretaceous kaolin deposits (averaging 17% in the 1-2 micrometer range) compare favorably with the diagenetic kaolin (averaging 15-20% in the 1.2-1.6 micrometer range) described by Henning (1986). On the basis of particle size distribution, it appears that the Cretaceous kaolin deposits have been influenced by diagenetic processes, and that the Eocene have been influenced very little by such processes.

CHAPTER VII

X-Ray Fluorescence

Instrumentation and Principles

Samples were analyzed using an EG&G ORTEC 6110 TEFA (Tube Excited Fluorescence Analyzer). X-ray Fluorescence (XRF) relies on the fact that elements generate characteristic X-rays when subjected to an ionization process with sufficient energy to free electrons in the K, L, and M shells. A characteristic X-ray is generated when a bound electron moves closer to the nucleus of the atom to fill the vacancy left by the freed electron. The detector of the instrument absorbs the energy from each X-ray photon that passes through its beryllium window and generates an electrical output with an amplitude proportional to the absorbed energy.

Sample Preparation

The pressed pellet method of sample preparation was chosen for the XRF analyses because this method is quick, reproducible, and provides stable samples which are easily handled. The two types of errors introduced by the specimen are matrix, or interelement effects, and improper surface preparation. Surface irregularities affect the path of primary exciting X-rays and have an even greater effect on the fluoresced X-rays. The mixing that occurs during comminution and particle size reduction during grinding in a Shatterbox helps reduce large scale heterogeneity in the surface of the sample.

A 12 gm sample was dried at 105^{0}C for 1 hour, placed in a SPEX Shatterbox (swingmill), and ground for 6 minutes. A few drops of FREON were add to serve as a grinding aid. To reduce density and compositional variations that occur when a sample is poured into a specimen holder, four grams of the ground material was placed inside a pellet die and pressed by hand to "pre-form" the pellet. Granular boric acid was poured into the die and on top of

the pre-formed pellet. The remaining parts of the die were assembled and placed into a Carver laboratory press. The die was pressed for 15 seconds at 10K psi and then 1 minute at 30K psi. The boric acid backed sample was labeled with the appropriate sample identification. The samples were stored in a desiccator until ready for analysis.

Interelement effects

Complex matrices can result in the measured intensities of elements not corresponding to the actual percentages present due to interelement effects. The interelement effects can cause enhancement and absorption. Enhancement and absorption effects are more apt to occur with elements that are close to one another on the periodic table. When the element of interest is excited by another element whose characteristic line is slightly higher in energy than the absorption edge of the analyzed element, enhancement occurs. When an element other than the element of interest has an absorption edge slightly lower in energy than the characteristic line of the analyzed element, absorption occurs. Energy level at the absorption edge is equal to the minimum amount of energy required to free a bound electron from its normal position within the atom and corresponds to the binding energy of the electron in that shell.

Results and Discussion

The bulk chemical compositions for all samples were determined using XRF analysis. Results for each of the samples can be found in Appendix 1 along with the mean and range for each element.

Note that the chemical analyses determined in this study reflect the composition of the entire sample, which included an appreciable amount of detrital quartz and mica in some cases. Elements such as Fe and Ti (reported as Fe_2O_3 and TiO_2, respectively) were present in minerals that occur as grain surface coatings and as micrometer sized, discrete minerals.

Several clay standards were analyzed along with the samples to check the accuracy and

precision of the equipment. Two of the standards utilized during this investigation were kaolin samples from east-central Georgia provided by the Clay Mineral Society (CMS) and labeled KGA1 (Cretaceous) and KGA2 (Eocene). These two standards were very similar in composition to the samples collected for this study and allowed direct comparison with reference materials. The average chemical compositions for the Eocene and Cretaceous samples are given in Table 7. The compositions of Clay Mineral Society Standards KGA1 and KGA2 are compared to the chemical compositions determined for these standards by Van Olphen and Fripiat (1979) which are also shown in Table 7. The results compare favorably with only slight differences, which could be due to the absence of >325 mesh material in the CMS standards. The average compositions of Cretaceous and Eocene samples (this study) are also given in Table 7. In general the Tertiary samples had higher Fe_2O_3 and TiO_2 contents than the Cretaceous samples.

In Table 8 the theoretical composition of kaolinite is compared to the chemical compositions determined for three other kaolinite samples. The Keokuk sample is precipitated kaolinite from within a geode and very nearly corresponds to the theoretical composition of kaolinite. The sample for St. Austell represents a kaolinite formed under hydrothermal conditions. It contains less SiO_2 and Al_2O_3 than the theoretical kaolinite. The sedimentary kaolin sample from Washington County, Georgia appears to be a Cretaceous soft kaolin. The Al_2O_3 content compares well with the hydrothermal kaolin, but is the most deficient in SiO_2 of all the samples compared.

As shown in Table 8, the composition of ideal kaolinite is 46.55% SiO_2, 39.49% Al_2O_3, and 13.96% H_2O. In this study, the Eocene samples averaged 46.00% SiO_2, approximately 0.5% less than "theoretical kaolinite", which compared quite favorably with the results of Jepson and Rowse (1975); however, in the case of Al_2O_3, the Eocene samples were

Table 7 - Comparison of Chemical Compositions

	1	2	3	4	5	6
SiO_2	44.2	45.71	46.08	43.90	44.85	46.00
Al_2O_3	39.7	37.76	37.58	38.5	37.09	36.33
TiO_2	1.39	1.55	1.63	2.08	2.14	1.81
Fe_2O_3	0.13	0.23	0.39	0.98	1.19	1.16
Na_2)	0.013	0.06	0.33	0.005	0.02	0.13
MgO	0.03	0.07	0.08	0.03	0.08	0.09
CaO	N.D.	0.01	0.08	N.D.	0.01	0.10
K_2O	0.05	0.03	0.15	0.065	0.04	0.11
Mn	0.002	N.D.	0.01	N.D.	0.01	0.01
P_2O_5	0.034	0.03	0.02	0.045	0.04	0.02
S	N.A.	0.08	0.05	N.A.	0.04	0.06
Ba	N.A.	0.01	0.02	N.A.	0.02	0.02
Cr	N.A.	0.01	0.01	N.A.	0.01	0.01
Rb	N.A.	N.D.	N.D.	N.A.	N.D.	N.D.
Sr	N.A.	0.01	0.01	N.A.	0.01	0.01
Zr	N.A.	0.13	0.15	N.A.	0.18	0.11

1. KGA 1 Clay Mineral Society Standard average composition (Van Olphen and Fripiat 1979)
2. KGA 1 Clay Mineral Society Standard average composition.*
3. Cretaceous samples average composition.
4. KGA 2 Clay Mineral Society Standard average composition (Van Olphen and Fripiat 1979)
5. KGA 2 Clay Mineral Society Standard average composition. *
6. Eocene samples average composition.

* Chemical compositions as measured during this study with XRF

N.A. - Not analyzed

N.D. - Not detected

Table 8 - Reported Analyses of Kaolinites From Different Areas

	1	2	3	4
SiO_2	46.55	46.40	46.2	45.2
Al_2O_3	39.49	39.52	39.2	39.2
TiO_2	*	0.09	0.23	0.17
FeO	*	*	*	*
Cr_2O_3	*	*	*	*
MgO	*	*	*	*
CaO	*	0.23	0.06	*
Na_2O	*	0.09	0.09	0.03
K_2O	*	0.01	0.21	0.02
H_2O	13.96	13.9	13.8	13.3

Chemical Constitiution of Clays (Newman and Brown, 1987)

1. Theoretical composition of kaolinite.
2. Kaolinite, Keokuk, Iowa, USA Keller *et al.*,(1966).
3. Kaolinite, St. Austell, Cornwall, UK. Contains 1-2% mica (Jepson and Rowse, 1975).
4. Kaolinite, Washington County, Georgia, USA. Contains 1-2% anatase (Jepson and Rowse, 1975).

(*) Not Reported

different, averaging 36.33% Al_2O_3 which is approximately 3.2% less than "theoretical kaolinite". The chemistry of Eocene samples in this study more closely resembled the Clay Mineral Society Standard (KGA2)material average composition.

The Cretaceous samples in this study averaged 46.08% SiO_2. Although the SiO_2 content was 0.5% lower than the theoretical SiO_2 content it was similar to the SiO_2 contents of other kaolinite samples as shown in Table 8. The Cretaceous kaolinite samples generally had higher Al_2O_3 contents than Eocene kaolinites, averaging only 1.91% less than "theoretical kaolinite", and contained less Al_2O_3 than the material reported by Jepson and Rowse (1975).

The soft kaolins were found to have consistently lower Fe_2O_3 and TiO_2 contents than the hard kaolins. Soft kaolins also contained more Al_2O_3 than the hard kaolins. Based on the work of Mestadagh (1980) and Hurst *et al.*,(1989), it is generally accepted that a small amount of iron substitutes for aluminum in kaolinite. As mentioned previously in the section concerning kaolin crystallinity, the substitution of iron for aluminum is thought to have a detrimental effect on crystallinity. The exact mechanism by which this might take place has been the subject of considerable study by Plancon and Tchoubar (1977).

CHAPTER VIII

Discussion and Conclusions

Several theories have been proposed to explain the origin of the Georgia kaolins and the differences between soft Cretaceous and hard Tertiary kaolins. The main objective of this study was to determine if the hard Tertiary kaolins were formed as a result of the reworking the soft Cretaceous kaolins. Whether or not the soft kaolins were the result of in situ kaolinization of source rocks or through the alteration of arkosic sediments was not of primary importance here.

As noted previously several hypotheses have been offered to explain the origin of the hard kaolins and why they differ from the soft kaolins. Briefly, they are:

1) Reworking of soft kaolins (Austin 1972, Murray 1976);
2) Deposition of feldspathic sandstones, which were later altered to kaolin (Kesler 1963, Jonas,1964);
3) Differential flocculation and laterization of hard kaolin (Smith, 1929);
4) Differences in depositional environmental (Hinckley, 1963);
5) Differences in the source rocks, that is a source granite for the soft kaolins, and a phyllite source for the hard kaolins (Dombrowski, 1989);

Several authors, including Austin (1972), Murray (1976) and Dombrowski and Murray (1984), have proposed that the fine particle-size, poorly crystalline kaolins commonly referred to as Tertiary kaolins, represent reworked Cretaceous kaolins. They suggested this for several reasons:

1) Tertiary (hard) kaolins occur stratigraphically above Cretaceous (soft) clays;
2) Tertiary kaolins typically have higher percentages of >2, 2-1, 1-0.5 and <0.5 micrometer material, indicating winnowing of the coarser grained Cretaceous kaolins;

3) Soft Cretaceous kaolins are typically bounded on top by an unconformity, above which clay balls and rip-up clasts indicative of reworking can be found.

The information gathered during this study confirmed consistent and measurable differences between Tertiary and Cretaceous kaolins. The samples of hard Tertiary kaolins were found to have higher iron contents and lower aluminum contents than the soft Cretaceous kaolin samples. The Tertiary samples had higher percentages of <0.5 micrometer material and lower percentages of >2, and 2-1, micrometer material than the Cretaceous samples. When examined with SEM the Tertiary kaolins exhibited an absence of books and vermiforms, and most of the clay particles were seen as compact aggregates arranged face-to-face compared to the face-to-edge arrangement of the Cretaceous kaolins which contain numerous books and vermiforms. X-ray diffraction revealed that the Tertiary kaolins had lower calculated crystallinity values indicating less internal structural order than indicated by the crystallinity values of the Cretaceous kaolins.

Sedimentary processes (including bioturbation) could account for some of the differences between the Cretaceous and Tertiary kaolins. The difficulty in interpreting these measurable differences was to decide whether any of the differences could not be accounted for by the proccesses of erosion, grain-size factionation, deposition, or bioturbation.

For hard kaolins to have been reworked from soft kaolins, the following conditions must have been met:

1) Iron must have been added;
2) Aluminum must have been lost;
3) The smaller particle-size fraction must have been separated and concentrated from the larger particle-size fraction of the Cretaceous kaolins;
4) Books and vermiform had to be eliminated or separated during reworking;

5) The internal structural order must have been diminished from well-ordered in the Cretaceous kaolins to poorly-ordered in the Tertiary kaolins.

The addition of iron to the Tertiary kaolins could easily have taken place by the influx of detrital material, or the precipitation of mineral and/or amorphous phases within the sediments or along joint and fracture planes. Because there are several potential methods of iron addition to clay sediments this factor was not considered useful in determining the origin of the Tertiary kaolins.

The fact that the Tertiary kaolins had less aluminum than the Cretaceous kaolins could have been caused by variations in the degree of loss of aluminum due to weathering. Again, this factor was not considered useful for answering the question at hand.

The original particle-size distribution of the Cretaceous sediments could have been altered by grain-size fractionation; however, the ability for sedimentary processes to significantly alter the particle-size distribution of a sediment decreases as the distribution of the grain-size population becomes more narrow. In the case of the soft versus hard kaolins the differences between the particle size distributions are very apparent in the <0.5 micrometer range.

Based on a study of the relative abundances of clay mineral species in the < 2 micrometer fractions from a crevasse splay in the Mississippi Delta, Dimarco *et al.*, (1986) concluded that the normal physical processes operating during sedimentation were incapable of fractionating clay mineral species in the <2 micrometer range. If the physical processes of sedimentation are incapable of fractionating different species of clay minerals which vary considerably in grain size, it seems unlikely that sedimentary processes exist which are capable of altering the particle size distribution of clay minerals that are nearly identical mineralogically.

Another method of altering the particle size distribution is size reduction by collision. This process becomes less effective as grain size decreases due to the decrease in probability

of an impact resulting in attrition of one or more particles. If this applies to kaolin the amount of grain-size reduction possible by grain-to-grain collision is very small. This would make it difficult to explain the absence of books, stacks, and vermiforms in the Tertiary kaolins by attrition. The particle-size distribution of the Cretaceous clays would have to have been significantly altered by grain-size fractionation or bioturbation if it was reworked to form Tertiary kaolins. It is uncertain whether sufficient attrition took place during erosion and sedimentation to have produced the particle-size distributions and particle morphologies seen in the Tertiary kaolins.

Since the differences in morphology (books, vermiforms) and the particle-size distributions could have been caused by grain-size fractionation and /or bioturbation these factors do not provide unequivocal evidence for or against the reworking of Cretaceous kaolins to form the Tertiary kaolins. Particle-size distribution and the morphology of kaolin minerals has been studied extensively and used as an indicator of clay genesis. Keller (1977) examined and described samples of kaolin from Georgia. He described the soft kaolins as having open, porous structures with numerous, expanded books and packets of kaolinite crystals indicating adequate space for growth either before or after deposition. Keller described the hard kaolins as compact, finer-grained, and characterized by face-to-face orientation of crystals with little room for crystal growth after deposition. Henning (1986) suggested that certain conclusions can be drawn concerning the nature of parent rocks based on the difference in the distribution of grain size. Henning also suggested (as Keller observed in 1977) that the texture of sedimentary kaolins is governed by processes of fractionation and sedimentation which result in particles being arranged parallel to one another. Comparing the samples examined in this study to the findings of Henning suggests that the Tertiary kaolins are sedimentary and that the Cretaceous kaolins have undergone some diagenetic alteration. Henning (1986) believes

that the vermiforms which occur in the sedimentary kaolins of Georgia are most likely products of diagenetic alteration.

To answer the question of whether the Cretaceous kaolins served as the source material for the Tertiary kaolins, internal structural order (as measured by the crystallinity index) was considered to be least likely to be altered by sedimentary processes. The crystallinity indicies of the samples clearly belonged to two distinct populations and corresponded to the ages of the samples (Cretaceous or Tertiary). The Tertiary samples all had calculated crystallinity values <0.5 and the Cretaceous samples all had values >0.5. Internal structural order has been used as a tool to determine the provenance of kaolinitic sediments. Based on X-ray diffraction and chemical analysis, Bristow (1968) concluded that Tertiary kaolinitic ball clays in fault basins of North and South Devon, England were derived from weathering mantles developed on the Culm Measures shales, instead of from hydrothermally altered granites. Bristow (1968) concluded that erosion and transportation would not have degraded the internal structural order of kaolinite. Only one factor, differences in internal structural order, seems capable of providing unequivocal information concerning the origin of the Tertiary kaolins. Based on this limited information the Tertiary kaolins do not represent reworked Cretaceous kaolins.

CHAPTER IX

Further Study

Other areas in which additional research might yield useful information are discussed below. Particle size distributions were consistently different between the Tertiary and Cretaceous kaolins. Since sedimentary processes can alter size distribution, these differences by themselves could not answer the question posed in this study. If more was known concerning the effectiveness of grain-size fractionation by sedimentary or bioturbational processes in kaolinitic clays, the significance of the differences measured during this study might be more fully understood.

A major problem which confronts every researcher of the Georgia kaolins is the difficulty in accurate and precise age determination of the kaolins due to the lack of fossils. Although a Tertiary age for the hard kaolins was determined on the basis of casts or molds of Eocene fossils found by Buie and Fountain (1967) in the upper portion of the kaolin, no other reported occurrence of fossils exists to this writer's knowledge. The age of the Huber Formation deserves confirmation through examination by lithostratigraphic or palynological techniques. Obviously, if two kaolins of differing characteristics (suggesting Cretaceous and Tertiary ages respectively) were in fact the same age, reworking becomes a moot point.

As noted by numerous authors, the chemical compositions of the Tertiary and Cretaceous kaolins differ consistently in iron, aluminum and quite commonly in titanium contents. A more thorough investigation into the nature and occurrence of these elements with TEM, SEM, and possibly electron microprobe could yield valuable information as to why they differ between Cretaceous and Tertiary kaolins. This might also aid in determining differences in source materials, and deposition and post-depositional processes. Such a study could also yield information related to the method of beneficiation most suited to removal of these

separate phases.

The role of reducing and oxidizing conditions on the depositional and post-depositional history of the kaolins also deserves attention. The post-depositional oxidation of Tertiary and perhaps Cretaceous kaolins may have played a role in producing the iron and titanium phases present in the kaolins today. The role of oxidation on the particle morphology, grain size, and mineralogy of the Tertiary and Cretaceous kaolins would certainly add to the understanding of the these deposits.

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APPENDICES

APPENDIX 1 XRF ANALYSES OF KAOLIN SAMPLES

ELEMENT	SAMPLE GK-1	SAMPLE GK-2	SAMPLE GK-3	SAMPLE GK-4	SAMPLE GK-5
Na_2O	0.23	0.16	0.13	0.11	0.45
MgO	0.01	0.02	0.09	0.04	0.04
Al_2O_3	36.38	38.37	33.57	36.56	38.11
SiO_2	45.56	45.97	50.65	45.21	46.20
P_2O_3	0.01	0.01	0.06	0.02	0.02
S	0.07	0.05	0.08	0.08	0.08
K_2O	0.08	0.01	0.04	0.0	0.02
CaO	0.28	0.02	0.07	0.09	0.03
TiO_2	1.56	1.58	1.41	1.76	1.68
Cr	136 ppm	117 ppm	152ppm	103ppm	126ppm
MnO	39ppm	0ppm	59ppm	77ppm	38ppm
Fe_2O_3	1.22	0.12	1.49	1.24	0.22
Ba	185ppm	165ppm	155ppm	180ppm	145ppm
Rb	18ppm	19ppm	21ppm	20ppm	17ppm
Sr	125ppm	87ppm	66ppm	117ppm	72ppm
Zr	419ppm	1727ppm	1586ppm	432ppm	1814ppm

ELEMENT	SAMPLE GK-6	SAMPLE GK-7	SAMPLE GK-8	SAMPLE GK-9	SAMPLE GK-10
Na_2O	0.33	0.21	0.16	0.01	0.09
MgO	0.06	0.09	0.03	0.09	0.12
Al_2O_3	37.76	35.70	38.12	34.82	29.99
SiO_2	45.85	46.78	45.71	47.39	55.95
P_2O_3	0.02	0.04	0.03	0.0	0.05
S	0.08	0.09	0.03	0.07	0.06
K_2O	0.0	0.03	0.14	0.11	0.87
CaO	0.02	0.11	0.03	0.69	0.0
TiO_2	1.35	1.64	1.71	1.34	1.07
Cr	114ppm	156ppm	141ppm	134ppm	153ppm
MnO	24ppm	0ppm	0ppm	27ppm	64ppm
Fe_2O_3	0.29	0.37	0.25	1.06	0.76
Ba	165ppm	147ppm	163ppm	173ppm	190ppm
Rb	20ppm	20ppm	22ppm	19ppm	36ppm
Sr	74ppm	53ppm	76ppm	114ppm	122ppm
Zr	1100ppm	2108ppm	1669ppm	488ppm	1126ppm

ELEMENT	SAMPLE GK-11	SAMPLE GK-12	SAMPLE GK-13	SAMPLE GK-14	SAMPLE GK-15
Na_2O	0.19	0.3	0.17	0.28	0.14
MgO	0.02	0.09	0.14	0.10	0.10
Al_2O_3	36.42	37.77	35.03	37.29	33.61
SiO_2	47.83	46.09	47.32	45.43	48.06
P_2O_3	0.0	0.0	0.0	0.04	0.0
S	0.06	0.05	0.06	0.05	0.07
K_2O	0.05	0.03	0.71	0.01	0.36
CaO	0.02	0.13	0.06	0.0	0.01
TiO_2	1.62	1.68	1.86	2.00	1.34
Cr	172ppm	139ppm	113ppm	105ppm	143ppm
MnO	0ppm	0ppm	57ppm	35ppm	105ppm
Fe_2O_3	0.16	0.24	1.09	1.06	2.12
Ba	139ppm	156ppm	212ppm	167ppm	269ppm
Rb	21ppm	22ppm	36ppm	19ppm	29ppm
Sr	81ppm	119ppm	92ppm	98ppm	84ppm
Zr	2077ppm	1508ppm	2604ppm	557ppm	1206ppm

ELEMENT	SAMPLE GK-16	SAMPLE GK-17	SAMPLE GK-18	SAMPLE GK-19	SAMPLE GK-20
Na_2O	0.17	0.1	0.08	0.08	0.08
MgO	0.31	0.11	0.0	0.16	0.08
Al_2O_3	36.53	35.86	37.98	36.63	37.49
SiO_2	47.01	46.83	46.13	46.85	45.47
P_2O_3	0.01	0.03	0.05	0.05	0.03
S	0.03	0.09	0.05	0.08	0.01
K_2O	0.35	0.02	0.0	0.05	0.07
CaO	0.45	0.02	0.08	0.39	0.05
TiO_2	1.57	1.89	1.38	1.44	1.73
Cr	112ppm	165ppm	145ppm	145ppm	135ppm
MnO	40ppm	95ppm	16ppm	51ppm	35ppm
Fe_2O_3	0.39	1.14	0.23	1.09	1.21
Ba	177ppm	183ppm	130ppm	194ppm	175ppm
Rb	28ppm	21ppm	21ppm	21ppm	18ppm
Sr	124ppm	85ppm	51ppm	57ppm	118ppm
Zr	1699ppm	3068ppm	999ppm	1645ppm	458ppm

ELEMENT	SAMPLE GK-24	SAMPLE GK-25	SAMPLE GK-26	SAMPLE GK-27
Na_2O	0.07	0.11	0.21	0.19
MgO	0.09	0.12	0.12	0.10
Al_2O_3	37.29	38.19	36.46	36.41
SiO_2	45.27	46.08	45.47	45.52
P_2O_3	0.04	0.02	0.0	0.01
S	0.03	0.03	0.05	0.05
K_2O	0.18	0.26	0.48	0.13
CaO	0.03	0.0	0.04	0.11
TiO_2	1.59	1.27	2.12	2.86
Cr	176ppm	175ppm	146ppm	141ppm
MnO	72ppm	8ppm	42ppm	47ppm
Fe_2O_3	1.133	0.40	1.03	1.06
Ba	274ppm	187ppm	200ppm	168ppm
Rb	25ppm	23ppm	30ppm	23ppm
Sr	187ppm	107ppm	118ppm	131ppm
Zr	370ppm	1079ppm	1592ppm	2430ppm

ELEMENT	SAMPLE A-1	SAMPLE A-2	SAMPLE A-3
Na_2O	0.20	0.25	0.14
MgO	0.12	0.10	0.04
Al_2O_3	37.47	37.78	35.98
SiO_2	45.87	45.87	45.58
P_2O_3	0.08	0.02	0.01
S	0.03	0.04	0.07
K_2O	0.91	0.60	0.08
CaO	0.04	0.01	0.05
TiO_2	1.67	1.48	2.03
Cr	163ppm	141ppm	144ppm
MnO	80ppm	49ppm	44ppm
Fe_2O_3	1.00	0.57	1.42
Ba	311ppm	197ppm	186ppm
Rb	44ppm	33ppm	18ppm
Sr	186ppm	94ppm	129ppm
Zr	1584ppm	2043ppm	985ppm

APPENDIX 2 STANDARD ERRORS OF CALIBRATION FOR CLAYS PROTOCOL

	KGA-1		DIFFERENCE	KGA-2		DIFFERENCE
Element	A	B	C	D	E	F	S.E.C
Na_2O	0.07	0.06	0.01	0.03	0.02	0.01	±0.02
MgO	0.01	0.13	0.12	0.05	0.04	0.01	±0.05
Al_2O_3	37.59	37.97	0.35	37.08	37.38	0.03	±0.36
SiO_2	45.45	45.97	0.52	45.83	45.11	0.28	±0.39
P_2O_3	0.03	0.03	0.00	0.05	0.03	0.02	±0.01
S	0.08	0.07	0.01	0.03	0.03	0.00	±0.03
K_2O	0.03	0.02	0.01	0.02	0.02	0.00	±0.01
CaO	0.01	0.03	0.02	0.02	0.00	0.02	±0.01
TiO_2	1.52	1.55	0.03	2.12	2.13	0.01	±0.34
Cr	0.01	0.02	0.01	0.01	0.01	0.00	±0.01
MnO	0.00	0.00	0.00	0.00	0.00	0.00	±0.00
Fe_2O_3	0.23	0.22	0.01	1.18	1.17	0.01	±0.55
Ba	0.01	0.01	0.00	0.02	0.02	0.00	±0.60
Rb	0.00	0.00	0.00	0.00	0.00	0.00	±0.00
Sr	0.00	0.01	0.01	0.01	0.01	0.00	±0.06
Zr	0.13	0.13	0.00	0.08	0.08	0.00	±0.03

APPENDIX 3 SAMPLE LOCATIONS AND ELEVATIONS

Sample #	Pit	Age	Elevations
GK-1	Sheppard	T	330
GK-2	Buffalo	K	220
GK-3	Buffalo	T	270
GK-4	Avant	T	320
GK-5	Tucker	K	230
GK-6	Tucker 54	K	230
GK-7	Tucker	T	310
GK-9	J.C. Shepherd	T	330
GK-10	Franklin West	T	325
GK-11	Franklin West	K	290
GK-12	Evans	K	300
GK-13	M-66	T	260
GK-14	M-92	T	330
GK-15	M-74	T	320
GK-16	M-56	K	300
GK-17	M-68	T	315
GK-18	M-24	K	265
GK-19	M-24	T	290
GK-20	Purvis	T	425
GK-25	Franklin East	K	290
GK-26	Martin	T	440
GK-27	Poss	T	440
A-1	Carrs Station	K	550
A-2	Union Camp	K	255
A-3	Youngblood	T	400

VITA

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