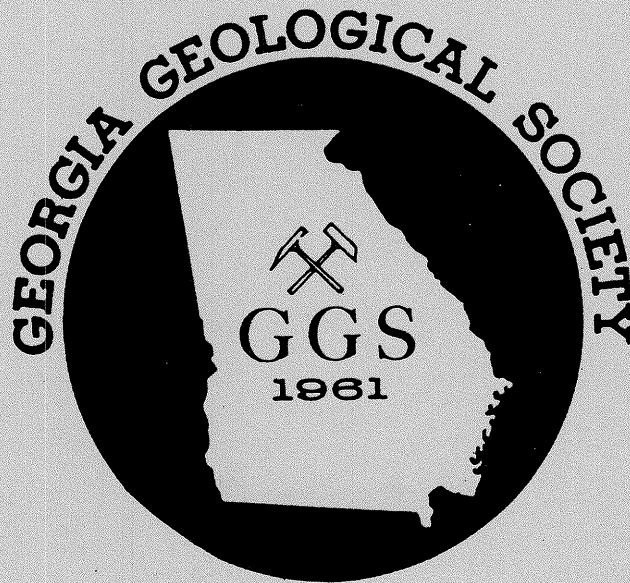


GEOLOGY OF THE COMMERCIAL KAOLIN MINING DISTRICT OF CENTRAL AND EASTERN GEORGIA

Jessica Elzea Kogel, Sam M. Pickering Jr.,

Evgenya Shelobolina, Jun Yuan, Timothy M. Chowns,

& David M. Avant Jr.



35TH ANNUAL FIELD TRIP
GEORGIA GEOLOGICAL SOCIETY
OCTOBER 6-8, 2000

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VOLUME 20, NUMBER 1, OCTOBER 2000

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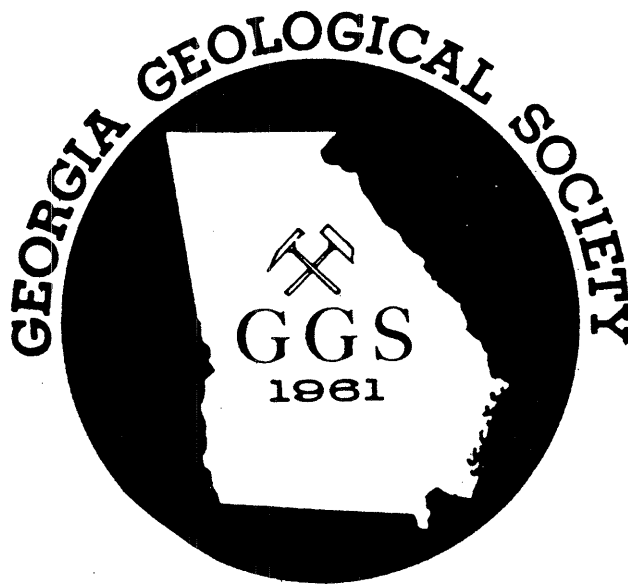
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GEOLOGY OF THE COMMERCIAL KAOLIN MINING DISTRICT OF CENTRAL AND EASTERN GEORGIA

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INTRODUCTION

This 2000 Georgia Geological Society meeting and field trip will mark the first time we have visited the main part of the Georgia kaolin mining district for some 25 years. In that time much progress has been made in understanding all aspects of the geology of the kaolin-bearing units, which we will outline in this guidebook.

Although the guidebook is a joint project, the various authors have focused on particular sections as follows:

Kaolin Stratigraphy and Its Use in Exploration....Pickering, Chowns and Avant
Kaolin Mineralogy, Quality and Product DevelopmentElzea Kogel
Kaolin Origin and AlterationYuan
Role of Microorganisms in Kaolin Genesis.....Shelobolina
Commercial Muscovite Mica From Kaolin Wastes.....Avant and Pickering

LOCATION

Commercial grade kaolins occur as discontinuous clay lenses in thick unconsolidated Upper Coastal Plain sand units. Pigment grade clay is mined from a district that extends just south of the Fall Line for a distance of about 150 kilometers along strike, from Macon, Georgia to near Aiken, South Carolina. Refractory kaolin and associated bauxite are mined in the Andersonville district of Sumter and Macon counties in western Georgia and at Eufaula in east Alabama.

The field trip will visit mines and reclamation areas in the Deepstep to Oconee area of western Washington County on Saturday. On Sunday we will visit the Georgia Industrial Minerals' mica mines and processing plant, and a kaolin mine and a fullers earth mine in the Wrens area of east Georgia. There will be opportunities to examine and sample hard (fine) and soft (coarse) kaolins, both in reduced and oxidized forms.

GEOLOGY OF COMMERCIAL KAOLIN

Several organic lignite zones of both Cretaceous and Early Tertiary age will be available to sample for fossil pollen studies. Mileage road logs locating each stop of both field trip days are in the Appendix at the back of this guidebook.

ACKNOWLEDGMENTS

The leaders wish to express their appreciation for the following companies, which have allowed participation by their scientific staff, field trip access to their mines and properties, and/or have given generous contributions to assist with our trip expenses:

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Imerys Pigments & Additives Group (Kaolin), Deepstep, Georgia
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Kind advice and assistance from Dr. David Prowell (USGS) and Dr. Ray Christopher (Clemson University) on allostratigraphy and palynology are also much appreciated. Mack Duncan of J.M Huber Kaolin Corp. was very helpful in advising on flint kaolins and associated fossiliferous sands in the Wrens area. Data presented in Chapter 4 were generated from work supported by NSF NATO grant DGE-9902554 which the author (ES) gratefully acknowledges. Portions of Chapter 2 were presented at the 37th Annual Meeting of the Clay Minerals Society Meeting during a workshop on Industrial Clay Mineralogy.

CHAPTER 1 – KAOLIN STRATIGRAPHY AND ITS USE IN EXPLORATION

THE KAOLIN INDUSTRY

Mining History and Productivity

Near-white, Coastal Plain kaolin clay has been mined intensively in central and eastern Georgia for more than a century, for use as a white industrial pigment and ceramic raw material. For at least the past 50 years the district has been the world center for this most widely used and valuable of industrial clays. The USGS estimates (Virta, 1998) that in 1998 9.6 million short dry tons of refined kaolin products were produced and sold from the Georgia district for a value of \$1.38 billion (or an average of \$144 per ton).

Necessity for Continuous New Exploration

Only the very highest quality and most easily accessible kaolin (probably only the very most favorable 1 percent or less of all that is encountered by regional exploratory drilling) is good enough to be used for mining to make acceptable commercial products. Since the average weight recovery of dry finished product from inground wet tons of crude clay mined is probably only about 50 percent, it is necessary for the industry to explore for, discover, and evaluate at least 19 million crude tons of new high grade kaolin each year.

Proven Kaolin Reserves

Most mining companies require a minimum of 20 years of assured proven future ore reserves. This is needed in order to justify the high capital expense for increasingly costly upgrades of plant equipment for improving product brightness, whiteness, viscosity, and particle size, in response to declining reserves of good quality kaolin.

Intensive mining of the best and most accessible known kaolin each year for the past 100+ years has resulted in high grade clays becoming increasingly scarce. As a result, the Georgia kaolin industry has begun turning inevitably to the superior quality clays of the eastern Amazon region of northern Brazil (Pickering and Linkous, 1997).

However, the very large investment already made here in skilled and dedicated employees, new clay exploration, costly processing plants, sophisticated beneficiation equipment, and a well-developed infrastructure, will likely enable the kaolin industry to remain active in central and eastern Georgia for at least the next several decades.

KAOLIN STRATIGRAPHY

Use Of Stratigraphy in Exploration

The effort necessary to discover the immense tonnage of new kaolin essential to industry survival requires a detailed knowledge of stratigraphy of the area. Of the ten or more

KAOLIN STRATIGRAPHY

Coastal Plain units encountered in this mining district, only two are known to contain significant deposits of useful kaolin. These two stratigraphic units contain remarkably different types of commercial grade kaolins, which have quite different industrial applications.

Precise stratigraphic correlation throughout the area has been difficult, due to the following factors:

- The absence of traditional marine guide fossils in these deltaic facies clastic sediments (biostratigraphic correlation has been possible only by use of fossil pollen in fresh unoxidized gray clays and lignites);
- The deltaic sands and kaolin clay sequences occur in strongly cross-bedded fining-upward cycles with little lateral continuity, and are separated by a multitude of high relief erosion surfaces;
- The kaolin district lies on the margin between the Atlantic and Gulf Coastal Plain Provinces, so stratigraphic terms used here have often been a confusing mix of Gulf and Atlantic units applied far from their original type sections;
- Natural outcrops of these unconsolidated sediments are rare and the excellent exposures in open pit kaolin mines are rapidly destroyed by land reclamation, and
- Intense weathering and alteration has significantly improved commercial clay quality, but has also profoundly obscured the original appearance, mineralogy, crystallinity, and chemistry of the sediments.

However, each year much new information becomes available as the industry drills tens of thousands of new core holes and opens dozens of new open pit mines. Periodically new palynological identifications from the gray clays and lignites are made, and this biostratigraphic information is used along with lithostratigraphy to refine existing stratigraphic correlations. In the past, the Georgia Geological Survey has offered careful new descriptions of local Georgia Coastal Plain units.

Further, major regional unconformities are used to divide similar sedimentary units into distinctive mappable sequences. These profound former erosion surfaces reflect global periods of major sea level lowering and consequent beneficial sub-aerial weathering of the kaolins. Accurate recognition of these worldwide events aids in regional chronostratigraphic correlation (Haq, 1988). This new type of correlation by mapping of major regional unconformities, called allostratigraphy (Prowell, *et al*, 2000), is proving very helpful.

All these activities have resulted in much new information over the past few years. This enables more exact correlation of units in the district. The intent of this section is to

summarize available data and outline a regional stratigraphic framework, as an aid to future mineral exploration, clay research, and new detailed geological and structure contour mapping of the kaolin-containing units.

SUMMARY DESCRIPTION OF STRATIGRAPHIC UNITS

The following is a brief chart of the stratigraphic units exposed in the field trip area, listed in order of age (Table 1.1; see also figure 1.1). Units used, and their terminology, reflect the authors' experience and opinions, and may not be in full agreement with other investigators.

GROUP	FORMATION	MEMBER	AGE
"Hawthorne Group"	unnamed	----	Miocene & later
Barnwell or Jackson Group	Tobacco Road Sand	----	Late Eocene
	Irwinton Sand	Sandersville Limestone	Late Eocene
	Twiggs Clay	----	Late Eocene
	Clinchfield Sand	Albion Mbr in east Ga.	Late Eocene
Oconee Group	Huber Formation	Jeffersonville Mbr.	Early-Mid Eocene
		Marion Mbr.	Late Paleocene
	Buffalo Creek Fm.	not yet subdivided	Late Cretaceous
not named	Pio Nono Fm.	not yet subdivided	Late Cretaceous
Piedmont Crystalline Complex	various gneisses, mafic & ultramafic	schists, phyllites, granites rocks, etc.	Pre-Cambrian & Paleozoic

*major regional unconformities are indicated as **bold** separating lines.

Table 1.1. Stratigraphic units exposed in the field trip area.

Piedmont Crystalline Rock Complex:

This term is applied to the much older pre-Cambrian and early to mid-Paleozoic metamorphic and igneous "basement" rocks cropping out north of the Fall Line. The most common rock types are metamorphic gneisses, amphibolites, schists, and phyllites intruded by later igneous granites and mafics. Today they are usually deeply weathered and often overlain by a 5 to 50 meter layer of saprolite.

Similar or thicker Late Cretaceous and Early Tertiary saprolites were the source for the Coastal Plain sand and clay units which make up the commercial kaolin district today. However, at that time the crystalline rock source area probably resembled or was higher than today's Blue Ridge Mountains. The considerable bulk of weathered rock, which was eroded from these ancestral Blue Ridge Highlands, amounting to thousands of feet in thickness, now makes up the sediment volume of today's Coastal Plain and continental shelf.

STRATIGRAPHY OF THE GEORGIA KAOLIN DISTRICT

Section (thickness not proportional)	Age	Group	Formation	Member	Description of Stratigraphic Units, Including Their Role in Groundwater Oxidation-Recrystallization of Kaolins
	Late Eocene	Jackson or Barnwell Group	Twiggs Clay Formation	-	Smectite fullers earth, denies recharging oxidizing ground water access to kaolin beneath unless breached by erosion.
	Early-mid. Eocene	Barnwell Group	Clinchfield Sand Fm.	Treadwell & Riggins Mill	Fine grained sand with occasionally abundant marine vertebrate fossils (shark & other fish teeth & bones, etc.)
	Late Paleocene	Oconee Group	Huber Formation	Jeffersonville Member ☆	Fining upward aquifer sand sequences capped by hard only partially altered finer particle size higher iron kaolin lenses.
	Latest Cretaceous	Oconee Group	Buffalo Creek Formation ☆	Marion Member	Soft gray to black unoxidized kaolin and lignite lenses in clayey sands, few to no commercial quality kaolin deposits.
	Late Cretaceous	-	Pio Nono Formation	not yet sub-divided	Many fining upward aquifer sand sequences, capped by soft coarse kaolin lenses which are today the most heavily mined.
	Paleozoic and Pre-C	-	"basement"	-	Arkosic clayey sand with no kaolin lenses, contains no known commercial kaolin deposits. Coarse gravel at base. Metamorphic-igneous complex; weathered granites, gneisses, and phyllites (?) were sources for commercial kaolins.

☆ - STRATIGRAPHIC UNIT WHICH PRODUCES IMPORTANT TONNAGES OF COMMERCIAL GRADE KAOLINS.

fk - Finer particle size hard kaolin (both un-oxidized and oxidized).
 ck - Coarser particle size soft kaolin (both un-oxidized and oxidized).
 kl - Gray kaolins and lignites.

U - Major unconformity
 - - - U - Subtle unconformity

Figure 1.1. Stratigraphy of the Georgia Kaolin District

The much older crystalline Piedmont rocks are separated from the Coastal Plain sediments by a profound unconformity (the Fall Line unconformity, carefully mapped in the Wrens to Thomson area of the CSRA by Hurst, Crawford, & Sandy, 1966) and by Hetrick & Friddell (1990, 1992). Topographic relief on this buried erosion surface is probably at least as irregular as the present land surface in the Fall Line area. Where the Piedmont rocks are gneisses and phyllites, which do not weather to kaolinite-rich saprolites, the Pio Nono Formation (which lacks kaolin lenses) is typically the oldest Coastal Plain unit. By contrast, where the low iron Sparta Granite with its primary kaolin saprolite crops out along the Fall Line, the Buffalo Creek Formation, with its coarse kaolin lenses, seems to overlie directly on the Piedmont rocks.

Pio Nono Formation

This unit was recently proposed (Huddlestun and Hetrick, 1991) for the coarse red to brown to yellow arkosic sands, sandy clays, and gravels which in many places directly overlie Piedmont "basement" complex rocks along the Fall Line. It is named for typical exposures along Pio Nono Road in Macon.

Huddlestun and Hetrick placed the Pio Nono Formation in the Oconee Group of sediments. In the present authors' opinion, the heterogeneous Pio Nono is very different from the Oconee Group deltaic sands with their common quite pure kaolin lenses and clay-ball clastic gravels, and should not be included with them.

No commercial grade kaolin clay deposits are known in the Pio Nono Formation, and its presence accounts for the lack of kaolin mining along the south edge of the Fall Line in the western part of the district. Where the Pio Nono is missing, Piedmont complex rocks may be unconformably overlain by either the Oconee Group kaolin-bearing Buffalo Creek Formation or the Jeffersonville Member.

There is a subtle unconformity and a prominent change in lithology at the contact between the Pio Nono Formation and the base of the overlying Oconee Group. No recognizable fossils of any type have been found in the Pio Nono. It is presumed to be a basal Late Cretaceous equivalent.

Oconee Group

Although informally used for a number of years, the Oconee Group was proposed formally by Huddlestun (1981) and Schroder (1982) as a replacement for the invalid use of "Tuscaloosa Formation" in Georgia. The type locality of the Oconee Group is the area of intensive kaolin mining on both sides of the Oconee River in northeast Wilkinson and northwest Washington counties. Typical mining operations include Thiele Kaolin Company's Avant mine area near the river in Washington County, and Engelhard Kaolin Company's Gibraltar mine area adjacent to the Oconee flood plain in Wilkinson County.

KAOLIN STRATIGRAPHY

Earlier investigators used the Alabama term "Tuscaloosa Formation" (Cooke, 1943, Kesler, 1957, Herrick, 1961, and Herrick & Vorhis, 1963), "Cretaceous, undifferentiated" (Eargle, 1955) or "Lower Tertiary & Cretaceous Undifferentiated" (Geologic Map of Georgia, 1976) for the various sand units containing prominent lens-shaped kaolin deposits in central and eastern Georgia. Decades ago it became evident (Bowie & Fountain, 1963, Pickering, 1971, and Austin, 1973) that the Georgia kaolins are quite different in age from the earliest Late Cretaceous Tuscaloosa sands of Alabama, and that a new stratigraphic framework was needed in the Georgia kaolin district. Application of the new term Oconee Group and its subdivided formations and members has been the result.

The term Oconee Group is a considerable improvement in consistent lithostratigraphic terminology, as the unit is restricted only to fining-upward sand/clay sequences over the wide range of geologic time from Early Late Cretaceous to Middle Eocene. It does not include the so-called "flint kaolin" of the Albion Member in the eastern Georgia Wrens area, which is properly part of the younger Barnwell Group.

In the present authors' view, the Oconee Group includes only the several mostly sand units with multiply repeated cross-bedded and fining-upward cycles often capped by discontinuous quite pure hard and soft kaolin lenses. For this reason, we disagree with Huddlestun and Hetrick (1991), and do not include the quite different arkosic Pio Nono Formation because it lacks these important sedimentary features.

The Oconee Group ranges in thickness from an eroded feather-edge at or near the Fall Line to as much as 800 meters before it begins a change to marine facies in the downdip subsurface south of a line from Cochran to Dublin to Wrightsville and Louisville. Typical Oconee Group cross-beds vary from 5 to 25 meters thick, and range from rounded quartz gravel with large kaolin clasts at the base, through increasingly fine and more clay-rich quartz sand, frequently to an upper lens-shaped cap of kaolin clay.

Oconee Group kaolin lenses may be as small as a few square meters and less than half a meter thick, or as large as hundreds of hectares and up to 30 meters thick. However, the industry is generally unable to mine kaolin less than 1.5 meters thick. The commercial grade kaolin lenses may contain less than 5 to 25 percent non-clay "grit" minerals coarser than 325 mesh (45 μ m), which are mostly quartz, muscovite, and heavy minerals. As will be shown, differences between the kaolins enable division of the Oconee into several distinctive sub-units, as follows:

Buffalo Creek Formation: The older, basal part of the Oconee Group was first proposed and described as the Buffalo Creek Formation by Pickering and Hurst (1989) and Hurst and Pickering (1989). The type locality is the area of intensive kaolin mining along the western side of Buffalo Creek from Deepstep to just north of the town of Oconee in western Washington County. The Buffalo Creek Formation has not yet been sub-divided into any recognizable members or sub-units.

The Buffalo Creek Formation typically consists of cross-bedded fining-upward channel fill deposits of: quartz and kaolin cobble-pebble gravel, sand, silt, and kaolin clay. Although occasionally gray, pink, violet, or yellow, these sands and clays are generally cream to near-white in color. The Buffalo Creek Formation is underlain by brightly multicolored clayey arkosic sands of the Pio Nono Formation, or by Piedmont crystalline rocks. Characteristics that distinguish between Buffalo Creek Formation kaolins and those in the Huber Formation are summarized in Table 1.2.

TYPICAL KAOLIN PROPERTIES	SOFT KAOLIN, BUFFALO CK. FM. & MARION MBR.	HARD KAOLIN FROM JEFFERSONVILLE MBR., HUBER FM.
Clay fracture type	Smooth, conchoidal	Rough, hackly or earthy
Pisolite structures (may be bauxitic or smectitic)	Rare	Common
Marginal marine burrows & trace fossils	Absent or very rare	<i>Amphorichnus</i> , <i>Thalassinoides</i> , <i>Ophiomorpha</i> common
Depositional environment	Fluvial, deltaic (mostly fresh water delta top)	Delta front (mostly marginal marine or lagoonal)
Degree of weathering alteration	Generally intensely recrystallized	Less altered by weathering, more likely to be organic
Degrittied clay particle size	Coarser than 65% <2 microns	Finer than 80% <2 microns
Kaolinite particle packing and association	Coarser vermiform crystals and books in an interlocked matrix of thin kaolinite plates	Tight face-to-face packing of fine kaolinite platelets, little void volume
X-ray diffraction disorder/defect type	high Hinckley index, 2 phase mixtures, 10-60% low defect phase	Low Hinckley index, single phase high defect kaolinite
Degrittied clay chemistry	Fe low, increases with decreasing particle size; Ti 2-3%, increases with decreasing particle size, low alkalis, high Th, low boron.	Fe higher, same for all size fractions; Ti high 2-3%; decreases with decreasing particle size; alkalis high, low Th, high boron
Geologic age and stratigraphic occurrence	Usually Cretaceous, in Buffalo Creek Fm. May be in Marion Mbr. of the Huber Fm.	Typically in early to mid-Eocene Jeffersonville Mbr. of the Huber Fm.

Table 1.2. Typical properties of soft and hard kaolins.

KAOLIN STRATIGRAPHY

Huddlestun and Hetrick (1991) regarded the Buffalo Creek Formation as only the uppermost coarse soft Cretaceous kaolin zone beneath the Huber Formation. He considered the Oconee Group sands and clays beneath this upper soft kaolin zone to be an extension of the Galliard Formation of the west Georgia Coastal Plain. However, in our opinion this is invalid as the kaolins are discontinuous, lens-shaped bodies which are seldom persistent over a distance of as much as one kilometer. The clear intent of establishing the Buffalo Creek Formation was and is to include the entire sequence of repeated local fining upward sand and clay units from the top of the Pio Nono Formation to the base of the Huber Formation.

Tshudy and Patterson (1975) and Zavada (1989) have published extensive listings of distinctive Late Cretaceous pollen from the Buffalo Creek Formation from central Georgia kaolin mines and core drill holes. All pollen assemblages are dominated by terrestrial plant forms, with very minor or no brackish or marginal marine floral components (Christopher, 2000, personal communication).

In general, pollen found in association with the Buffalo Creek Formation commercial kaolins in Georgia indicates correlation with the Late Campanian Stage of the Upper Cretaceous, and is contemporary with South Carolina's pollen zone "B" and biochronologic zone CC 22 (Prowell and Christopher, personal communication, 2000). This is the local updip non-marine equivalent of the Gulf Coast marine Ripley Formation (near Ripley, Tippah County, Mississippi, Hilgard, 1860).

The soft coarse particle size kaolins of the Buffalo Creek are the mainstay raw material of the Georgia kaolin industry. They probably make up approximately 70 percent of all kaolins mined in Georgia today, and are selectively used for the bulk of No. 1 and No. 2 paper coating clay products, all delaminated and most paper filler products, and most sanitaryware, automobile catalytic-converter body, fiberglass, and dinnerware ceramic products. New reserves of well-oxidized, high quality, coarse kaolin, under reasonable overburden thickness, are eagerly sought by all the mining companies.

The top of the Buffalo Creek Formation is a profound regional unconformity, which represents a considerable period of early Paleocene erosion. However, the base of the Marion Member of the Huber Formation usually contains quartz pebbles and kaolin clasts and is seen cutting into the upper stratum of coarse-particle-size soft kaolin.

Huber Formation: Bowie and Fountain (1967) named the Huber Formation for slightly sandy and kaolinitic sediments which they recognized as significantly younger than the underlying sands and kaolins known to be of Late Cretaceous age. They were also the first to recognize that the upper part of the Huber Formation is the only known southeastern U.S. source for hard kaolins of very fine particle size.

The Huber Formation, like the underlying Buffalo Creek Formation, is a series of fining upward sand-clay sequences, which are cross-bedded and superposed over each other. Although it thickens downdip, its total thickness is considerably less than the Buffalo

Creek. As has been mentioned and listed in Table 1.2, the upper hard fine particle kaolins differ significantly from the typical coarser clays of the Buffalo Creek and the basal Huber. Overall, the sands of the Huber Formation tend to be somewhat finer than Buffalo Creek sands, and contain considerably more heavy minerals.

The Huber Formation is distinctive and can be recognized in mine exposures, at outcrop, and in the subsurface, from Andersonville in west-central Georgia to at least Hepzibah in eastern Georgia. Interestingly, on the basis of its kaolinitic lithology and palynology, it has also been recognized far updip, in a small fault-bounded basin lying across the Towaliga Fault near Warm Springs, Georgia (Christopher et. al. 1979, 1980; Reinhardt, 1984). This Coastal Plain outlier is some 29 miles north of the present Fall Line. Further, palynology studies by Darrell (1966) of numerous bauxite and kaolin filled limesinks in Cambrian rocks in Northwest Georgia show considerable lithologic and biostratigraphic similarity to the Huber Formation.

The Huber Formation is usually much less altered by oxidative weathering than the older Buffalo Creek, usually grayer, and, at its base, more lignitic than the Buffalo Creek. Newell, *et al* (1980) described rather abundant Late Paleocene to Middle Eocene pollen from numerous organic clays in the Huber Formation. In comparison with the palynology of the Buffalo Creek, the Huber shows a much more brackish and marginal marine aspect. There has been almost no kaolinite recrystallization in the Huber clays.

Huddleston (1991) recognized a consistent natural twofold division of the Huber Formation with a more organic and lignitic lower unit which he called the Marion Member, and an upper Jeffersonville Member characterized by the distinctive upper, hard, fine particle size kaolin. Although he described the type sections for these units in Twiggs County, the present writers have found this subdivision of the Huber to be recognizable eastward at least to the Wrens kaolin-mining district.

Marion Member

This unit consists of at least one fining-upward sequence beginning with the basal quartz pebble and kaolin clast conglomerate which rests on the top of the Buffalo Creek Cretaceous/Tertiary unconformity. This coarse high-energy zone fines-upward into clay zones which are often dark, pyritic, and rich in organics and lignite seams. Pollen from these dark organic clays correlates with nannofossil biochronozones NP 4 and NP 5 of the Danian and Thanetian Stages of the Paleocene (personal communication, Prowell and Christopher, 2000). This is correlative with the Gulf Coastal Plain Wilcox Group (Wilcox County, Alabama, Crider, 1906)

The interface between the Marion Member and overlying Jeffersonville Member is a subtle unconformity and not easily distinguished.

KAOLIN STRATIGRAPHY

Jeffersonville Member

Distinctive hard, fine particle size kaolins occur in Georgia only at the top of the Jeffersonville Member. They are commonly burrowed by intertidal and brackish water shrimp and other organisms which left only trace fossils (Schroder, 1982). Microscopic bioturbation textures throughout the hard Jeffersonville kaolins make it evident that the entire unit has been passed through the digestive tracts of multiple burrowing organisms. The geochemical environment of this digestive bioturbation must have made for interesting clay mineral diagenesis.

Pollen from the Jeffersonville Member in the Georgia kaolin district correlates with nanofossil biochronozone NP 14 of the Ypresian and Lutetian Stages of the Middle Eocene (Prowell & Christopher, personal communication, 2000). This is the equivalent of the Gulf Coastal Plain, Claiborne Group (at Claiborne Bluff, Alabama, Conrad, 1847).

Another interesting feature of well-oxidized Jeffersonville Member kaolins is that they show a pale apple-green color on a fresh fracture surface, particularly when examined in bright sunlight. This greenish color fades within a few minutes upon exposure to the atmosphere. This is probably caused by rapid oxidation of iron salts on the freshly broken clay surface.

The Jeffersonville Member fine particle size kaolins are not as highly valued for mining as the coarse Buffalo Creek kaolins. However, they do make up approximately 30 percent of all the Georgia kaolins mined, and are selectively used for calcine feed, providing gloss on coated paper, blending to improve high shear viscosity, and as a functional rubber reinforcing filler.

The top of the Jeffersonville Member and Huber Formation is a very prominent unconformity marking the erosion surface between the Middle and Late Eocene. It also marks the boundary between the brackish deltaic intertidal/marginal marine conditions of the Huber Formation and the distinctly marine aspect of the overlying Barnwell/Jackson Group. There are no commercial kaolins above this prominent unconformity, which is therefore a prime stratigraphic target for kaolin exploration.

Barnwell/Jackson Group

The Barnwell Group (Sloan, 1905) is an Atlantic Coastal Plain term for largely marine units which are recognized to be of Late Eocene age. The type area is near the town of Barnwell in Barnwell County, South Carolina. The correlative Jackson Group of the Gulf Coastal Plain (Murray and Withbert, 1950) was named for a type section near Jackson, Mississippi.

Considerable confusion has come from attempting to stretch stratigraphic terms from distant type localities. Local terms for Barnwell/Jackson sub-units recognizable in the field trip area are:

Clinchfield Sand Formation. The Clinchfield Sand was first recognized and applied to a type section in Houston County in central Georgia by Pickering (1970). This fine grained sand is recognizable above the Huber Formation throughout the kaolin district at least as far east as Deepstep, where it commonly contains shark and other fish teeth, small pectens and other mollusk shells.

We will see an interesting unit, which may be an eastern facies of the Clinchfield Sand at Stop 2 on Sunday in the overburden at Huber's Bracewell kaolin mine. Here a siliceous "flint kaolin" is well exposed in a fossiliferous sand at the same stratigraphic position as the normal Clinchfield Sand. This opal CT cemented kaolin and sand may pose a real challenge to those who try to reconstruct sedimentary environments. These types of sands and siliceous "flint clay" have been referred to the Glascock and Albion Members (Carver, 1980; Moskow, 1988).

Twiggs Clay Formation. The Twiggs Clay is a continuous thick stratum of marine fuller's earth, which is recognizable from Cordele in west-central Georgia to at least Hepzibah in eastern Georgia. Cooke and Shearer (1907) named the Twiggs Clay for exposures in Twiggs County, Georgia that had previously been equated with the South Carolina Congaree Clay. The Twiggs Clay is exposed as overburden in most mines in the kaolin district throughout this area.

As will be mentioned later, the Twiggs Clay has had a profound effect on the commercial quality of the underlying kaolin clay. Where the Twiggs is continuous and has not been breached through by erosion, it forms an impermeable hydrologic seal. This seal has prevented oxidizing surface waters from recharging the Oconee Group sand aquifers and bleaching the gray pyritic kaolins. Where gaps have been eroded in the overlying Twiggs Clay, the kaolins have been altered by ground water oxidation to cream, pink, purple or tan tints and residual acids from pyrite and organic matter have been flushed out. Such kaolins which have been naturally well-leached by oxidizing ground water are of much better commercial quality and are considerably easier to process to meet paper coating standards.

Interestingly, the Twiggs is frequently deeply weathered to a brownish red mottled residuum, which bears little resemblance to its normal blue-gray unweathered appearance. We will see this weathering change in the Twiggs at several of our field trip stops. The weathering begins as a color change from blue-gray to yellowish gray, and then becomes deeply oxidized and mottled.

There are a number of younger stratigraphic units recognizable above the Twiggs Clay, but they have little effect on the kaolin quality or mining and therefore will not be described here.

KAOLIN STRATIGRAPHY

ALLOSTRATIGRAPHY OF THE GEORGIA KAOLIN DISTRICT

Allostratigraphy, or subdivision of sedimentary units by their bounding regional unconformities, is a particularly useful concept for kaolin exploration on the Georgia Coastal Plain. First, only three major regional unconformities bound the entire commercial kaolin sequence. These unconformities can be structure-contour mapped to predict the range of elevations that would allow core drilling to intersect each kaolin unit under reasonable overburden. Second, each major unconformity represents a considerable gap in sediment deposition due to sea level decline and/or rising land surface, which marks the time interval when the kaolins were subject to maximum beneficial weathering alteration. And, third, recognition of these regional unconformities present welcome opportunities for reliable time correlations in these commonly unfossiliferous sediments.

The first regional unconformity of interest occurs at the base of the Pio Nono Formation or Buffalo Creek Formation where the Pio Nono is absent, and coincides, in the kaolin district, with the Fall Line. Naturally, no commercial kaolins of sedimentary origin can be discovered beneath this profound unconformity. Even where the Piedmont rocks have been deeply weathered to nearly featureless mottled saprolite, they are easily recognized by the presence of persistent quartz veins and subtle crystalline rock texture.

The second regional unconformity is at the base of the Marion Member of the Huber Formation. Although subtle, this unconformity usually defines the upper limit of soft, coarse, well-crystallized kaolin that makes up approximately 70 percent of the commercial grade clay mined in the district today. It is therefore a key surface to be located during the first phases of exploration.

The third regional unconformity is at the base of the Clinchfield Sand and Twiggs Clay of the Barnwell Group and truncates the Jeffersonville Member of the Huber Formation. This easily recognized unconformity separates kaolin-bearing terrestrial to marginal marine sediments from much more marine, often highly fossiliferous, non-commercial overburden. There is no chance of discovering commercial pigment-grade kaolins above this unconformable surface. Determining its elevation is therefore a primary goal of exploration in a new kaolin area.

SEQUENCE STRATIGRAPHY OF THE OCONEE GROUP

The scenario proposed in Chapter 3 for the origin of the kaolins of the Oconee Group relies on the alternation of episodes of marine transgression and highstand during which clastic sediments were deposited in a variety of marginal marine, deltaic and alluvial settings, with episodes of intense weathering during lowstands. Unconformity-bounded sequences of sediment (alloformations) deposited during highstands, were thoroughly leached and altered by pedogenesis during lowstands. In the process muds containing a heterogeneous suite of clay minerals resembling those currently being deposited by rivers flowing from the Piedmont were converted to almost monomineralic kaolinite mudstones.

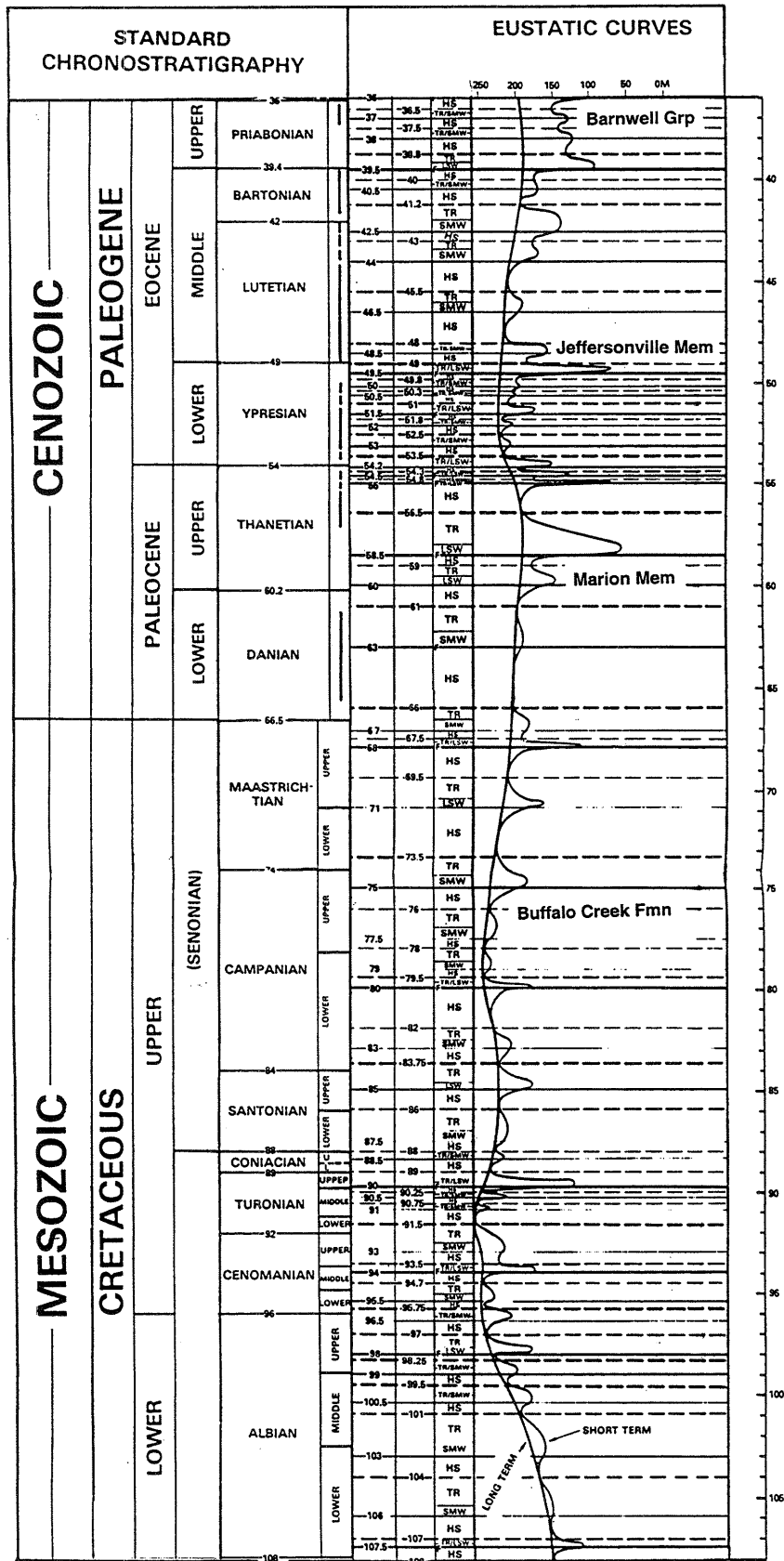


Figure 1.2. Eustatic Sea Level and Chronostratigraphy of Late Cretaceous-Eocene Epochs (from Haq et al 1988)

KAOLIN STRATIGRAPHY

Alloformations are deposited and preserved depending on the balance between the creation of accommodation space and the rate of sediment infilling. Accommodation space in turn is controlled by changes in eustatic sea level and basin subsidence (relative sea level). Typically alloformations consist of three parts or systems tracts, called the lowstand, transgressive and highstand systems tracts. At the base they are defined by an unconformity formed during lowstand. Above lies a thin transgressive systems tract formed during the period of most rapid relative sea level rise when the creation of accommodation space commonly outstrips the rate of sediment supply. During this interval water depths increase and the shoreline migrates landward but very little sediment accumulates. Subsequently, towards highstand, the rate of relative sea level rise slows and sedimentation begins to outpace accommodation space. As a result, water depths decrease and the shoreline progrades seawards, typically laying down thick sequences of shallow marine or deltaic sediment, which constitute the highstand systems tract. This entire package is then truncated by erosion during the ensuing lowstand. For more detail see papers by the Exxon group in Wilgus and others (1988) and Van Wagoner and others (1990).

The Oconee Group includes the most proximal sediments deposited at the northern limits of the Georgia Coastal Plain. It also coincides with some of the highest highstands identified by Exxon stratigraphers (Haq et al. 1988). Eustatic curves show sea levels around 250m above modern sea level during the Late Cretaceous and at least 200m above the modern during the Early Eocene (figure 1.2). These are the highest highstands of the Mesozoic and Cenozoic and coincide respectively with the age of the Buffalo Creek Formation and the Jeffersonville Member of the Huber Formation. During deposition of the Late Paleocene, Marion Member, highstands topped out about 175m above modern sea level. Such highstands created large amounts of accommodation space that was infilled by clastic sediments. Locally in Georgia, the Late Eocene was also a major highstand, but accompanied by marine smectite clays (Twiggs Clay) rather than fluvial to marginal marine kaolin.

Equally important, for the same time intervals, eustatic curves show major lowstands, during which sea level dropped by at least 100m. Especially impressive forced regressions occur in the late Turonian, late Maastrichtian, Late Paleocene (two), and at the Early-Middle Eocene boundary. Lowstands would have led to erosion and unconformities, but would also have exposed large areas of new coastal plain to weathering and leaching by groundwater; this during an interval of geologic time when greenhouse climates prevailed.

The combination of elevated sea levels interrupted by short but pronounced lowstands, with warm humid climate would seem to offer the ideal conditions for the formation of kaolin on a gently sloping coastal plain derived from the Piedmont.

CHAPTER 2 - KAOLIN MINERALOGY: KEY TO RESOURCE QUALITY, PROCESS RESPONSE, AND PRODUCT DEVELOPMENT

INTRODUCTION

Each year approximately 40 million tons of processed kaolin is sold into markets ranging from brick making to paper coating. This functional versatility is a direct consequence of natural variability in deposit quality, which is controlled by mineralogy, and the degree of processing. Poorer quality deposits containing relatively large quantities of impurity minerals are sold locally for use in cement, brick, lightweight aggregate, and refractories. Typically these clays are not processed or are only minimally processed. High purity kaolins are extensively processed for more technically demanding applications such as paper coating and filler. These high-grade kaolin products account for 33% of world kaolin production and represent 70% of the value (Harben and Virta, 2000).

Over the past 10 years the US, the UK and Brazil have been the major producers of high grade kaolin (figure 2.1). The US has been the dominant producer with an annual average production rate of 10 million short tons/year. The UK has consistently produced 2 to 3 million tons/year over this time period while Brazil's production has increased from approximately 1 to 2 million tons/year. Brazil's increase in production capacity reflects the construction of 2 new processing plants located in the Amazon basin along the Capim River where there are extensive deposits of coarse sedimentary kaolin that rival the quality of the Georgia deposits. Until recently Australia was also a significant producer of paper coating kaolin products but the processing facility there is currently shut down.

Most of the kaolin mined in the United States comes from a series of laterally discontinuous kaolin beds located in Georgia and South Carolina. The major mining district follows the Fall Line, which marks the boundary between pre-Cretaceous metamorphic and igneous rocks of the Piedmont Province to the northwest and younger Coastal Plain sediments to the southeast (figure 2.2). The commercial kaolins occur here as 2 to 15 m thick lenses and horizontal beds in sedimentary rock sequences representing deposition in prograding and retrograding fluvial, marginal marine and shelf environments including deltas, estuaries, and lagoons. The commercial quality deposits are restricted to Cretaceous, Paleocene and Eocene age strata.

TYPES OF COMMERCIAL KAOLIN

Two types of kaolin are mined in Georgia. These are commonly referred to as hard and soft kaolin. Each type has distinctive characteristics as previously described in Table 1.2. The soft kaolins are relatively coarse, have a soapy texture, and break easily with a conchoidal fracture. The hard kaolins are finer grained, have an earthy texture, and are more difficult to break. In general, the soft kaolins are found in Cretaceous and Paleocene age strata and are best described as mixtures of interlocking fine to coarse euhedral kaolinite platelets and larger kaolinite stacks or vermiforms. This clay type has undergone

KAOLIN MINERALOGY

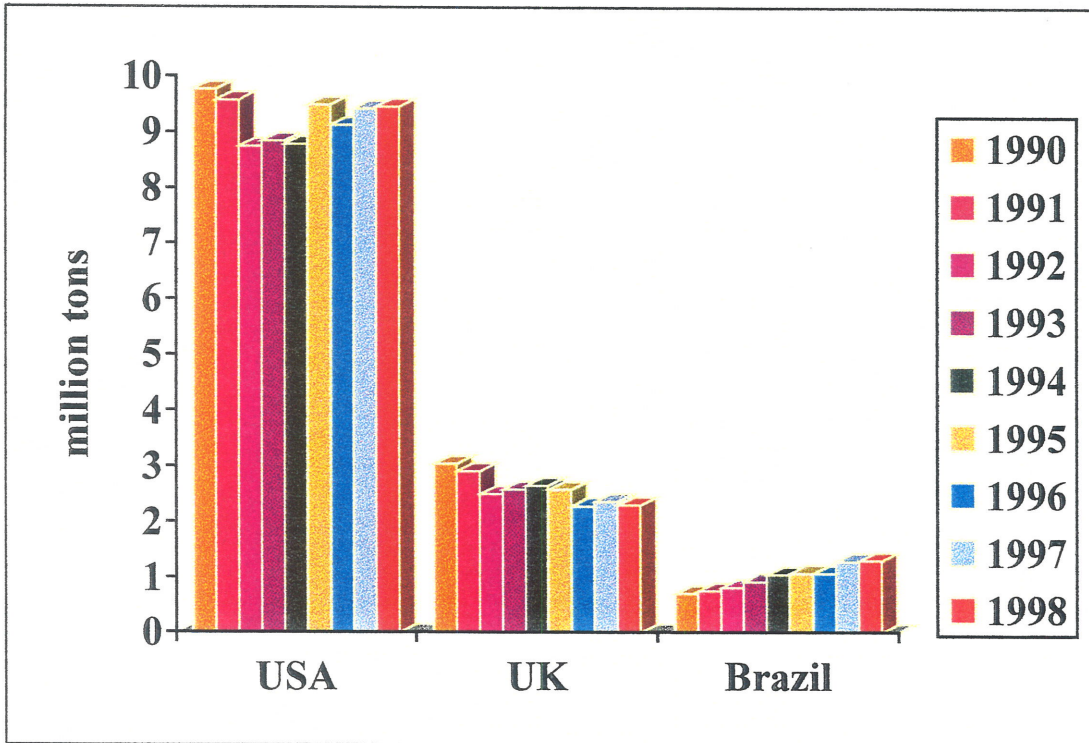


Figure 2.1. The U.S. dominates world production of processed kaolin products (data from Harben and Virta, 1999).

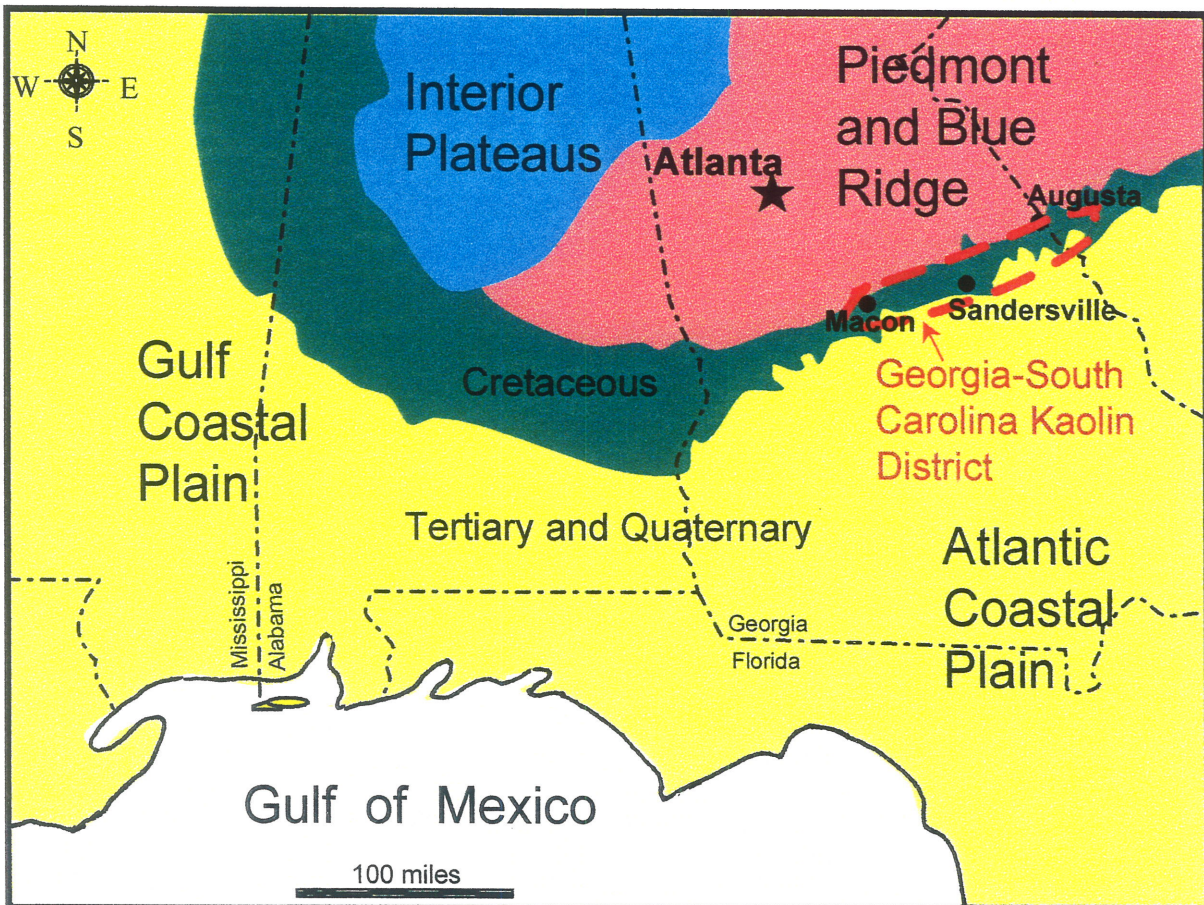


Figure 2.2: Location of Georgia-South Carolina Kaolin District as related to principal geological features in the southeastern United States.

KAOLIN MINERALOGY

extensive in-situ recrystallization leading to coarsening of individual kaolinite crystallites. Hard kaolins are restricted to Early to Middle Eocene age marginal marine-strata and formed as a result of flocculation in salt water which caused tightly packed face-to-face association between submicron sized clay platelets. Vermiforms are rare in the hard kaolins, which have undergone little recognizable in-situ recrystallization.

MINERALOGY

Mineralogy of the commercial grade kaolins may be described in terms of two general categories: 1) kaolin group minerals and 2) coexisting impurity minerals. Kaolin group minerals generally constitute 90 to 95% of the crude kaolin while impurity minerals account for the remaining 5 to 10%. Coexisting minerals may be further subdivided into two additional categories: 1) those that control rheology and 2) those that impact color and brightness. Describing the mineralogy of the kaolins in this manner is useful from the producer's point of view for two reasons. One is that mineralogy determines end use and the other is that mineralogy controls process response. The primary objective of processing is to remove coexisting minerals and concentrate kaolinite. For most applications either a pure kaolinite free of coexisting minerals is desirable (i.e. as in paper coating) or a product with controllable quantities of certain coexisting minerals such as smectite is desirable (i.e. as in certain high green-strength dinnerware ceramic applications).

Kaolin Group Minerals

Kaolinite is the major mineral constituent and is the principal kaolin group mineral present in these deposits. Two types of kaolinite are found in the Georgia deposits. Low defect kaolinite, also referred to as high Hinckley Index kaolinite, is typically found in the soft kaolins. This type of kaolinite is characterized by a low abundance of crystal structure defects. High defect kaolinite, also known as low Hinckley Index kaolinite, is most often associated with the hard kaolins. Kaolinites in this category contain a high abundance of structural defects. Trace quantities of nacrite and dickite are also present (Johnston et al., 2000), as is metaholloysite.

Low Defect Kaolinite. Low defect kaolinite is typically low in structural iron content (0.10 to 0.45 wt% Fe_2O_3), tends to be coarser in particle size, forms crystallites with a mean thickness of 30 nm and often occurs as large vermiforms and equant crystals (figure 2.3). This type of kaolinite has intense, well defined X-ray diffraction peaks in the 0,211 and 2,013 domains (figure 2.4) and typically exhibits elevated endo- and exothermic differential thermal analysis (DTA) peak temperatures compared to high defect kaolinite. Low defect kaolinite was formed by recrystallization of relatively iron-rich, high defect kaolinite. Because the kaolins have undergone differential weathering and consequently varying degrees of recrystallization, mixtures of high and low defect kaolinite are common especially in the soft kaolins. Kaolins that have undergone more intense oxidative weathering typically contain a higher percentage of low defect kaolinite and therefore have a higher Hinckley Index.

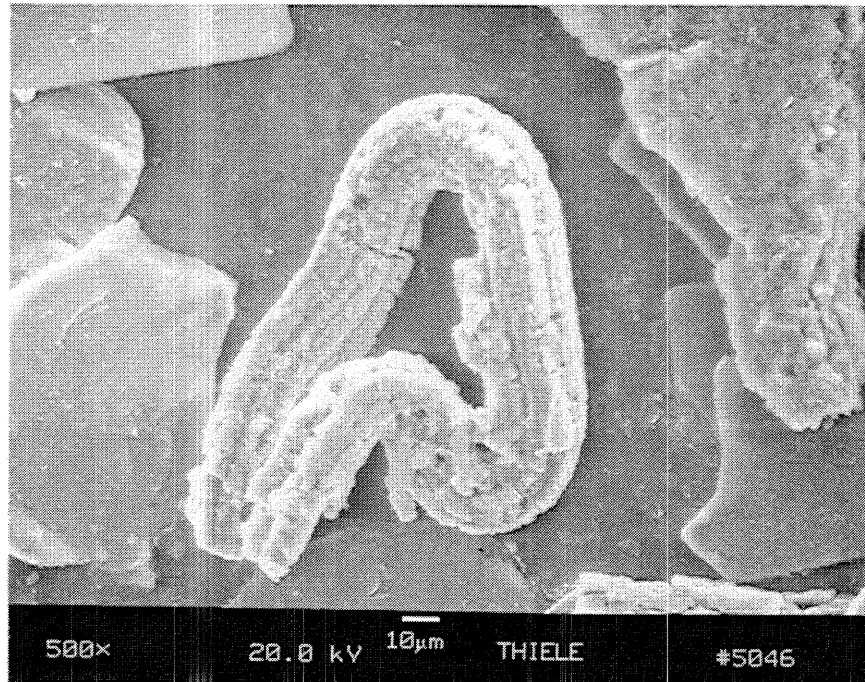


Figure 2.3. Scanning electron micrograph of vermiform kaolinite in soft kaolin

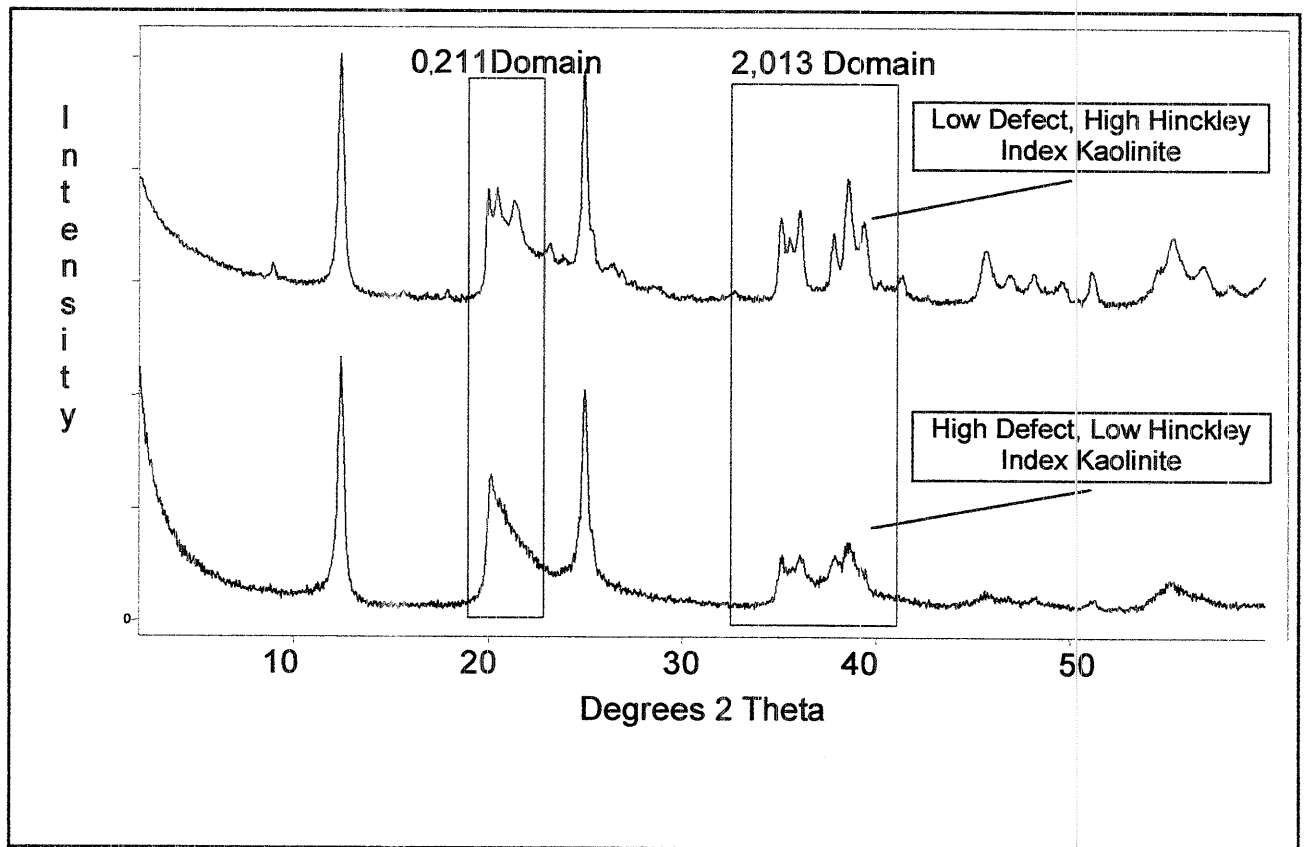


Figure 2.4. Typical X-ray diffraction patterns of low (top) and high (bottom) defect kaolinite

KAOLIN MINERALOGY

High Defect Kaolinite. This type of kaolinite is recognized by broad X-ray diffraction bands rather than well-resolved individual peaks in the 0,211 and 2,013 domains (figure 2.4). It occurs as fine single crystallites with mean thicknesses of 15-20 nm and is the principal component of the hard kaolins. Translation defects are the most common defect type and are probably related to the high structural iron content (0.70 to 1.00 wt% Fe₂O₃) that is characteristic of this type of kaolinite.

Metahalloysite. Metahalloysite is a common minor constituent of both the commercial and noncommercial grade kaolins. This mineral was inherited from erosional debris derived from the weathering of Piedmont source rocks. It is generally ubiquitous, occurs as tubes and is found in trace quantities in the commercial grade kaolins. Using transmission electron microscopy (TEM) it may be observed in one of several stages of recrystallization to kaolinite.

Nacrite and Dickite. Trace quantities of nacrite-like and dickite-like phases have recently been discovered in both the hard and soft kaolins using low temperature Fourier transform infrared (FTIR) spectroscopy. This technique detects these minerals but gives no information regarding whether they occur as discrete phases or stacking sequences within the kaolinite. In the case of the soft kaolins, these minerals are generally concentrated in the finest fraction. Conditions leading to the formation of nacrite and dickite are generally thought to involve hydrothermal temperatures and pressures (Brindley, 1980); however, the Georgia kaolins have not been subjected to such conditions. According to oxygen and hydrogen isotope analysis these kaolins crystallized over a temperature range of approximately 20 to 35° C (Hassanipak and Eslinger, 1985). Maximum confining pressure has probably never exceeded a sedimentary cover load of approximately 200 to 300 meters.

Coexisting Impurity Minerals That Degrade Rheology

Commercial grade Georgia kaolins contain trace quantities of several 2:1 phyllosilicate minerals including smectite, mica and illite. These minerals, along with particle size distribution and shape, control slurry rheology, which is critical, because many of the kaolin products sold for paper and ceramic applications are shipped and used as slurries.

Micas and Illite. Mica and illite are ubiquitous and occur in all size fractions of the kaolins. The coarse muscovite and the finer illite are predominantly dioctahedral 2M₁ polytype. Illite, which is probably a degradation product of coarser detrital muscovite, has a chemical composition between muscovite and vermiculite and contains 5 to 8% K₂O (Malcom 1994). The detrital muscovite is also commonly deficient in potassium which gives it unique physical properties compared to commercial micas derived from pegmatites (see Chapter 5). Typical percentages of mica and illite in the commercial kaolins range from 5 to 25%. Alteration of mica to coarse kaolinite is common and examples of various stages of this alteration sequence can be observed in the soft kaolins. Typically detrital mica first alters to kaolinite along the edges and cleavage planes, producing splayed crystals (figure 2.5).

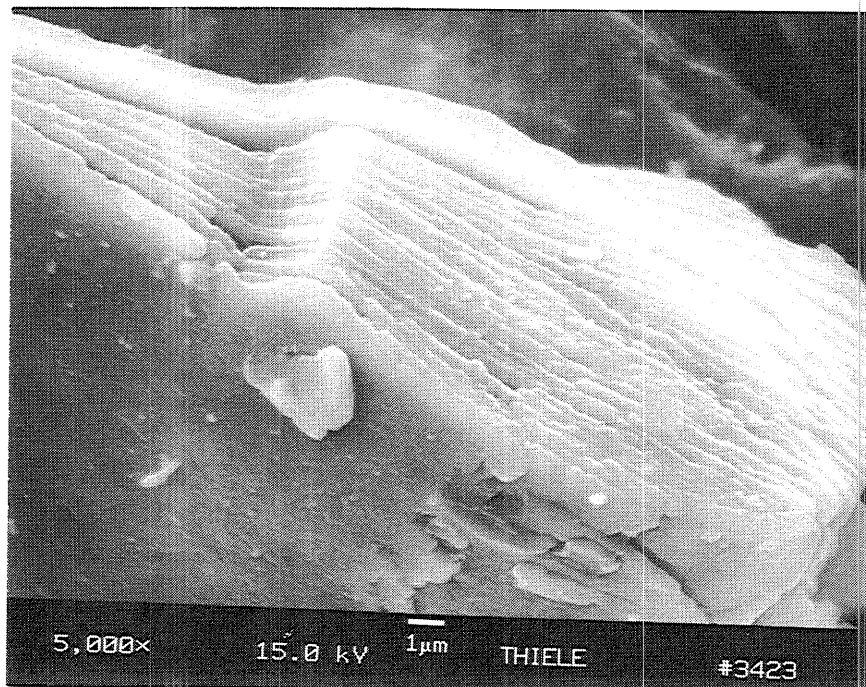


Figure 2.5. Scanning electron micrograph showing alteration of detrital muscovite to kaolinite

Smectite. Smectite is found in both the hard and soft commercial-grade kaolins in quantities ranging from trace to less than 5% for paper coating grade kaolins and closer to 20 or 30% in high green-strength ceramic kaolins. The smectite is best characterized as a 15 to 17Å montmorillonite with Ca and Mg as the principal exchangeable cations (Lowe et al. 1993). This montmorillonite has a high layer charge and is typically concentrated in the fine fraction of paper coating grade kaolins. In some cases it is attached to the (hkl) and (001) faces of kaolinite. It also occurs as discrete particles forming a matrix around kaolinite (Jones 1988).

Mixed Layered Clays. Mixed layered illite/smectite has been reported as a minor constituent in some Georgia soft kaolins (Lowe et al. 1993). There is some evidence that mixed layered kaolinite/smectite may be present.

Coexisting Impurity Minerals That Degrade Brightness and Color

Fe And Ti Oxide Minerals. There are a number of impurity oxide minerals in kaolin that discolor the clay and therefore must be removed during processing. The two major groups of minerals that function as pigments are Fe-contaminated anatase and iron oxide minerals. Iron oxide minerals account for approximately 2 to 30% of the total iron in Georgia kaolins. The anatase, which is discolored due to substituted Fe, comprises 1 to 2% of the soft kaolins and 1 to 3% of the hard kaolins.

KAOLIN MINERALOGY

Iron oxides most commonly associated with the Georgia kaolins are goethite and hematite (Angel and Vincent 1978). In addition, Malengreau et al. (1994) identified ferrihydrite from second derivative diffuse reflectance spectra collected on a well-ordered soft kaolin (KGa-1). Goethite is the most common iron oxide mineral in the commercial grade kaolins and is disseminated throughout the clay deposit. Hematite, by contrast, is usually less abundant. Compared to hematite, goethite is less easily removed by the standard reductive leaching process that is used in the kaolin industry so alternative methods of removal have been developed (Hall and Elzea, 1999).

Goethite commonly forms discontinuous coatings on anatase and kaolinite. Discrete colloidal goethite crystallites are also common and typically form single laths. These laths, which are usually less than 1 μm in length, may also form clusters or stellate intergrowths (figure 2.6). Hematite tends to be coarser than goethite and most often occurs as subhedral to anhedral pseudohexagonal crystallites that range in size from 0.05 to 0.2 microns in diameter. Both hematite and goethite contain trace quantities of transition state metals besides Fe including Ti and V. Trace quantities of Al, Si and P may also be present in these minerals.

Anatase, like goethite, is ubiquitous in the kaolins, and is generally submicron in size. Besides Fe, anatase contains trace quantities of Cr, Zr, and Nb (Pruett et al. 1996). Typical crystal morphology includes submicron euhedral pseudocubic crystals and coarser equant cube-shaped skeletal crystals. Crystallite size and shape suggest that this mineral is authigenic in origin and most likely altered from ilmenite or some other Ti-bearing precursor mineral such as biotite or even Fe contaminated rutile. Alteration presumably occurred during the oxidative weathering of the kaolinitic sediments. Rutile is less abundant and occurs as much larger detrital grains.

Iron Sulfide Minerals. Pyrite and marcasite are most prevalent in unoxidized kaolins. Pyrite exhibits a range of occurrences from very small, disseminated, typically octahedral crystals and framboids to large masses of cubic crystals. Both minerals line ancient burrows and replace ancient plant roots. Marcasite is found in the center of the pyrite-lined burrows. These iron sulfide minerals oxidize and re-precipitate as hematite and goethite. This oxidation is most notably visible as a change in color from gray (unoxidized) kaolin to pink and tan (oxidized) kaolin (figure 2.7).

Organic Matter. Organic matter is a minor component of the commercial grade kaolins; however, even trace quantities of organic matter may significantly impact color and brightness. Organics are one of the components responsible for the gray to gray-brown coloration that is characteristic of reduced kaolins. Commercial grade oxidized kaolins contain from 0.01 to 0.04% organic matter, and reduced kaolins contain from 0.06 to 0.08% organic matter. In general, the hard kaolins are more organic-rich than the soft kaolins, and further updip kaolins are typically much less organic than those in downdip locations.

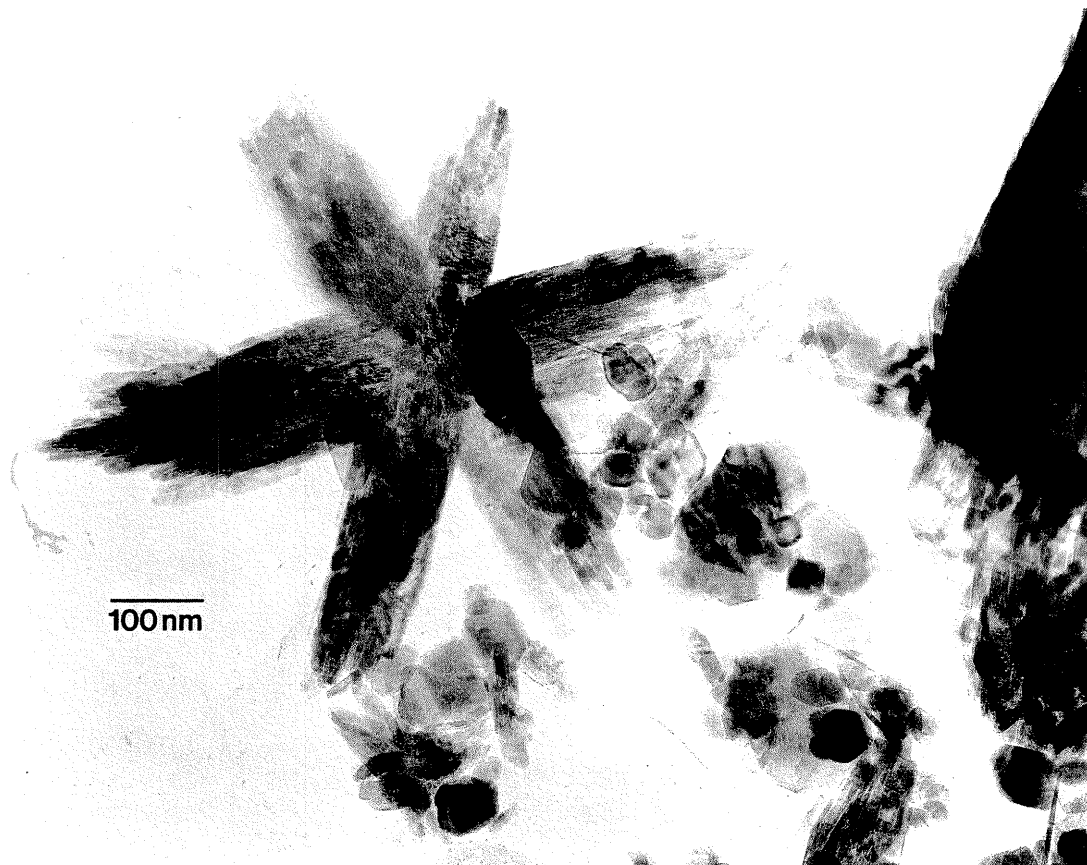


Figure 2.6. Transmission electron micrograph of stellaform goethite crystal.

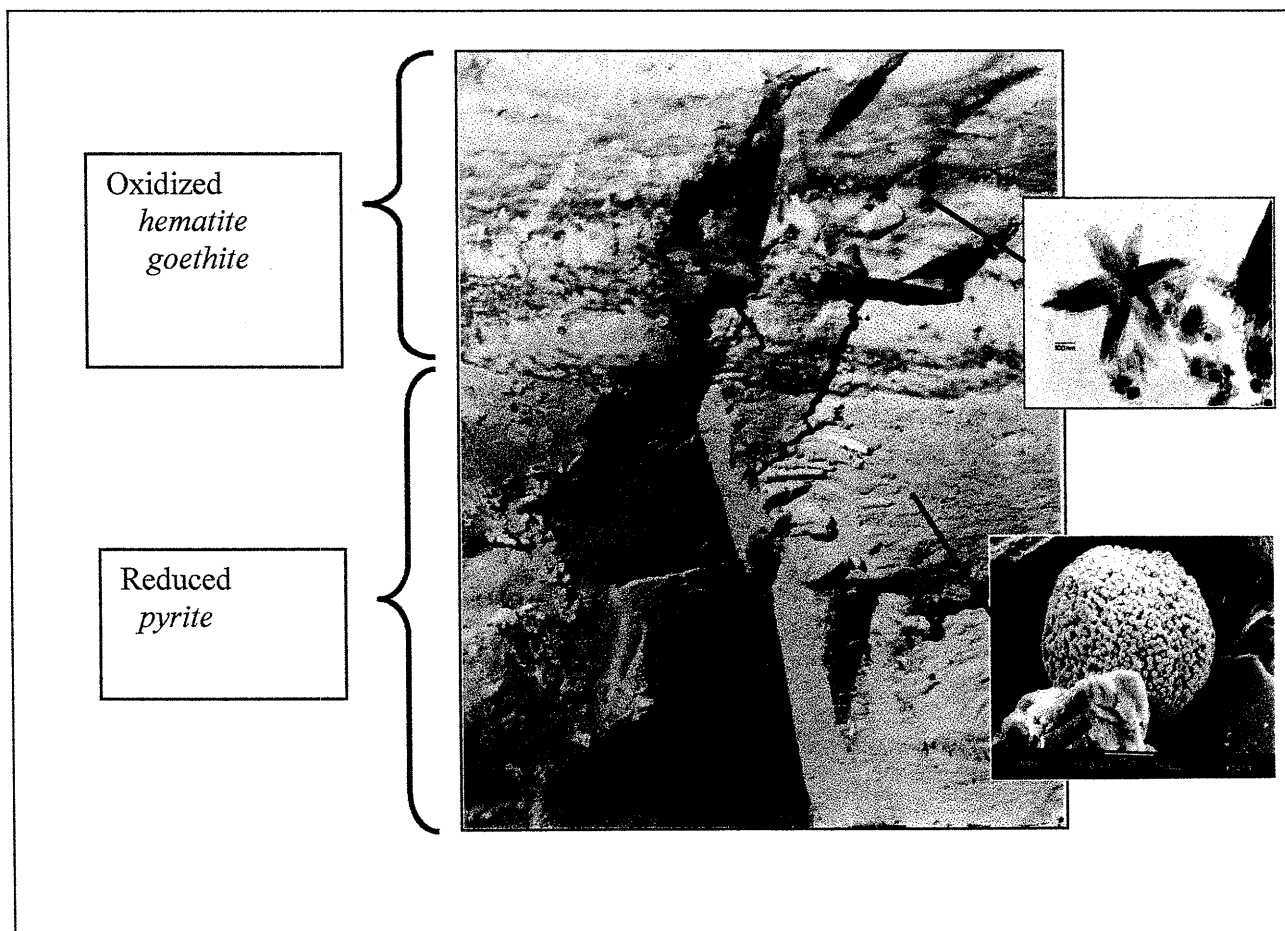


Figure 2.7. Example of a typical redox boundary between reduced gray kaolin and oxidized tan and pink kaolin. Outcrop height approximately 1m.

Other Accessory and Trace Minerals

Heavy Minerals. Sand size and finer heavy minerals present in the kaolins include ilmenite, leucoxene, rutile, tourmaline, zircon, epidote and kyanite. These minerals are inherited from the original feldspathic crystalline source rocks. They occur in trace quantities that are typically below XRD detection limits and are removed during the degritting stage of processing so are generally not of concern for the majority of commercial applications. Heavy mineral concentrations in degritting compounds may represent a future source of titania and zirconia.

Phosphate Minerals. A rare earth-bearing aluminum phosphate mineral has been identified in the hard kaolins. Compositionally this mineral is best described as a Ceflorencite containing Ba, Sr, Pb, La, and Nd. Electron and X-ray diffraction data are consistent with this identification. A crandallite-group mineral has also been identified in KGa-1 (Bish et. al., 1999).

Post-Depositional Mineral Reactions

A number of post-depositional mineralogical transformations have occurred in these deposits (Pickering, et al. 1997). These reactions, which cause observable changes in microtexture and mineralogy, are largely responsible for altering the original predominantly kaolinitic muds containing abundant associated minerals into almost pure white kaolinite. The mineralogy of the original sediment is unknown but was probably similar in composition to currently exposed Pleistocene clay deposits found in the present Coastal area. One such deposit contains abundant metahalloysite, organic matter, mica, quartz, pyrite, smectite and kaolinite along with trace quantities of various heavy minerals (Elzea et. al, 1997).

Examples of commonly observed post-depositional alteration reactions include the following: 1) dehydration of halloysite to metahalloysite, 2) oxidation of pyrite and replacement by goethite and hematite, 3) replacement of detrital mica by kaolinite (figure 2.5), and 4) coarsening of kaolinite. There are also a number of likely mineralogical transformations that we do not have direct evidence for. These include 1) the dissolution of Ti-bearing precursor minerals (i.e. ilmenite, biotite) and the subsequent precipitation of authigenic anatase (Schroeder and Shiflett, 2000), 2) weathering of feldspar to kaolinite, 3) weathering of biotite to smectite with vermiculite as an intermediate phase and 4) alteration of smectite to kaolinite.

Many of these reactions are driven by microbial action (see Chapter 4) and also occur in response to changes in the local geochemical environment as a result of fluctuating redox and pH conditions. For example, sharp boundaries between gray reduced kaolin containing abundant pyrite framboids and oxidized tan kaolin are sometimes exposed in newly opened mine faces (figure 2.7). This boundary marks an abrupt cm-scale change from reducing to oxidizing conditions. Besides color there are a number of other features that define this boundary. These include pH, particle size, mineralogy, and bulk chemistry.

KAOLIN MINERALOGY

Because alteration was not uniform, mineralogy and subsequently physical properties vary laterally and especially vertically within the deposits. This variability has led to diverse market applications for the commercial grade kaolins mined in the southeastern US.

COMMERCIAL APPLICATIONS

Different grades of kaolin are mined and processed for the following major applications: paper (filler and coating), ceramics (sanitaryware, dinnerware) and fiberglass. These are the highest volume consumers of kaolin mined in the SE US. Paper alone uses approximately 80% of the high grade kaolin sold each year while ceramics, largely sanitaryware, uses 6% and fiberglass uses 5%. There are also many lower volume applications, which account for the remaining 14% of kaolin sold. These include paint, rubber, adhesives, catalyst, pharmaceutical, brick and refractory uses. Each of these applications requires kaolin with specific properties, which are determined by the mineralogy of the raw material and processing. Product specifications vary depending on application and often by customer.

Paper Coating Grade Kaolin

Kaolin is applied to the surface of paper and board to improve smoothness, printability, opacity, gloss, and color. A typical paper coating formulation consists of water, pigment, binder and small quantities of other additives such as dispersants, lubricants and biocides. This mixture contains up to 65% solids. Pigments most commonly used for coating include kaolin, calcium carbonate, titanium dioxide (anatase and rutile) and calc. In the US, kaolin is the primary pigment in the coating system.

Paper coating grade kaolin must be relatively white and free of discoloring impurities such as Fe-oxides. Particle size, particle shape and particle size distribution must also fall within a desired range to achieve efficient light scattering and opacifying properties. Kaolinite between approximately 0.2 and 2 microns provides optimum light scattering. Low abrasivity, excellent dispersion characteristics, and low viscosity are additional requirements. Because the coating is applied to the paper surface at speeds of 1500 to 2000 meters/minute, rheological behavior under high shear (Hercules viscosity) is critical to the paper maker. If Hercules viscosity is too high the coating blade may drag across the surface and cause streaks, gaps and even rips. Brookfield, or low shear viscosity, is also important because it determines slurry behavior under low shear conditions such as those encountered during pumping and unloading from rail cars.

Paper coating grade kaolin products are divided into 3 basic categories: standard, delaminated and calcined (Table 2.1). The standard and delaminated products are referred to as hydrous or water washed kaolins because they are refined using wet processing to enhance brightness and color and modify particle size. Standard brightness products are subjected to high intensity magnetic separation and reductive leaching while high brightness products undergo further brightness enhancement using froth flotation and selective flocculation. Calcined kaolin is heated to temperatures ranging from 900 to

1100⁰C depending on the desired brightness of the final product. Heating causes the kaolinite particles to form aggregates, which give rise to higher void volume and consequently improved light scattering and opacity. A variety of coating grade products designed for specific applications are available to the papermaker. For example, if the papermaker desires a high gloss finish, a high brightness fine particle size product would be selected. For lightweight periodicals where fiber coverage must be accomplished with the least amount of coating possible, a delaminated product is most suitable. Low coat weights help offset the high cost of mailing.

Product	Particle Size (% <2 μm)	GE Brightness	Brookfield Viscosity (cP) (%solids/spindle/rpm)	Average Price/ ton
STANDARD				
Regular Brightness				
#1 fine	95	86.0-87.5	300 (70/1/20)	\$75-85
#1	90-94	86.5-88.8	300 (70/1/20)	\$75-85
#2	80-82	85.5-87.0	300 (70/1/20)	\$60-70
#3	73	85.0-86.5		
High Brightness				
#1 fine	95	90-92	600 (70/2/20)	\$130-140
#1	90-94	90-92	300 (70/1/20)	\$130-140
#2	80-82	88-90	300 (70/1/20)	\$115-125
DELAMINATED				
fine delaminated	95	87-89	400 (67.5/3/20)	} \$85-95
regular delaminated	80	88-90	400 (67.5/3/20)	
coarse delaminated		84-89	400 (67.5/3/20)	
CALCINED				
low brightness	86-92	80-83	500 (50/2/20)	} \$280-320
standard brightness	86-92	92.5 min	500 (50/2/20)	

Table 2.1: Standard Coating Grade Products for the Paper Industry

Paper Filler Grade Kaolin

Filler grade kaolin is generally coarser and not as bright as coating grade kaolin (Table 2.2). Most filler grade products are water washed while some are dry processed or air floated. Water washed filler products are derived from coarse kaolin generated from the processing of #1 and #2 coating kaolins. Discoloring impurity minerals are concentrated in the coarse fraction, leading to a lower brightness product. The air floated fillers are lower in brightness because they are not as extensively refined and therefore contain more impurities. In the past 15 to 20 years competition from precipitated calcium carbonate (PCC) has greatly reduced sales of paper filler kaolin products.

KAOLIN MINERALOGY

Product	Particle Size (% <2 μm)	GE Brightness	Average Price/ ton
AIR FLOATED			
standard	50-60	76-79	} \$35-75
premium	50-60	79-83	
fine standard brightness	82-95	81-83	
fine high brightness	82-95	84-86	
WATER WASHED			
standard	60-70	82-84	
premium	60-65	83-85	

Table 2.2: Filler Grade Product Specifications

Kaolin filler is added to the pulp to fill voids between the wood fibers thus improving the appearance and printing characteristics of the paper. Filler also serves to reduce cost by substituting relatively inexpensive kaolin (\$40 to \$60/ton) for significantly more expensive pulp (\$630/ton). Because the strength of the paper is compromised by the addition of filler, the upper limit for the amount of filler added to the paper is 20 to 30%. Critical properties for filler grade kaolin are brightness and particle size. Particle size is critical because kaolin that is too fine will not be retained in the sheet.

Ceramic Grade Kaolin

Kaolin mined in Georgia is sold for use in two main ceramic applications. One is sanitaryware and the other is dinnerware. Each application has relatively specific clay quality requirements dictated by the manufacturing process.

Sanitaryware, including toilets, wash basins and bathtubs, is made by pouring a clay slip comprised of approximately 30% kaolin, 25% Ball Clay, 25% silica and 20% feldspar into a plaster mold. Once in the mold, the slip dewateres by capillary action or by applying external pressure (pressure casting). The resultant filter cake is then allowed to dry before it is removed from the mold. Kaolin improves casting performance by controlling slip rheology and dewatering rate. Coarse kaolin free of smectite impurities is typically used for this application because it forms a porous filtercake that dewateres rapidly; however, fast casting kaolins tend to have poor green strength due to their low smectite content. This can be remedied by adding a plastic component to the composition, such as ball clay, or by selecting kaolin containing low levels of smectite. Although the primary function of kaolin is to enhance casting rate, it must also meet other specifications. It must be white when fired and consequently free of discolored impurity minerals such as iron oxide and titanium dioxide.

Dinnerware is produced using a process called jiggering. Clay is placed in a rotating mold and is then pressed into the mold with a profiled knife. Both jiggering and slip casting are useful techniques for quickly producing large numbers of identical pieces. Kaolins suitable for jiggering must have high green strength because they are subjected to high shear conditions. High green strength kaolins are those that contain moderate

amounts of smectite. Instead of measuring green strength, the dinnerware kaolin producer determines cation exchange capacity (CEC), which is a good indicator of smectite content and therefore green strength. These kaolins must also possess high-fired whiteness and translucence. Clays that meet these performance requirements typically contain low levels of iron oxide and anatase and therefore low Ti and Fe contents.

Specifications for typical ceramic grade kaolin products from Georgia are shown in Table 2.3. These products differ in terms of particle size, chemical composition and smectite content, which is reflected in the CEC.

Property	Velvacast [®]	HWF Kaolin	Pioneer [®]	6 Tile [™]
Particle Size (% < 2 μm)	38-40	20	55-65	54-65
325 mesh residue (% max)	0.15	0.50	0.75	1.0
color (fired cone 8, 50/50 clay/nepheline syenite)				
Brightness	65.5	71.2	58.5	60.8
Whiteness index	15.2	---	28.6	25.9
CEC (meq/100g)	1.0-1.5	2.0	4.5-5.5	8.5 min.
Fe ₂ O ₃	0.3	0.3	0.4	0.3
TiO ₂	1.4	0.5	1.4	1.4
K ₂ O	trace	0.5	0.1	---
Na ₂ O	0.1	0.1	0.04	0.04
MgO	0.2	0.1	0.1	0.5
CaO	0.1	0.1	0.2	0.4
Product Type	ww	ww	af	af
Application Best Suited for	sc	sc	c,p,e	p,j

ww = water washed, af = air float

sc = slip casting, c = casting, p = pressing, e = extrusion, j = jiggering

Table 2.3. Selected Properties of Typical Ceramic Grade Products from Georgia

Fiberglass Grade Kaolin

Kaolin is used in the manufacture of fiberglass as an inexpensive source of alumina. It is added to the glass composition to improve durability and strength. Ideally the glass manufacturer would use chemically pure aluminum oxide but kaolin is much less expensive; however, kaolin introduces chemical variability to the glass melt which must be carefully controlled. Consequently specifications for fiberglass grade kaolin are based primarily on chemical composition. For example, Fe and Ti are closely monitored to control overall chemistry of the glass melt and redox conditions in the furnace. Carbon content is also critical for redox conditions in the furnace. Carbon may also react with the platinum trays or "bushings" through which the glass is extruded to form fibers. Alkali content must be carefully monitored to control fluxing. Key quality parameters are wt% SiO₂, Al₂O₃, TiO₂, Fe₂O₃, CaO, MgO, Na₂O, K₂O and LOI.

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Kaolin for fiberglass must also meet certain particle size specifications. The kaolin must be free of coarse particles (> 325 mesh) because these particles may not completely dissolve in the glass melt and could potentially plug the platinum bushings. Consistent quality is key for fiberglass production. Typical specifications for fiberglass grade kaolin are shown in Table 2.4.

Property	Typical Fiberglass Grade Kaolin Product
SiO ₂	<45.0 ± 0.6 wt%
Al ₂ O ₃	>38.5 ± 0.5 wt%
Fe ₂ O ₃	<0.50 ± 0.05 wt%
TiO ₂	<1.4 ± 0.03 wt%
CaO	<0.2 ± 0.05 wt%
MgO	<0.3 ± 0.1 wt%
Na ₂ O	<0.03 ± 0.01 wt%
K ₂ O	<0.20 ± 0.1 wt%
LOI	>14.0 ± 0.5 %
Carbon	<0.015 ± 0.01 wt%
+ 60 mesh residue	0.025 % max
+ 200 mesh residue	0.150 % max
+ 325 mesh residue	1.500 % max

Table 2.4. Selected Properties of Typical Fiberglass Grade Kaolin Product from Georgia

RESERVE ANALYSIS

Whether a particular kaolin deposit is mined for paper, fiberglass, ceramics, or some other application depends on a number of factors including crude clay quality, processed clay quality, cost of processing, and available processing equipment. In most cases the decision to process a particular kaolin deposit for one end use as opposed to another depends primarily on raw material quality which is controlled by mineralogy and is determined by performing a series of tests on core samples.

Prospecting and Mining

Kaolin deposits are located by drilling in areas and at elevations where deposits are likely to occur at reasonable depth. A combination of approaches is used to select these areas including location of active mines, historical mining and drilling activity, geography and topography. Once a deposit has been discovered, quality and size of the deposit is determined by testing core samples drilled on a grid pattern. A minimum of 50 to 100 holes per 100 acres provides a reasonable indicator of the size and quality of the deposit. It is not uncommon to drill 200 feet below the surface at a cost of \$1,500 to \$2,000 per core. Closer spaced drilling, usually on 100 to 200 foot centers, is required for more detailed reserve analysis and is only undertaken when the wider spaced drilling proves that the quality and size of the deposit is sufficient to warrant mining.

Other considerations that must be taken into account prior to making the decision to mine include: 1) overburden stripping ratios (overburden thickness/ kaolin thickness), 2) distance to processing plant, 3) wetlands, 4) land lease or ownership status and 5) potential for groundwater problems.

After the decision to mine an area has been made, a detailed mine plan is developed and approved. The land is cleared and overburden removal begins. The overburden may be over 100 feet thick. Historically overburden has been thinner but most of the high quality kaolin with little overburden has already been mined. Consequently there is a trend towards mining deeper deposits in more downdip areas.

Once the kaolin surface is exposed the clay is excavated using draglines, backhoes or scrapers. The clay is often removed in benches and, because clay quality varies both vertically and horizontally, selective mining is used to separate different quality kaolins into stockpiles. Controlled blending of these stockpiled kaolins is used to achieve a desired raw material quality prior to processing.

Individual mine blocks or cuts typically range in size from 40 to 200 feet deep and 2 to 12 acres in area. The amount of commercial quality kaolin recovered from a single mine cut typically ranges from 50,000 to over 400,000 wet crude tons depending on the thickness of the ore body and the size of the cut. Most companies operate more than one mine, which increases their blending options, thus allowing optimized resource utilization, improved quality control and an expanded product line.

Laboratory Testing

Kaolin samples are tested in the laboratory to determine quality. Testing is completed on cores drilled for exploration and mine planning. Grab samples from the mine and stockpiles may also be tested. The extent of testing depends on whether the sample is an exploration sample or a daily mining sample. Many of the tests are standard industry analyses while others are proprietary and company or customer specific.

Typically the core is brought in from the field, trimmed, and laid out to dry. After drying the core is then divided into intervals and each interval is tested. The amount and type of testing varies from company to company and is determined, in part, by the products that each company makes. In other words, a company that processes kaolin only for paper coating products may limit testing to that specific end use whereas another company might test the kaolin to determine its suitability as a raw material for ceramics and fiberglass. Another company might be interested in all three end-use markets. Historically companies have focused on one or two of their main target markets, which usually means that testing is biased towards their particular current application(s).

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Evaluation of Kaolin for Paper Coating/Filler Applications. Kaolin used to fill and coat paper must meet certain minimum quality specifications in terms of the following properties:

- Particle Size (% finer than 2 microns)
- Brightness (% reflectance at 457 nm)
- Color (Hunter Values – L,a,b)
- Brookfield Viscosity (low shear)
- Hercules Viscosity (high shear)
- Residue Content (% coarser than 45 microns)

These properties are measured on the raw material and/or after wet processing using standard test procedures, many of which are published by the Technical Association of the Pulp and Paper Industry (TAPPI) as official test methods for the paper industry. Generally, paper-coating kaolins possess good flow properties, are relatively white and bright, and have minimum grit content. Filler grades are coarser, more viscous and not as bright as paper grade kaolins (Table 2.5).

Once it is determined that a kaolin is likely to meet paper coating or filler grade specifications, it is then processed in the lab to determine process response. This step is critical because process response cannot be accurately predicted from crude clay properties. This is because paper coating grade kaolins are extensively refined using a multistep wet process that substantially removes discolored impurity minerals and modifies particle size distribution. What may appear to be a highly discolored poor quality kaolin before processing often turns out to be a good quality coating grade kaolin after processing.

Although kaolin is not routinely evaluated for mineralogical composition as such, the properties listed above are controlled by mineralogy. Generally, the impurity minerals are the minerals that interfere with the performance of the kaolinite and therefore must be removed or somehow modified. Impurity minerals control deposit quality; however, the relationship between mineralogy and quality is not always as straightforward as we would like. This is largely because these impurity minerals occur in trace quantities and are consequently difficult to analyze on a routine basis.

Because kaolinite is the primary functional component of the product it is essential to understand its fundamental properties. For paper coating kaolin, the most important and most routinely analyzed properties are particle size distribution, particle shape, surface area, structural order, and bulk chemistry. For specialized products, such as calcined clays, properties such as surface chemistry and thermal behavior might be included in the mineralogical analysis. These routine measurements are commonly performed on degrittred or fractionated kaolin containing trace quantities of coexisting phases along with the kaolinite.

Particle size distribution is a key characteristic of kaolin that directly controls performance in paper coating systems. In fact standard coating products are defined by less than 2 micron particle size (Table 2.1). Although kaolin is naturally fine, processing is usually required to meet particle size specifications. Recently there has been a trend towards creating what are termed engineered pigments and these typically have a narrower particle size distribution than the natural clay. These products provide certain desirable properties to the paper maker and have evolved in response to the Brazilian products which naturally have a very narrow particle size distribution with few fines. Particle size of the raw material is important in deposit evaluation but because particle size distribution is easily manipulated using centrifugation, delamination or blending, it only defines quality in cases where particle size classification is not used in the process.

Evaluation of Kaolin for Ceramics. Kaolins used as raw material for ceramics are generally coarse kaolins containing relatively low levels of iron and titanium oxide. This grade of kaolin is tested for rheology, CEC, particle size distribution, chemistry and nitrogen BET surface area. These tests give an indication of how the kaolin will perform in various ceramic applications. Typically ceramic grade kaolins are dry processed although there are several products on the market that are wet processed. Kaolins for casting applications are coarse, have a relatively low BET surface area and low CEC. Because CEC is measured using a methylene blue test it is sometimes reported as the methylene blue index (MBI). Other tests that may be completed depending on the particular grade and application include fired brightness and color, green strength, fired strength and shrinkage.

Evaluation of Kaolin for Fiberglass Applications. The key quality parameter for fiberglass applications is chemistry determined by standard x-ray fluorescence. A secondary consideration is the percentage of coarser than 325-mesh residue. Process response is generally not a consideration for kaolin destined as a raw material for fiberglass. This is because all fiberglass kaolin is dry processed which means that coarse impurities (also called grit) are mostly removed using an air classifier. Because this airfloat process essentially removes only grit and does not alter clay particle size or brightness, it has a limited impact on final product quality, especially compared to the water washed process. Consequently, crude kaolin properties must be very close to final product quality. Fiberglass manufacturers may request additional testing including chemical oxygen demand, a measure of remnant organic matter.

Grading and Mapping

After the laboratory data have been collected, results are entered into a database and maps showing clay grade are generated. These maps illustrate how clay quality varies both horizontally and vertically within the deposit. Grade variations are related to sedimentation or weathering controlled mineralogy. Variations in quality related to deposition of the original kaolinitic sediment tend to be horizontal in nature. Particle size and distribution of detrital minerals such as mica and quartz are examples of original depositional features that control quality. Post-depositional weathering processes also impact quality and often without a predictable relationship to stratigraphy. Consequently,

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abrupt changes in clay quality may occur across relatively short lateral distances. Distribution of iron oxide minerals is an example of a weathering induced quality modification.

In order to mine the deposits efficiently and cost effectively, it is essential to have access to geostatistical mapping software capable of accurately predicting horizontal and vertical quality changes from drill core data that is spaced at lateral distances from 50 to 200 feet.

LINKING MINERALOGY TO END-USE

Mineralogy is the key to end-use. In general the more extensively altered soft kaolins are best suited for the demanding requirements of the paper coating market. These coarse, relatively pure kaolins typically have excellent rheological properties because they are free of smectite. They also possess superior brightness and color characteristics due to low levels of iron oxide contamination. These same kaolins are utilized for certain ceramic applications. Coarse particle size, optimum particle shape characteristics, high void volume and lack of smectite yield good slip casting properties while low iron and titanium content yield a white product after firing. White-firing coarse soft kaolins that contain sufficient smectite to improve green strength are sold as a raw material for dinnerware manufacture. Coarse and fine kaolins are also used as a raw material for fiberglass.

The fine hard kaolins are processed for paper coating as well as filler products. Coating grade products derived from these clays are known for their superior glossing properties due to their fine particle size. Filler grade kaolins tend to be those that have poor rheological properties due to small quantities of smectite and/or mica. Many of the calcined products use gray hard kaolin as a feed material. This type of clay produces a relatively low abrasion product with desirable color characteristics. The fine hard kaolins are also blended with coarse soft kaolins in order improve the viscosity of marginally poor rheology soft kaolins that otherwise would not meet rheology specifications for paper coating. The hard kaolins are generally not used for ceramics because they have poor casting performance due to slow dewatering characteristics as a result of their fine particle size and low void volume.

CHAPTER 3- ORIGIN OF THE GEORGIA-SOUTH CAROLINA COMMERCIAL KAOLINS

TERMINOLOGY

Many terms are used to describe the different types of kaolin found in the Georgia-South Carolina kaolin district (Table 3.1). Two of the most common terms are soft kaolin and hard kaolin. Others include oxidized kaolin (cream, pink, tan, or purple in color), reduced kaolin (various shades of gray color), micaceous kaolin, non-micaceous kaolin, sandy kaolin, and kaolinitic sands. Additionally, terms such as flint kaolin, bauxitic kaolin, and pisolitic kaolin have also been used frequently (e.g., Pickering and Hurst, 1989). A weathering residual type of kaolin or saprolitic kaolin has been explored recently.

Definitions for soft kaolin and hard kaolin have evolved over time. Attempts to substitute the term Cretaceous kaolin for soft kaolin and the term Tertiary kaolin for hard kaolin have not been very successful because occasional Tertiary kaolins have soft kaolin textures and unusual Cretaceous kaolins have somewhat hard textures (Pickering and Hurst, 1989). Austin (1998) also noted that the Tertiary kaolin clays in Georgia could be as coarse as 50% finer than two microns, which would be coarser than many of the typical Cretaceous kaolins.

The diverse types of kaolin from the Georgia-South Carolina kaolin district reflect the complexity of the environments under which these kaolins formed. Even though numerous studies have been devoted to understanding the genetic relationships of the different types of kaolin, there is still no universally accepted explanation for their origin. Controversy has centered around the following questions:

- What causes the differences between the two main types of kaolins in Georgia-South Carolina, i.e., soft versus hard kaolins?
- What is principally responsible for the formation of the commercial kaolin deposits: sedimentation or post-depositional alterations?

These questions essentially are about three key variables related to the formation of the kaolins: the source materials; the sedimentary environment under which the source materials were deposited; and the post-depositional processes that have changed the original sediments to commercial kaolin deposits (Pruett, 1993; Pruett and Yuan, 1998). In the following sections we will attempt to critically review the theories regarding these key systems and the evidence supporting different views.

SOURCE MATERIALS

It is generally agreed that the ultimate source for the commercial kaolin deposits and their host sediments are the igneous and metamorphic rocks of the Piedmont Province (Ladd, 1898; Veatch, 1908; Smith, 1929; Kesler, 1963; Grim and Wahl, 1968; Murray, 1976;

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Term	Description	References
Soft Kaolin	Originally used for white to cream color clays, though gray coarse clays are soft. They break easily into friable blocks having sharp angles and smooth flat or massive conchoidal fracture faces. Generally coarser than 65-70% <2 microns but can be finer.	Stull and Boles, 1926; Smith, 1929; Pattern and Murray, 1984; Pickering and Hurst, 1989
Hard Kaolin	White to light drab, cream or gray in color; breaks into irregular chunks with rough or hackly fracture. Burrow structures common. Generally finer than 80% <2microns.	Stull and Boles, 1926; Smith, 1929; Pattern and Murray, 1984; Pickering and Hurst, 1989
Semihard Kaolin	Intermediate between soft and hard kaolins.	Stull and Boles, 1926.
Cretaceous Kaolin	Kaolin in undifferentiated Cretaceous sedimentary strata.	Buie and Fountain, 1967; Buie et al., 1979
Tertiary Kaolin	Kaolin in early Tertiary sedimentary strata locally named the Huber Formation.	Buie and Fountain, 1967; Buie et al., 1979
Oxidized Kaolin	Cream, white, tan, pink, or purple colored kaolin. Iron is often in oxidized form such as oxides and hydroxides. Organic matter not abundant.	Pickering et al., 1997
Reduced Kaolin	Synonymous with gray clay. Color due to organic matter and disseminated or nodular pyrite and marcasite.	Pickering et al., 1997
Micaceous Kaolin	Kaolins with mica/illite content greater than 5%. Generally interbedded with commercial kaolin or sand. Breaks easily into irregular chunks.	
Sandy Kaolin	Generally refers to kaolins having more than 15-20% of 44 µm or larger size quartz particles. Gradation from very sandy to very pure kaolin with little quartz sand is common.	Buie et al., 1979
Flint Clay	Rock-like massive clay which is composed largely of kaolinite. Often white in color. Breaks with conchoidal or irregular fracture.	Stull and Boles, 1926
Pisolitic Kaolin	Kaolin clays showing the unique texture of concentric rims with a size up to 1 inch in diameter. May be gray or white. May or may not contain bauxitic mineral.	Buie et al., 1979; Horstmann, 1983
Saprolitic Kaolin	Weathered residual quartzose kaolins formed <i>in situ</i> and retain the original texture of granitic or gneissic rocks.	
Ball Clay	Plastic kaolinitic clay with minor to abundant organic matter. Produces ceramic-ware that generally fires white with high green strength and fired shrinkage. From old English practice of rolling clay into 25 cm balls.	Burst and Hughes, 1994
Fuller's Earth	Any fine-grained earthy material with bleaching and absorbent properties. Originally applied to material used to remove lanoline and dirt from wool.	Elzea and Murray, 1994

Table 3.1 Terms used to describe kaolins in the Georgia-South Carolina Mining District

Pickering and Hurst, 1989; Dombrowski, 1993; Pruett, 1993; Hurst and Pickering, 1997; Austin, 1972, 1998). Evidence supporting this conclusion includes:

- present-day elevation gradient from the Piedmont to the Coastal Plain,
- distribution of kaolins along a narrow belt adjacent to the Fall Line (Figure 2.1),
- wedge-shaped geometry of the kaolin-bearing Coastal Plain sediments which pinches out against the crystalline basement and thickens downdip,
- some kaolin beds rest directly upon deeply weathered Paleozoic crystalline rocks of the Piedmont Plateau,
- K-Ar age of muscovite associated with the kaolins in the Cretaceous and early Tertiary sediments averages 286 m.y., which is similar to that of mica from the crystalline rocks of the Piedmont (Hassanipak, 1980), and
- the apparent provenance of the minerals found in the Coastal Plain sediments (e.g., Dombrowski, 1993; Pruett, 1993, and Pruett *et al.* 1996).

According to Hurst and Pickering (1997), kaolin minerals have been the dominant component of detritus from this source area ever since Cretaceous time. River water borne detritus flowing seaward from the Appalachian Highland in South Carolina and Georgia today is as much as 80% kaolinite. Abundant kaolinitic materials provided the necessary detrital mineral supply for the formation of what are now massive commercial kaolin deposits.

Recent trace element data from Dombrowski (1993) suggests that soft and hard kaolins may have been derived from different source rocks on the Piedmont. Dombrowski concluded that granite and gneiss were the source rocks for the soft kaolin deposits while phyllites such as those from the Little River Group were responsible for the hard kaolins in East Georgia and South Carolina. Hard kaolins in Middle Georgia showed components from both the granite-gneiss source rocks and the phyllite source rocks. Dombrowski's conclusion differs from the conventional view that the differences between the two major types of kaolins are due to depositional environment and/or post-depositional changes.

Buie (1964) proposed the possibility of volcanic origin for the Georgia kaolins to account for the following characteristics: purity of the clay deposits, absence of body fossils, lack of bedding, presence of anatase crystallites, and presence of elongate bevel-edged particles which seemed to him to have the form of glass shards. However, isotopic evidence (Hassanipak, 1980) does not support this mode of origin. Many of the characteristics cited by Buie as evidence for a volcanic origin are much more easily explained by post-depositional alteration.

DEPOSITIONAL ENVIRONMENT

Most investigators agree that the hard Tertiary kaolins were initially deposited in a transitional to near shore marine environment similar to the present coast of Georgia and South Carolina (e.g., Hinckley, 1961; Kesler, 1963; Austin, 1972; Schroder, 1979; Patterson and Murray, 1984; Dombrowski, 1993; Hurst and Pickering, 1997). Much evidence supports this conclusion: lithological facies of the Tertiary sediments, geometry

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and lateral extent of kaolin deposits, fine particle size, good sorting, and face-to-face association of the hard kaolin platelets, abundance of pyrite, presence of opal-CT lepispheres, bioturbated zones, as well as the presence of marine trace and microfossils. Schroder (1979) identified nine trace fossil species from Huber Formation sediments and concluded that this assemblage could only have developed under brackish or shallow marine conditions. Horstmann (1983) classified the depositional environment of the kaolin deposits in the Huber Formation as intertidal salt marshes, citing evidence such as the heavy mineral assemblage, abundance of mica flake, marginal marine ichnofossils, nodular iron concretions, plant rootlet structures, massive character, and high boron content. Patterson and Murray (1984) stated that the lithology of the Huber Formation is typical of a tidal-flat environment of deposition. Hurst and Pickering (1997) proposed that the original sediments were mainly neritic and were deposited in a dysoxic environment ("Dysoxic" refers to molecular oxygen concentration too low to be toxic to anaerobes or cause abiotic oxidation; less extreme than "anoxic").

The soft Cretaceous kaolins are characterized by their high degree of purity, the scarcity of bedding or other sedimentary features, and the lack of trace fossil remains. These features make it difficult to determine their depositional origin. It is generally agreed that the typical sedimentary structures in these sediments were lost due to post-depositional alteration.

The majority of investigators believe that Cretaceous kaolins were non-marine in origin (Stull and Boles, 1926; Hinckley, 1961; Kesler, 1963; Austin, 1972; Dombrowski, 1993; Pickering, Hurst and Elzea, 1997). Stull and Boles (1926) pointed out the absence of "lime, gypsum, and manganese nodules" in Cretaceous sediments. Hinckley (1961) and Kesler (1963) cited fresh water origin to account for the random orientation of kaolinite crystals in soft kaolins and the absence of marine fossils. Pickering and Linkous (1997) drew the similarities between Brazilian Jari clay and Georgia hard kaolins and between Brazilian Capim clays and Georgia soft kaolins. They suggested that the Georgia soft kaolins might have formed in a similar environment as the Capim clay, i.e., in a fresh-water deltaic site. Cramer (1974) analyzed the subsurface facies pattern in Cretaceous Coastal Plain and concluded that the kaolin-bearing sediments were of the deltaic nature.

POST-DEPOSITIONAL ALTERATION

The location and timing of the kaolinization of the source materials is one of the most debated aspects regarding the origin of the Georgia and South Carolina kaolins.

The earliest theories assumed that kaolinite was formed primarily by *in situ* weathering alteration of feldspar and mica in granitic and gneissic rocks of the Piedmont Plateau and that the kaolinite was subsequently transported by river to the near shore environment for deposition (Ladd, 1898; Veatch, 1909; Smith, 1929). The purity of the kaolin deposits was attributed to sorting in the sedimentation process. This explanation was logical at the time, given the fact that the Piedmont crystalline rocks are deeply weathered and that the occurrence of kaolin bodies in sands and gradational sequence of the sediments would imply sorting by a sedimentation process.

Some later workers argued, however, that kaolinization took place primarily after detrital sediments were laid down (Kesler, 1963; Jonas, 1964; Grim and Wahl, 1968; Austin, 1972, 1998; and Murray, 1976). Three processes were thought to have significantly contributed to kaolinization, i.e., "winnowing", diagenesis and subaerial weathering. "Winnowing" was proposed by Kesler (1963) and supported by Grim and Wahl (1968). It stressed the rapid deposition of arkosic sands in a deltaic environment and their subsequent alteration to kaolinite, which would then be segregated and re-deposited as kaolin bodies.

Winnowing is not a true post-depositional process because it occurs prior to the final deposition. Post-depositional processes such as diagenesis and weathering were thought by some authors to be mainly responsible for the differences between soft kaolin and hard kaolin, that is, soft kaolin was considered to have undergone more severe alteration than hard kaolin (Jonas, 1964; Austin, 1972, 1998; and Hurst and Pickering, 1997). Geological aging of kaolinite was also considered along the same line. Hurst and Pickering (1997) insisted that compositional variations in the kaolins relate not so much to differences in source area and depositional environment as to location within the groundwater system and differing degrees of kaolinization and diagenesis. They listed twelve post-deposition alteration sequences that were evidently part of the process for the formation of commercial kaolins. These include bacteria-mediated stripping of Fe, destruction of organic matter, recrystallization of kaolin minerals and coarsening of kaolinite, *in situ* weathering of feldspar to kaolinite, alteration of Ti-bearing minerals to anatase, alteration of illite to kaolinite, diagenetic transformation of biogenic silica to opal-CT and quartz, and others. Evidence for post-depositional alteration also includes:

- where found beneath high Twiggs Clay smectite overburden or in downdip areas, soft and hard kaolins alike are usually quite gray and impure,
- presence of pisolitic or bauxitic kaolin or bauxite at the top of some commercial kaolin deposits,
- coarser particle size and better crystallinity in older age kaolins (i.e., Cretaceous) than younger age kaolins (i.e., Tertiary),
- many soft and hard kaolin deposits show upward transition from gray to pink to cream or from cream to purple kaolins. Mottling is heavy near the surface of some deposits,
- generally, kaolins closest to the fall line are most oxidized and the ones farthest downdip are gray, and
- textural features such as etched and corroded quartz grains, and oxidation of pyrite to iron oxide or hydroxide, support the idea that these deposits have undergone post-depositional leaching alteration.

Even though there is much evidence for post-depositional modification, kaolin deposits were not necessarily formed by these processes alone. For Tertiary hard kaolins, it seems convincing that much of the kaolinite formed prior to burial and post-depositional processes may have improved the purity of the kaolin bodies (Patterson and Murray, 1984). Evidence for this is strong including, for example, good sorting of sediments, good preservation of original sedimentary features, mineralogical composition of present-day

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marsh sediments which contain up to 80% kaolinite, occurrence of abundant gray kaolins, and well-preserved sedimentary sequence from sand, to micaceous kaolin, and to kaolin.

Smith (1929) and Murray (1976) suggested that Tertiary hard kaolins may have been reworked and re-deposited from older soft Cretaceous kaolins, based on the presence of rounded kaolin balls in the Tertiary sediments. However, these kaolin balls are most common in the sediments immediately above the Cretaceous-Tertiary boundary. Some of the hard kaolins may have originated from reworked soft kaolins, but the contribution would be limited, particularly for kaolin deposits of Eocene age. Major differences in X-ray diffraction patterns make it difficult to explain how soft kaolins were reworked and re-deposited as hard kaolins.

The effect of post-depositional processes on the kaolinization of Cretaceous kaolins is less clear. Austin (1972) after carefully analyzing kaolin and bauxite deposits along the Fall Line came to the conclusion that laterization was primarily responsible for the formation of Cretaceous kaolins. He reasoned that the Cretaceous kaolins resulted from a Paleocene or Early Eocene laterization of Cretaceous sediments and that the Tertiary kaolins resulted from erosion and redeposition of these sediments. In other words, he considered the Cretaceous kaolins to be residual and the Tertiary kaolins sedimentary. He further suggested that a significant portion of the commercial kaolins resulted from episodic desilicification and resilicification of bauxite as supported by the relatively common pisolitic texture in commercial kaolins.

Laterization is indeed capable of forming kaolin deposits such as the Australian Weipa kaolin and Brazilian Jari and Capim kaolins. However, how much laterization contributed to the formation of Georgia-South Carolina kaolins is debatable. Brazilian Rio Capim kaolin deposits show a remarkable upward fining sequence starting from kaolinitic sands at the bottom to coarse particle size kaolin in the middle to hard and finer particle size stained kaolin at the top. The question is whether sedimentation or weathering was responsible for the gradational lithology.

Although the geological ages of the eastern Amazon region Brazilian kaolins are largely unknown, one has much finer mean particle size than the other. Both Capim and Jari Brazilian kaolins seem to have consistently better shaped euhedral crystals and also fewer colloidal particles finer than 0.25 μm size than do the comparable Georgia kaolins. Both of these features are probably due to the considerably higher degree of lateritic alteration which the Brazilian kaolins have experienced during their moist and tropical climatic weathering history (Pickering, written comm., 2000). This more intense alteration has likely led to a higher degree of "Ostwald ripening" growth and recrystallization of the coarser Capim kaolinite crystals, and consequent chemical dissolution of the colloidal-size crystallites (Eberl *et al.*, 1990).

The most recent debate has focused on the idea that present kaolin deposits in Georgia were very far from commercial quality when they were first deposited. The original sediments were likely poorly crystallized dark organic and pyritic clays, perhaps similar to today's ball clays of west Tennessee and Kentucky. Subsequent alteration and

recrystallization by oxidizing acidic groundwaters were necessary to slowly remove impurities and develop the nearly monomineralic high quality kaolin required by the industry today.

SEQUENCE OF EVENTS RESULTING IN COMMERCIAL KAOLINS:

The following is a simplified summary of the significant events which are now thought to have occurred in the formation of commercially useful kaolins in the Georgia Coastal Plain district:

STAGE I (oxidizing conditions, pH about neutral)

Deeply weathered crystalline granitic rocks of the ancestral Blue Ridge mountains were the source for the clay minerals which became today's commercial kaolins. Weathering of the granitic source rocks led to development of a thick alteration saprolite. Weathering reactions involved the removal of Ca, Na, and K from feldspars and micas, and their replacement by hydroxide to form hydrous aluminum silicate kaolin group minerals (feldspars & micas⇒halloysite/illite⇒kaolinite/illite). This saprolite/soil formation process was assisted by aerobic bacterial action. Ferro-silicate minerals (biotite, etc.) altered to high iron smectites. The pervasive anatase found in well-oxidized pink and purple kaolins today may have begun from biotite alteration. Erosion of saprolite and transport by relatively high energy streams to major river systems allowed clay minerals to arrive as muddy water at broad deltas along the edge of the Late Cretaceous and Early Tertiary sea.

STAGE II (reducing conditions, pH about neutral)

Clay minerals arrived in a very low energy, low gradient swampy environments with lush plant growth. They were deposited by flocculation in ponds and lagoons on the delta along with abundant dead plant material (leaves, pollen, woody fragments). Clays (especially the hard Jeffersonville Member) may have been encouraged to flocculate by periodic incursion of semi-saline water during storm conditions. Lens-shaped organic mud/clay deposits were formed by the recurrent fining-upward process of clastic sedimentation. Rotting plant matter in the restricted sediment basins effectively removed available oxygen from river water, allowing crystallization of pyrite in the muds. Anaerobic bacterial action begins.

STAGE III: (oxidizing conditions, pH becoming acidic)

During several emergent sea level cycles after kaolin deposition, there were stages of intermittent sub-aerial lateritic weathering and erosion, development of unconformities on exposed surfaces of the clay lenses, and development of pervasive paleosol horizons. Kaolinite recrystallization began in the poorly crystalline kaolinite-illite muds. Intertidal burrowing bioturbation by shrimp, worms, etc. was intense both within and on the surface of the exposed unconformity at the top of Jeffersonville Member kaolins. This consumption of organic matter and the chemistry of their digestive tracts may have been

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important factors in kaolinite alteration. Aerobic bacterial action intensified due to exposure to oxidizing conditions. Lateritic leaching and removal of soluble Na, Ca, and K resulted in removal of nearly all remaining feldspar, and muscovite began undergoing alteration to kaolinite. Pyrite oxidation to hematite and goethite began, and reddish-purple anatase may have begun to crystallize from titania-rich remnant biotite.

STAGE IV: (reducing conditions, pH remaining acidic)

A rise in sea level and/or sinking land elevation in Late Eocene caused shoreline retreat with a major advance of sea over the formerly deltaic kaolin/sand sequence. Deposition of Clinchfield Sand and then Twiggs Clay fullers earth smectite (20 to 40 meters thick) occurred during this time. The presence of a continuous layer of relatively impervious smectite sealed off the top of the deltaic sequence from further ground water recharge, assuring a long period of reducing conditions and slow bacterial action which consumed some of the less refractory organic matter. Growth of authigenic (?) muscovite may have been actuated by regrowth on detrital mica fragments in carbonaceous and lignitic zones at the base of the clay lenses.

STAGE V: (oxidizing conditions, pH remaining acidic)

Neogene to Recent erosion breached through the continuous layer of Twiggs Clay smectite cover, allowing oxygenated slightly acidic ground water to enter the deltaic sequence via the sand units and to saturate the clay lenses. Wherever the overlying impermeable Twiggs Clay aquiclude was breached by erosion, removal of organic matter resumed by both chemical oxidation and bacterial action. Kaolinite recrystallization was re-initiated. Partial alteration of muscovite by ground water removal of potassium resulted in development of very coarse accordion-shaped vermicular kaolinite and hybrid kaolinite-rimmed muscovite crystals. Pyrite was converted by oxidation to hematite/goethite. Anatase may have crystallized from biotite remnants.

CHAPTER 4 – ROLE OF MICROORGANISMS IN DEVELOPMENT OF COMMERCIAL GRADE KAOLINS

“Without the multitude of living reactions as channels for energy and electrons and without the enormous capability of life to transfer with and against chemical gradients, there would be practically no or at least a very reduced geochemical rock cycle on this planet”. (Krumbein and Dyer, 1985, p.157)

MICROORGANISMS AS GEOLOGIC AGENTS

Definition of Different Types of Microorganisms

Microorganisms are small, individual organisms that are invisible to the unaided eye. This diverse group of organisms includes bacteria, fungi, algae, protozoa, and their symbiotic associations such as lichens. The microorganisms comprise two distinct groups: prokaryotic organisms, including bacteria, and eukaryotic organisms, including fungi, algae and protozoa. Prokaryotic bacteria are the oldest living organisms as evident from microfossils 3,500 million years old (Schopf, 1993). They are characterized by the lack of a nuclear membrane and by the absence of membrane-bound organelles. Eukaryotic microorganisms are more evolutionarily recent; their first occurrence in the geological record has been estimated at 900 to 2,500 millions of years ago (Hallbauer et al., 1977, Cloud, 1978, Margulis, 1981, Ehrlich, 1981, Sterflinger, 2000).

In order to grow and reproduce, microorganisms need inorganic or organic compounds that can be oxidized (AH₂, electron donors) to provide utilizable energy (ΔG). They also need inorganic or organic electron acceptors (B). They must also utilize inorganic and organic compounds for the formation of their cell structure. A general reaction can be written as:



Type of organism	Carbon source	Energy source
<u>Autotrophic</u> microorganisms: photolithotrophic cyanobacteria, algae and chemolithotrophic bacteria.	photolithotroph	CO ₂ electromagnetic energy (photons)
	chemolithotrophs	CO ₂ inorganic components (Fe ²⁺ , S ⁰ , NH ₄ ⁺)
<u>Heterotrophic</u> organisms: all the fungi and most of the bacteria	photoorganotrophs	organic compounds electromagnetic energy (photons)
	chemoorganotrophs	organic compounds organic compounds

Table 4.1. Classification of microorganisms according to their sources of energy and carbon

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Microorganisms are classified depending on the nature of their carbon and energy sources (electron donors) and on the type of electron acceptors utilized (Table 4.1 and 4.2).

Type of organism	Electron acceptor
aerobic	oxygen
anaerobic	inorganic electron acceptor other than oxygen (NO_3^- , SO_4^{2-} , CO_2 , Fe^{3+} , Mn^{4+} and many others)
fermentative	organic compounds

Table 4.2. Classification of microorganisms according to the nature of the electron acceptors

Role of Microorganisms in Geological Processes

Microorganisms are widespread in all natural environments except those at true volcanic temperatures. A wide range of microorganisms has been investigated with respect to their impact on geological processes, including alteration, solubilization, accumulation of minerals and the conversion of fossil organic matter (Kuznetsov et al., 1963; Karavaiko, 1978, Berthelin, 1988, Berthelin et al, 1999, Ehrlich, 1996a, 1999; Banfield and Nealson, 1997, McIntosh and Groat, 1997, Dorn, 1998, Sterflinger, 2000, Lovley, 2000). As outlined by H.L.Ehrlich (1996b), the reason microorganisms colonize rocks and dissolve or form minerals is that it favors their survival.

There are two interrelated mechanisms by which microorganisms may cause weathering alteration in rocks: biochemical and biomechanical. Biochemical weathering occurs when compounds created by microorganisms etch mineral surfaces or produce changes in the bulk chemical composition of the mineral. Biomechanical weathering involves the physical disintegration of minerals and rocks. Some microorganisms dissolve minerals to use them as a (1) source of energy, (2) terminal electron acceptor in respiration, or (3) trace element source (Ehrlich, 1996b). Other microorganisms may dissolve minerals producing inorganic acids, organic acids, reducing compounds and alkaline compounds.

For example, thionic bacteria dissolve pyrite, using the sulfide ion as an electron acceptor. Autotrophic bacteria (nitrifying and thionic) are also producers of inorganic acids (nitric and sulfuric respectively). Fungi, lichens and some heterotrophic bacteria are producers of organic acids and complex-forming compounds.

Microorganisms may also play a role in mineral formation. Microorganisms may form minerals authigenically (from dissolved species, one or more of which are generated by microbes) or diagenetically (resulting from transformation of one mineral into another). Microbial mineral formation may involve direct enzymatic intervention or metabolic production of specific chemical reactants that cause precipitation of minerals, or it may be a passive process, carried out by microbial metabolites (Ehrlich, 1999).

ROLE OF MICROORGANISMS IN DEVELOPMENT OF COMMERCIAL GRADE KAOLINS IN GEORGIA

Kaolin clays are most often formed by alteration of aluminum silicate minerals in a warm, humid environment. The most common source mineral for kaolinite is feldspar. The postdepositional weathering and diagenesis of kaolin has recently been shown to play a key role in upgrading its quality (Pickering and Hurst, 1989). When conditions were favorable for weathering, kaolin of good commercial quality was produced: dark organic matter was leached out, pyrite and iron silicate and carbonate minerals were altered to iron oxides, and soluble salts were rinsed away. The importance of microbial mediation in these weathering reactions is just beginning to be understood (Chapelle et al. 1988; Chapelle and Lovley 1990; Ehrlich 1996b, Hurst and Pickering 1997). Recent data on microbial-rock interactions and the discovery of numerous microbial fossils in subsurface environments (Barker and Hurst, 1992, 1993, Pedersen et al, 1997, McKinley et al., 2000) may provide insight into the role of microorganisms in the development of commercial grade kaolin.

Weathering Of the Piedmont Granitic Rocks

Weathering of the granitic rocks of the Piedmont generated large volumes of kaolinitic clays, quartz sand and mica, as well as minor amounts of other minerals, especially iron and titanium oxides. Feldspar, a major component of granitic rocks, is considered to be the parent material for most of Georgia's sedimentary kaolins. Removal of Ca, Na and K from feldspars and replacement by hydroxide led to formation of kaolin group minerals. Microbes played an important role in this process.

Microbial biofilms commonly coat granitic rock surfaces and are important agents of weathering (Dorn, 1998). Phototrophic organisms (such as cyanobacteria algae) and autotrophic bacteria (thiobacilli nitrifying bacteria) are usually the first microorganisms colonizing fresh rocks. Once organic matter is accumulated by phototrophic and autotrophic microorganisms, lichens establish and heterotrophic fungi and bacteria develop.

Lichens are common weathering agents on the rock surface. Lichens are symbiotic organisms, composed of a photosynthetic component (algae or cyanobacteria) and a fungal component. In such symbiotic organisms the photosynthetic host is shielded from excessive sunlight, desiccation, and mechanical injury, and receives water and inorganic substances via its fungal associate. In return, the fungus receives organic nutrients from the photosynthetic organism. The lichens that coat and invade rock surfaces weather minerals through a variety of processes including their secretion of oxalic, citric and other organic acids and also mechanical action. The lichens *Rhizocarpon geographicum*, *Xanthoparmelia conspersa* and some species of *Umbilicaria* show a special affinity for granitic and siliceous rocks (Brodo, 1973). *Xanthoparmelia conspersa* was particularly effective in reacting with biotite-rich granite substrates (Schatz, 1963).

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According to the model proposed by Barker and Banfield (1998), 4 zones of biogeochemical weathering may be found at the interfaces between rock and lithobiotic communities (including lichens and bacteria): (1) the photosynthetic zone is represented by the upper thallus of lichens and is devoid of mineral transformations; (2) the direct biochemilithic zone is localized in the lower thallus and characterized by physical disaggregation of minerals to a depth of 10 mm and by association of all mineral surfaces with microorganisms, extracellular polymers and weathering products – Fe-rich clays and Fe oxyhydroxides; (3) the indirect biochemilithic zone occurs within the intact substratum beneath the lichen community and shows slowly progressing biochemical weathering reactions (with feldspars almost unweathered and biotite altered to vermiculite); and (4) the physiochemilithic zone includes minerals subjected to predominantly inorganic reactions. Based on laboratory and field studies Barker and Banfield (1998) suggest that geomicrobiological weathering rates are several orders of magnitude faster compared to inorganic weathering rates.

Lee and Parson (1999) observed the following sequence of weathering processes within lichen-encrusted granitic rock: (1) biochemical and/or mechanical weathering of bare rock surfaces leading to widening intergranular and intragranular pores; (2) colonization of lichen and beginning of penetration of the fungal hyphae into the interior of the rock (with the rate of penetration at the studied locality of more than 0.002 mm/ year); (3) biomechanical weathering of minerals by penetration of fungal hyphae into intragranular pores along cleavage and fracture planes increases the surface area/volume ratio of the grains; and (4) biochemical weathering of fragmented mineral grains leads to leaching of biotite, etching of feldspar and deposition of a silica-rich clay substance.

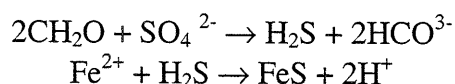
Ueshima and Tazaki (1998) observed accelerated bioweathering of K-feldspar and biotite by iron-oxidizing bacteria (*Toxothrix* sp. and *Galionella* sp.) in thin sections of granite in fresh water. Microbial mats were formed on the surface of the thin section after 3 and 10 days. After 2 months kaolinite crystals were formed on the surface of feldspar. The release of K and Si into solution was documented. Field (Nesbitt and Markovics, 1997) and laboratory (Nesbitt and Young, 1984, Muir and Nesbitt, 1997) studies showed that the major biochemical effect on feldspar weathering was release of H⁺-ions (organic and inorganic acids) that in turn promoted feldspar decomposition. As discussed by Muir and Nesbitt (1997), H⁺ penetrated the feldspar surface, destabilizing Na-, Ca-, and Al-oxygen bonds, and temporarily substituting for these elements in the feldspar structure.

Transportation and Deposition of Weathered Clays

Washed into a major river system, the weathered clays of the Piedmont were transported to a very low energy, low gradient environment with lush plant growth and deposited by flocculation in ponds and lagoons along a deltaic shoreline, with abundant dead plant material (leaves and woody fragments). At the time of deposition at least the southern half of Georgia was covered by an ocean and the seacoast stretched across Georgia well north of the present Fall Line.

Geochemical transformation of minerals continued in pond and lagoon sediments. During microbial decomposition of leaves and woody fragments a complex mixture of organic materials formed: sugars from pectins, gums and mucilages; amino acids from proteins; fatty acids from lipids; and phenolic acids from lignins and tannins. At the same time humic acids were synthesized from the interaction of phenolic acids with microbial proteins (Kononova, 1965). Sugars and amino acids were metabolized to fermentation acids and hydrogen. Due to consumption of oxygen by aerobic heterotrophic microorganisms, conditions at the bottom of sediments became favorable for anaerobic bacteria. Successive zones of fermentation, denitrification, iron-reduction, sulfate-reduction and methane production developed. Microbial iron reduction may have resulted in the formation of magnetite (Lovley et al, 1987) or siderite (Coleman et al., 1993) and pyrite formed in the zone of microbial sulfate-reduction.

Iron sulfide is considered the most common metal sulfide deposit attributed to biogenic activity (Southam, 2000). The following reactions, mediated by dissimilatory sulfate-reducing bacteria, may have taken place:



The immobilization of FeS on the surface of sulfate-reducing bacteria is promoted by a combination of the ionic interaction of Fe^{2+} with the anionic cell surface polymers and with biogenic H_2S (Fortin et al, 1994). After initial FeS immobilization, mineral transformations continue resulting in the formation of pyrite. Compared to the purely abiotic process, the bacterially mediated transformation of FeS into FeS_2 has been shown to be a more efficient process (Donald and Southam, 1999).

Biologically mediated formation of (Fe, Al)-silicates may have also taken place. Bacterial populations in different freshwater environments form clay-like material of variable composition and structure (Ferris et al., 1987, Konhauser et al., 1993, 1998, Tazaki, 1997). Laboratory studies demonstrate that biogenic (Fe, Al) silicates develop through the following sequence of events: (1) adsorption of cationic iron to anionic cellular surfaces, (2) precipitation of ferric hydroxide phase on the cell surface, (3) reaction with dissolved silica and aluminum and (4) growth of an amorphous clay-like phase (Ferris, 1997, Konhauser and Urrutia, 1999).

Exposure to Air

Sometime after deposition the sediments were uplifted and subaerally exposed to weathering and erosion which led to development of unconformities on the surface of clay lenses. Kaolinite recrystallization from poorly crystalline kaolinitic source clays probably began during this stage. Microbial weathering intensified due to exposure to air and led to leaching and removal of soluble Na, Ca, and K, and to destruction of almost all

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remaining feldspar. Pyrite oxidation with formation of hematite/goethite also took place during this stage.

Burial of Clay Lenses

Changes in sea level interrupted the sequence of transformation and deposition of kaolin from the Piedmont. Deposition of a continuous layer of relatively impervious smectite began and sealed off the top of the deltaic sequence from ground water recharge, starting a long period of deep burial of the kaolin lenses and slow microbial action. The term "subsurface" is used for strata effectively isolated from the surface for time scales of many years and designates environments that can be considered extreme. As conditions became more and more unfavorable, the diversity of microbial types diminished.

Until recently deeply buried subsurface sediments were considered to be devoid of life. But now it is apparent that the subsurface harbors an impressive diversity of microorganisms (Balkwill et al., 1989, Fredrickson et al., 1991, 1996, Ghiorse, 1997). A variety of aerobic, fermentative, acetogenic, sulfidogenic, iron-reducing and methanogenic bacteria have been reported from these investigations. A number of remarkable examples of long-term microbial survival in subsurface systems are known. Fredrickson et al. (1995) identified sulfate- and Fe(III)-reducing bacteria from Miocene-aged fluvial, lacustrine and paleosol subsurface sediments ranging in depth from 173 to 197 m at a site in south-central Washington state. The concentration of soluble electron acceptors for microbial respiration was low, while total biomass and organic carbon were highest. The authors suggested that the low hydraulic conductivity of these sediments probably contributed to the long-term maintenance of both bacteria and organic carbon by limiting the supply of soluble electron acceptors for microbial respiration. The results suggest that the current subsurface microbial population was derived from organisms that were present during lake sedimentation approximate to 6-8 million years ago.

Krumholz et al (1997) conducted assays for sulfate reduction in rocks obtained from Cretaceous shales and sandstones at depths of up to 250 m. The rocks had apparently been isolated from contact with the surface for at least 10,000 years based on groundwater ages. Microbial activity was readily detected in crushed material incubated in slurries and in relatively undisturbed freshly exposed rock faces. Krumholz et al (1997) also documented stimulation of sulfate reduction in sandstones by organic matter contained in added shales. In this analysis, the response of sulfate-reducing bacteria was relatively rapid, and indicated the active state of microbial cells.

Resumption of Contact with Groundwater

Erosion breached the continuous layer of Twiggs Clay smectite cover during Late Pliocene and Pleistocene and groundwater entered the deltaic sequence via the sand units and contacted the kaolin lenses. The contact with oxygenated, slightly acidic groundwater led to the accelerated removal of organic matter and transformation of iron minerals.

Kaolinite recrystallization was re-initiated at this stage. Partial alteration of muscovite by ground water resulted in very coarse accordion-shaped vermicular kaolinite crystals. Pyrite oxidized and hematite/ goethite formed. Anatase may have crystallized from biotite remnants.

Contact with groundwater probably had a great impact on the activity of respiring anaerobic bacteria by switching the terminal electron accepting process. For their respiration anaerobic respiring bacteria need not only electron acceptors (for example, SO_4^{2-} for sulfate-reducing bacteria, Fe^{3+} for iron-reducing bacteria and NO_3^- for nitrate-reducing bacteria), but also mechanisms for electron acceptor regeneration. It is generally considered that in an anaerobic sedimentary environment organic matter is metabolized by a succession of anaerobic terminal-electron-accepting processes (TEAPs) (Reeburgh, 1983). Nitrate reduction is usually the first TEAP in sediments along the groundwater flow path (Lovley and Goodwin, 1988, Lovley and Chapelle, 1995). After depletion of nitrate, nitrate reduction is usually followed by zones of Mn(IV) reduction. Then Mn(IV) reduction is followed by Fe(III) reduction, sulfate reduction and methanogenesis as each successive electron acceptor is depleted. This separation into zones is often not absolute: environmental heterogeneity may generate microzones and several TEAPs may take place within a small area, and in fluctuating conditions several TEAPs may overlap (Lovley and Goodwin, 1988). However, in sediments under steady state conditions one TEAP generally dominates the geochemistry within each zone (Reeburgh, 1983). Introducing electron acceptors with the groundwater or its regeneration will stimulate the development of bacteria carrying out corresponding TEAP. For example, dissolved oxygen that is introduced with groundwater into zones in which methane production or sulfate reduction is the TEAP, can oxidize Fe(II) in the sediments and increased Fe(III) concentration can switch the TEAP to Fe(III) reduction (Vroblesky D.A., Chapelle F.H., 1994).

Although the rate of microbial metabolism in subsurface clayey sediments was found to be lower than in adjacent sandy aquifers (Fredrickson et al. 1989; Sinclair and Ghiorse, 1989; Chapelle and Lovley 1990), the decomposition of organic matter and transformation of iron compounds in clay lenses may be attributed to direct or indirect microbial activity. Chapelle and Lovley (1990) have estimated the *in situ* rate of microbially catalyzed carbon dioxide production in several deep anaerobic aquifers in South Carolina. The turnover rate constants of $^{14}\text{CO}_2$ production from $[2-^{14}\text{C}]$ acetate were below the detection limit. The turnover rate constants of $^{14}\text{CO}_2$ production from $[U-^{14}\text{C}]$ glucose per year were estimated as 0.05 for clayey sediment from the Black Creek Formation (240 m depth) and 7.7 for clayey sediment from the Middendorf Formation (305 m depth), while the turnover rate constants in adjacent sandy sediments were 74 and 15 respectively. The turnover rate constant was calculated as $k=f/t$, where f was the fraction of added label evolved as $^{14}\text{CO}_2$ over time (t) during the initial time points when $^{14}\text{CO}_2$ production was linear.

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The authors speculated as to whether this bacterial population was a remnant of microorganisms present at the time of deposition some 70 to 80 million years ago or possibly organisms transported with the groundwater that entered the subsurface between 10,000 and 50,000 years before the present. Fredrickson et al. (1996) proposed that, at geologic time scales, indirect organic matter decomposition in clayey beds through diffusion into adjacent, more permeable sandstones (having greater and interconnected pores and much more abundant bacterial activity) may be more valuable than a direct process carried out in the clayey beds themselves.

RECENT MICROBIAL ACTIVITY THAT MAY HAVE INFLUENCE ON THE COMMERCIAL QUALITY OF KAOLIN

One of the most important conditions for the industrial use of kaolin is a low content of discoloring iron impurities. Iron is present as Fe(III) oxides and hydroxides, as iron coatings on clay particles, and as structural iron in kaolinite, smectite and mica in soft and hard kaolins. It is present mainly as pyrite in gray reduced kaolin. Therefore, the microbial processes for enhancing commercial quality of kaolin are microbial iron reduction of soft and hard kaolin, and pyrite and organic matter oxidation for gray kaolin.

The biological reduction of Fe(III) may be carried out by anaerobic iron-respiring bacteria. Fe(III) respiration is important in anoxic, nitrate-depleted environments. A wide diversity of microorganisms are capable of Fe(III) respiration: all representatives of the *Geobacteraceae* family, as well as *Geothrix fermentans*, *Geovibrio ferrireducens*, *Ferribacter limneticum*, *Shewanella* spp., *Ferrimonas* spp and *Aeromonas* spp. (Lovley, 2000). Fermentative organisms can also transfer a small amount of their electron flow to Fe(III) during primary fermentative metabolisms. Amorphous and soluble forms of iron are known to be preferable electron acceptors for iron-reducing bacteria. But recent literature suggests that in the presence of humics or humic analogs, crystallized Fe(III) oxides and hydroxides may also be significantly reduced (Lovley et al. 1998). Iron-respiring bacteria may also reduce the structural Fe(III) in ferruginous clay minerals (smectites) (Kostka et al., 1996). In some environments sulfide can nonenzymatically reduce Fe(III).

Well known re-oxidation processes of Fe(II) include its chemical reactions with molecular oxygen under neutral conditions (Stumm and Morgan, 1981), and its biological utilization as an electron donor by aerobic acidophilic (Ehrlich et al, 1991), or neutrophilic bacteria (Wood, 1988). In the absence of oxygen, Fe(II) can be oxidized chemically (with Mn(IV) oxide), or biologically by bacteria using nitrate as the electron acceptor and ferrous iron as the electron donor (Straub et al. 1996). Studies of anaerobic Fe(II)-oxidizing nitrate-reducers found that these organisms were widespread in a variety of sediments (Straub et al., 1998).

Often the representatives of both directions of the microbial iron cycle exist in the same subsurface microbial community. For example, a microbial consortium able to form siderite in anaerobic conditions and ferrihydrite in aerobic conditions was derived from a microbial biofilm formed on a subsurface granite vault (Sawicki et al., 1995, Brown et

al., 1996). The following groups of microorganisms have been found in kaolin samples from deposits in Russia and the Ukraine: aerobic heterotrophic bacteria, 10^2 - 10^5 cells per gram; fermentative bacteria, up to 10^2 cells per gram; denitrifying bacteria, up to 10^2 cells per gram; sulfate-reducing bacteria, up to 10 cells per gram, and iron-reducing bacteria, up to 10 cells per gram (Shelobolina et al., 1999).

The structure of the microbial community in kaolin from the Prosyankovskoe site in the Republic of Ukraine was investigated in more detail: aerobic and facultatively anaerobic microorganisms were represented by bacteria of the genera *Bacillus*, *Pseudomonas*, *Nocardia*, *Caulobacter* and *Deinococcus* and microscopic fungi of the genus *Acremonium*. Anaerobic microorganisms were represented by bacteria of the genera *Clostridium*, *Bacteroides*, *Desulfovibrio*, *Desulfobacter* and by a strain of iron-reducing bacterium (Turova and Osipov, 1996).

Stimulation of bacteria growth in a slurry of this kaolin by addition of a carbon source led to the development of sequential respiring processes (with aerobic heterotrophic bacteria followed by fermentative bacteria, iron-reducing, sulfate-reducing and methanogenic bacteria). By the end of the experiment, gradients in color, Eh, pH, and total Fe were observed down the kaolin sediment column with mainly aerobic heterotrophic and fermentative bacteria on the top of the column and anaerobic bacteria in the middle and bottom part. Such stimulation led to development and interaction in both directions of the microbial iron cycle: iron-oxidation and iron reduction processes (Fig.1) and resulted in neosynthesis of magnetite (Fe_3O_4), pyrite FeS_2 and thermodynamically unstable ferric hydroxides (ferrihydrite $5\text{Fe}_2\text{O}_3 \cdot 9\text{H}_2\text{O}$, akaganeite $\beta\text{-FeOOH}$, and lepidocrocite $\gamma\text{-FeOOH}$) (Vodyanitskii et al.1997).

In order to learn more about how the bacterial iron cycle might be involved in weathering alteration of kaolins, different types of Georgia kaolins were collected. Large pieces of subsurface kaolin samples were wrapped with plastic and immediately sent by overnight delivery service to the laboratory and placed in an anaerobic glove box filled with N_2 .

The following samples were chosen for experiments and analysis:

- 1) **W1.** Gray colored reduced soft kaolin associated with dark lignite from the Marion Member of Paleocene age. The sample was collected from an adjacent Wilkinson Kaolin Company mine on the northeast side of extensive Dry Branch Kaolin Company mines, 1000 meters east of the intersection of Georgia Highway 18 and an unpaved mine road 4 miles south of Georgia Highway 57. This kaolin has not yet been bleached by oxidizing, acidic ground water, and may not be well recrystallized.
- 2) **DB2.** Cream-pink soft kaolin taken from Dry Branch Kaolin Company's Brooks mine just north of Asbury Church Road. Kaolin was adjacent to burrows of shrimp/worms and filled by organic sediment containing pyrite.
- 3) **Th3.** Reduced hard kaolin from the Jeffersonville Member of the Huber Formation, relatively unaltered by oxidizing, acidic ground water. Sample was taken from Thiele's General Refractories clay mine about 2 miles south of Tabernacle Church (Stop No. 2 on our Saturday field trip).

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The samples were analyzed for bacterial content and both Fe-reducing and Fe-oxidizing bacteria were found in the kaolin samples studied (Table 4.3).

Sample	Anaerobic iron-reducing bacteria	Anaerobic nitrate-reducing iron-oxidizing bacteria	Aerobic acidophilic iron-oxidizing bacteria
W1	410 ± 230 cells/gram	4.6×10 ³ ± 1.7×10 ³ cells/gram	2.15×10 ⁴ ± 0.8×10 ⁴ cells/gram
DB2	3.2 ± 1.8 cells/gram	21.5 ± 8.1 cells/gram	< 0.03 cells/gram
Th3	11 ± 8 cells/gram	2.15×10 ³ ± 8.1×10 ³ cells/gram	< 0.03 cells/gram

Table 4.3. Most probable number analysis for bacteria of iron cycle (cells per gram of sample).

Sample	Organic Carbon, %	Short Organic Acids, mmoles/kg				
		Acetate	Formate	Pyruvate	Lactate	Oxalate
W1	1.6	ND	30.6	15.5	ND	141.7
DB2	0.1	0.1	3.6	1.6	1.7	ND
Th3	0.1	ND	1.6	0.4	0.4	ND

Not detected (ND): succinate, fumarate, propionate, butyrate, citrate.

Table 4.4. Organic Carbon and Short Organic Acids

The numbers of iron-reducing and iron-oxidizing bacteria were greatest in the gray reduced kaolin (sample W1), which also contained a large amount of organic carbon (Table 4.4). All kaolin samples had low concentrations of 0.5M HCl-extractable iron "available for bacteria" as compared with "total" iron (Table 4.5).

Sample	HF-extractable Fe(II), mmoles/kg	HF-extractable Fe(III), mmoles/kg	HCl-extractable Fe(II), mmoles/kg	HCl-extractable Fe(III), mmoles/kg
W1	29.4 ± 0.2	22.2 ± 0.2	2.3 ± 0.0	0.5 ± 0.1
DB2	5.3 ± 0.0	19.7 ± 0.1	0.2 ± 0.0	0.9 ± 0.0
Th3	6.6 ± 0.1	48.6 ± 0.1	0.4 ± 0.0	0.3 ± 0.0

* Komadel and Stucki (1988)

** Lovley and Phillips (1986)

Table 4.5. HF*- and 0.5M HCl**-extractable Fe(II) and Fe(III) in Georgia kaolin samples.

To determine how stimulation of the bacterial participants of different directions of microbial iron cycle can change the behavior of iron in the kaolin samples, experiments with crushed kaolin incubated in slurries were performed.

To stimulate the development of anaerobic iron-reducing bacteria, kaolin slurries were incubated under anaerobic conditions with addition of a complex-forming agent (nitriloacetic acid, 1 mmole/l slurry). Nitriloacetic acid was used to increase the availability of iron minerals in the kaolins for bacteria. To stimulate the development of anaerobic nitrate-reducing/iron-oxidizing bacteria, kaolin slurries were incubated under anaerobic conditions with the addition of 4 mmoles/l of NO_3^- (electron acceptor) and 1 mmole/l of nitriloacetic acid. Slurries in the control tubes were autoclaved and then the same compounds as for experimental tubes were added and the same incubation performed.

The incubation of slurries at 30°C during 30 days led to significant changes in the oxidation-reduction state of iron in the experimental tubes (Table 4.6). No reduction or oxidation, but slight dissolution of iron was observed in the control tubes.

The results suggest that bacteria involved in both directions of the iron cycle were present in soft, hard and gray Georgia kaolins and may have affected the commercial quality of the kaolin.

PROPOSED BIOTECHNOLOGICAL METHODS FOR ENHANCING THE QUALITY OF KAOLINS

A number of microbiological processes connected with the removal of iron impurities from kaolin have been developed, but to date they have only been applied on laboratory or pilot scale. Some of these are described below.

A spent fermentation liquid from the cultivation of different strains of the heterotrophic fungus *Aspergillus niger* was used as a leaching agent (Cameselle et al., 1995, 1998, Groudev, 1987, 1999, de Mesquita et al., 1996). Groudev (1987) developed a combined chemical-biological method using the fermentation liquid from *A. niger* cultivation, diluted with water and acidified to pH 0.5 with hydrochloric acid. The iron contents of different kaolins treated by this method were lowered from the range of 0.65% - 1.49% Fe_2O_3 to the range of 0.44% - 0.75% Fe_2O_3 . Cameselle et al. (1995, 1998) and de Mesquita et al. (1996) used a filtered fermentation liquid that removed up to 47 % of the iron. De Mesquita et al. (1996) showed that the brightness of biotreated kaolins was higher than kaolins treated with the conventional methods (treatment with sodium ditionite, aluminium powder, zinc powder or ozone), with the additional advantage of producing less-aggressive effluent into the environment.

ROLE OF MICROORGANISMS

A semi-industrial technology for removing Fe(III) impurities from kaolins has been developed by Hintz et al. (1977). A mixed culture containing the heterotrophic bacteria *Enterobacter* (formerly *Aerobacter*) *aerogenes* and *Leuconostoc mesenteroides* was inoculated into a nutrient medium containing molasses, urea and kaolin. As Fe(III) impurities were reduced, the supernatant was periodically siphoned off to remove the dissolved Fe(II) that was generated, and fresh medium was added. Depending on the kaolins utilized, the bacteria removed from 27.5 to 43.9% of the initial Fe(III). The treatment did not cause any unfavorable modifications in the chemical and physical characteristics of the kaolin.

Recent trends in biotechnology highlight the use of techniques that stimulate naturally occurring microbial communities instead of using microbial mono- or mixed cultures. Microbial communities are capable of self-regulation and complex modification of various compounds, they are resistant to changes in the environment, and they utilize simple and cost-effective procedures. The method developed by Avakyan et al. (1997) included stimulation of the development of bacteria present in the kaolin by addition of a source of carbon, with subsequent extraction of iron by magnetic separation. Stimulation of the development of bacteria resulted in a decrease in the degree of crystallinity of silicate and aluminosilicate minerals and in an increase in the amount of iron extracted by subsequent magnetic separation (from 7 - 12 to 42 - 57% of the total Fe content in the kaolin).

These promising studies on microbiological processes for enhancing the quality of kaolin, combined with an increasing understanding of microbial impact in geological processes, may lead to the development of industrial biotechnologies for kaolin beneficiation in the near future.

CHAPTER 5 - COMMERCIAL GRADE MUSCOVITE MICA FROM KAOLIN WASTE MATERIALS

In 1995 GGS member David Avant (BS in geology, Ga. Southern Univ., 1979) began producing high brightness white muscovite mica and industrial grade quartz sand from kaolin mine overburden and clay processing waste products. For some 16 years previously David had worked as an exploration geologist for two of the largest of the kaolin companies. He had always believed that there was an excellent opportunity to develop valuable by-product minerals from the clay industry's waste materials. For the past five years his new company, Georgia Industrial Minerals Inc., has done just that near the town of Deepstep.

Georgia Industrial Minerals mines their crude mica and sand ore from three different sources:

- From micaceous viscous kaolin that is left as waste at the bottoms of worked-out kaolin mines. Muscovite is naturally concentrated at the base of the kaolin lenses, either as part of the fining-upward sedimentation process and/or by authigenic recrystallization from micron-size detrital micas. Micas coarser than a few microns particle size are very harmful to the low and high shear viscosity necessary for paper coating kaolin products. Typically, the waste kaolin left in the bottoms of many worked-out mines contains: 25 to 60 percent viscous kaolin, 10 to 50 percent quartz sand, and 8 to 40 percent +200 mesh muscovite. Mica from these bottom clays tends to be finer in particle size, lower in potassium, and higher in natural aspect ratio than the sand micas. Compared to typical pegmatite micas the micas from the Coastal Plain sediments are depleted in potassium (Table 5.1). Mica from the Jeffersonville Member hard fine kaolins may contain small amounts of dark graphite, which is rare in micas from Buffalo Creek Formation soft coarse kaolins.

	Pegmatite Mica ⁺	Mica #1	Mica #2	Mica #3	Mica #4	Mica #5
SiO ₂	45.55	47.52	52.15	48.79	48.73	51.20
Al ₂ O ₃	36.89	37.68	35.66	38.86	38.32	37.50
TiO ₂	0.26	0.83	0.94	0.63	0.62	0.36
Fe ₂ O ₃ *	1.25	0.88	0.67	1.51	0.80	0.61
MgO	0.58	1.39	0.86	1.13	1.31	1.24
Na ₂ O	0.80	2.46	0.90	3.88	3.52	1.94
K ₂ O	10.17	9.24	7.16	5.20	6.70	5.72

* assumes all Fe as Fe₂O₃

⁺ muscovite from GA pegmatite (Ernst, 1963)

Table 5.1. Chemical composition of typical pegmatite muscovite compared to chemical composition of 5 individual mica crystals from Coastal Plain sediments.

COMMERCIAL GRADE MUSCOVITE FROM KAOLIN WASTE

- From waste sand overburden that is being removed from active new kaolin mines. There are many such mines in the Deepstep area, so Georgia Industrial Minerals is able to pick the better grades of white sand being excavated during nearby mine development. The composition of these sands averages approximately: 70 to 80 percent white quartz sand, 20 to 25 percent kaolin clay, and 2 to 5 percent muscovite mica. The sand micas are usually coarser in particle size, higher in potassium, and more difficult to delaminate than micas from the bottom clays.
- From by-product material dredged from waste degritting impoundments that hold coarse non-clay "grit residue" minerals separated from the kaolin. The mineral content of these impounds varies with distance from the waste discharge point. Coarse quartz sand settles nearest the discharge, thin flakes of muscovite settle somewhat farther away depending on their particle size and aspect ratio, and the kaolin lost during the degritting process settles farthest down the impound toward the dam. Thus, if there has been only a single discharge point, the dredge can be placed to produce almost any desired mineral concentration. Impounds for storing kaolin degritting waste are costly to build, take up otherwise valuable land, and always seem to fill sooner than expected, so dredging them provides needed new holding capacity.

The general process by which the crude ore is processed is to wet slurry sieve through a 5/16th inch screen to remove the coarsest silica sand. The commercial size sand, mica and kaolin are then separated by further wet screening and hydraulic classification. Mica and kaolin are separated by a patented proprietary process.

Georgia Industrial Minerals has also obtained a patent on cleavage delamination and commercial sale of mica from sedimentary sources. Their operation is thought to be the first example of mining and producing wet ground mica products from sedimentary source material. Also, the same chemical and bacterial alteration which has so whitened and removed iron from the kaolin and sand has made the mica unusually bright and white. GE Brightness is measured by a Technidyne Brightmeter TB-1c with green filtration at 550 nm wave length illumination. Georgia Industrial Minerals' mica products offer brightness in the 78 to 86 GE range. Color measurement is done by the Hunter L,a,b system.

Georgia Industrial Minerals is just completing a considerable expansion of their mica production capacity. When completed, the expanded plant will be one of the world's largest and will be capable of making approximately 52 thousand dry tons per year of refined mica. There are currently two general types of mica products made at Georgia Industrial Minerals; filler grade and ultrafine grade. Filler mica makes up about seventy percent of their production, and ultrafine about thirty percent.

Filler grade wet ground muscovite mica product is principally sold as a white mineral component of wallboard joint cement for interior home and office construction. It is used to fill and smooth the joints between gypsum plaster wallboard. The flat mica flakes are essential to give the board joints a very smooth finish, provide reinforcing stiffness to

avoid sagging before the cement sets and strength to resist age-cracking, and furnish a non-absorbing surface which bonds well but does not soak up excessive paint. A further advantage is that the mica acts as a relatively inexpensive extender mineral to minimize the percentage of much more costly adhesive needed in the joint cement.

Ultrafine grade wet ground mica is cleavage delaminated to greatly reduce its thickness and aspect ratio. One of the major advantages of sedimentary mica is that the finer flakes have been naturally leached of some of their potassium content. This has had the effect of enhancing their ease and perfection of cleavage into far thinner, finer flakes. The result is a range of ultrafine mica products of various particle sizes, which also have an exceptionally high aspect ratio (ratio of diameter to thickness). The finest range of mica flakes resulting from this process may be so thin that they could approach only a few atomic unit cells in thickness. Particle size and shape are measured by Malvern laser diffraction Mastersizer, after ultrasonic mechanical dispersion.

Ultrafine grade mica is used as a white pigment in paint and plastic, as a pearlescent base for paints, plastics, and cosmetics, for a release compound in rubber and other molded products, as thermal and electrical insulation in plastics and epoxies, etc. The ultrafine delaminated grades of mica attract much higher prices than the filler grades, and are frequently sold in the range of several dollars per pound.

We will visit Georgia Industrial Minerals' office, laboratory, and plant processing facilities, and two of their micaceous kaolin mines. Fortunately, one of these mines now exposes a rare example of dark organic clay and lignite, which is believed to be of Cretaceous age. Samples of this material will be of interest for study of fossil pollen.

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CHAPTER 4

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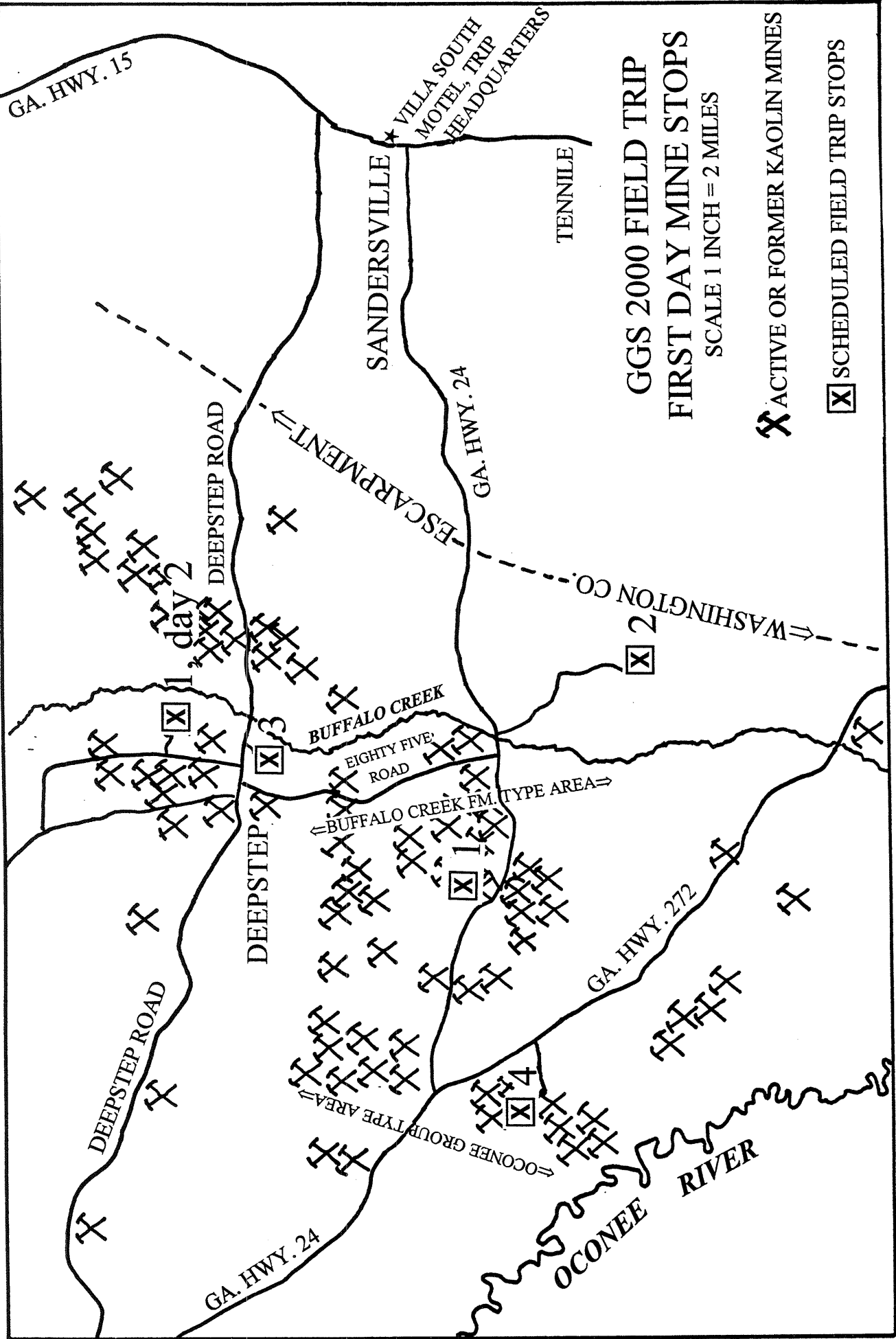
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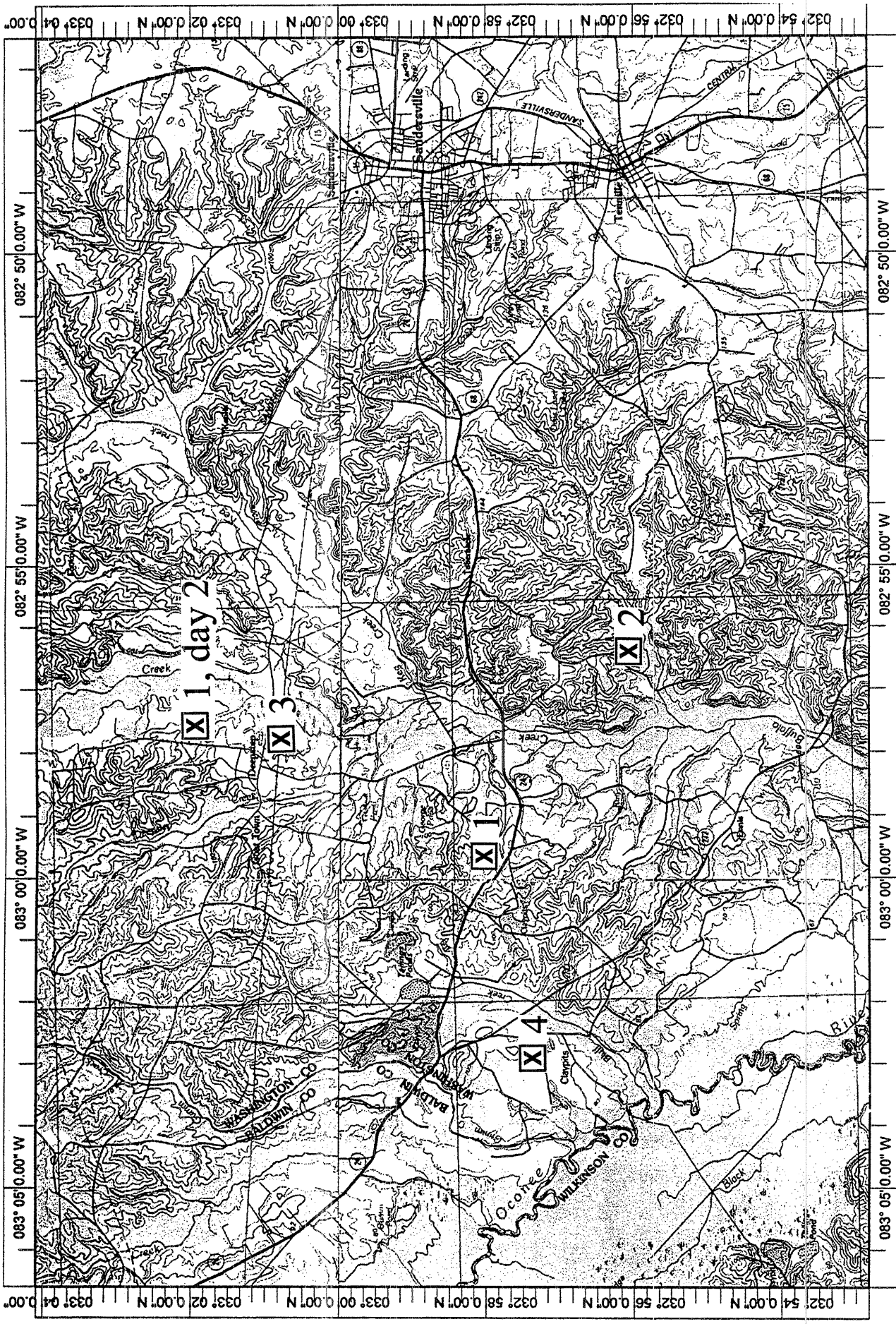
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**GGG 2000 FIELD TRIP
FIRST DAY MINE STOPS**
SCALE 1 INCH = 2 MILES

X ACTIVE OR FORMER KAOLIN MINES

X SCHEDULED FIELD TRIP STOPS



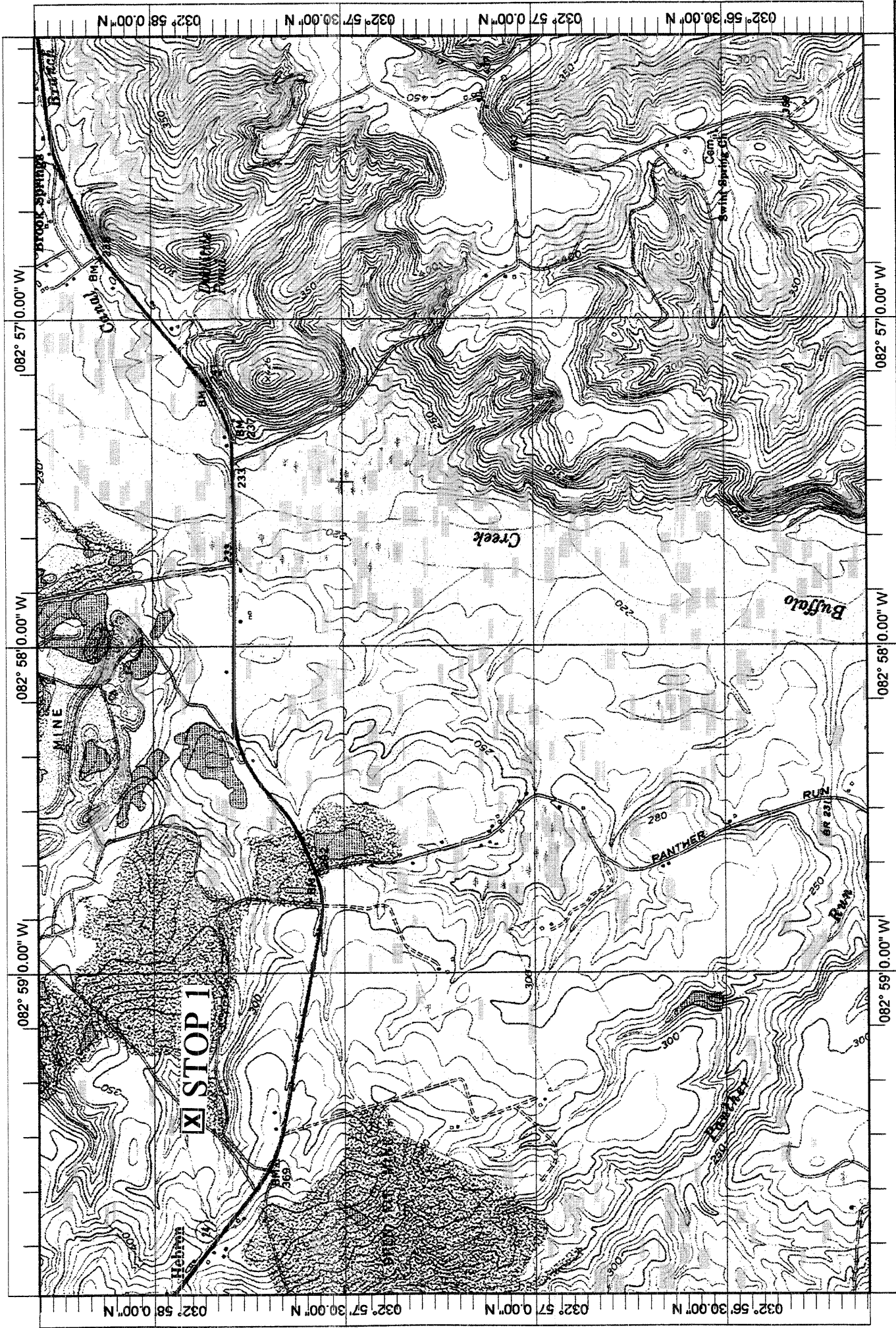
Name: DUBLIN
 Date: 9/13/100
 Scale: 1 inch equals 1.972 miles

Location: 032° 58' 28.1" N 082° 56' 32.1" W
 Caption: 2000 GGS FIELD TRIP, FIRST DAY.

FIELD TRIP ROAD LOG

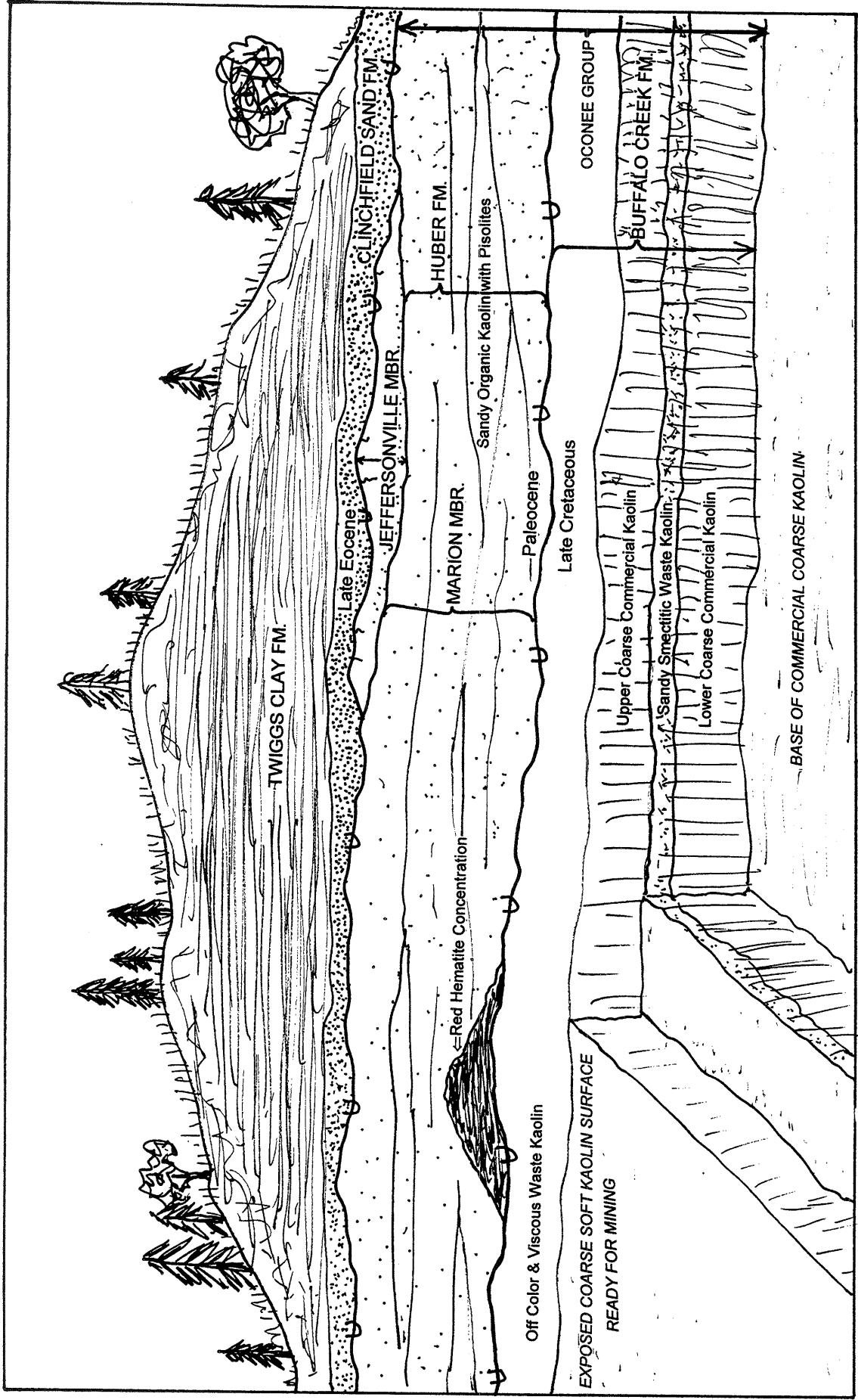
FIRST DAY:

Cumulative mileage, rounded to nearest mile:	Waypoints and Stops
0 miles	Leave field trip headquarters at the Villa South Motel, Sandersville, turn left on Ga. 15 south.
1 mile	Turn right on Kaolin Road.
2 miles	Turn right just beyond Thiele Kaolin Co., and pass between the Thiele and Huber (formerly ECCI) waterwash kaolin plants. These were first built in the 1940's, and have been continually upgraded with new technology and clay fractionating, brightening, and whitening equipment. The plants each have a capacity for refining and shipping between 500,000 and 1 million short tons of finished kaolin per year, at an average value of about \$110 per short ton. Much of the product for the North American market is shipped out as dispersed, liquid slurry (70% solids) in rail tank cars. This is the form in which it will be used by paper mills, for sheet and board coating. Paper will not take sharp printing impressions until it has received a fine particle size coating of mineral pigment. One to three long kaolin unit-trains are made up each day in central Georgia for shipment to customers centered in the western Great Lakes area. The approximately one-third of kaolin production which is exported, principally to western Europe and southeast Asian paper markets, is rail hauled dry in covered bulk hopper cars to ship-loading warehouse centers at Savannah and Charleston.
3 miles	Cross railroad tracks at the Huber railcar loading area on left. Note that the Huber and Thiele plants are quite different. Huber receives most of its raw kaolin from the mines by truck in solid lump form. Thiele gets all its crude kaolin as a degrittied liquid slurry by underground pipeline directly from blungers like those we will see near the mines. Huber's crude clay is stored in covered sheds until needed. It is blended then blunged at the plant by vigorously mixing with water and a small amount of dispersant chemical.
4 miles	Drive by Burgess Pigment Co. plant and offices on right. Burgess specializes in a calcined kaolin product. Raw kaolin, received from Thiele, is heated to 900° to 1100° C., which drives off the 14 percent formula water, and increases brightness and opacity. Burgess' primary calcined clay market is the paint industry.



Name: TABERNACLE
 Date: 9/19/100
 Scale: 1 inch equals 2000 feet

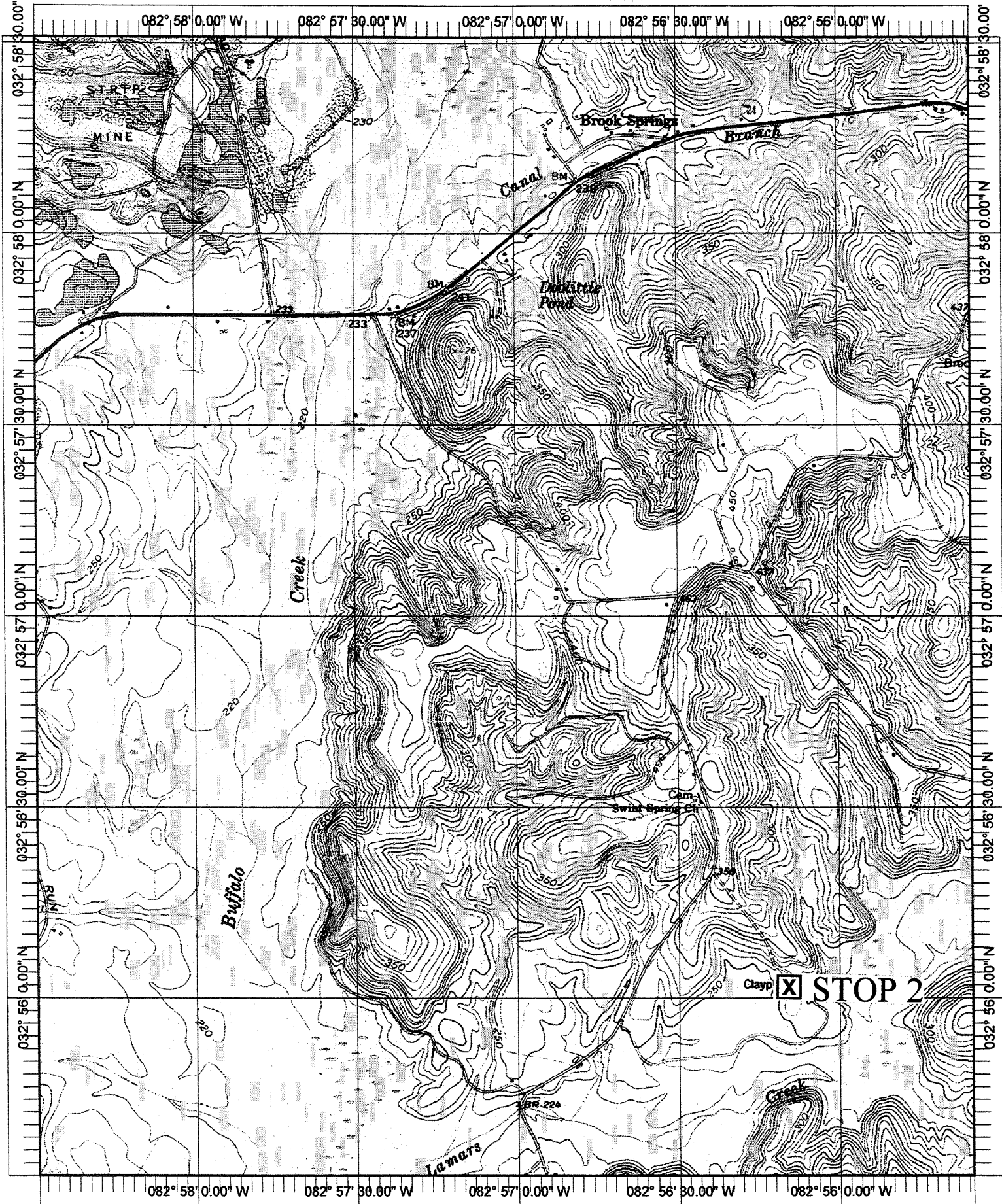
Location: 032° 57' 12.9" N 082° 58' 03.5" W
 Caption: STOP 1, IMERY'S KAOLIN MINE AT TYPE AREA OF BUFFALO CREEK FM. JUST NORTH OF GA. HWY. 24.



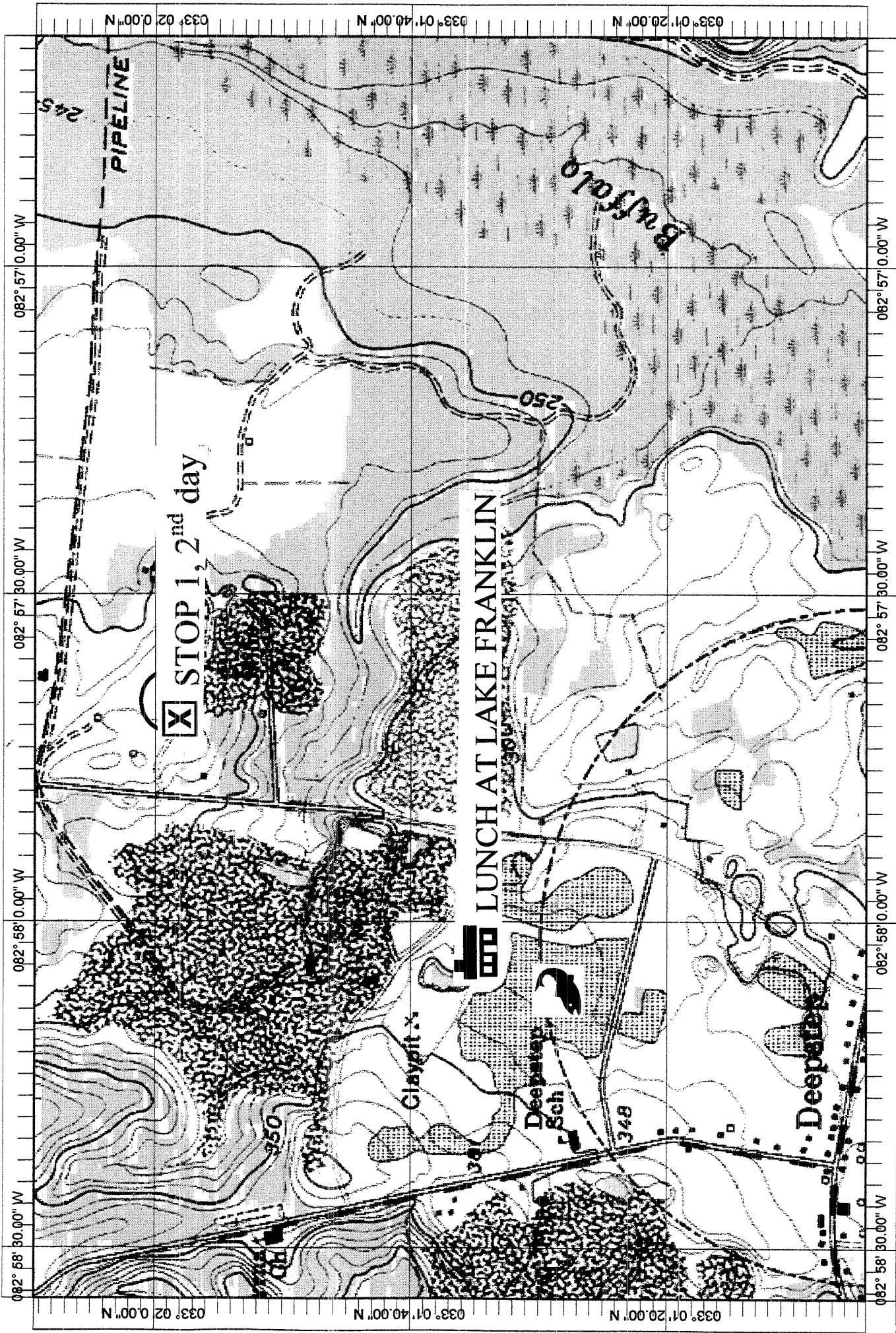
STOP NO. 1: IMERY'S SHEPPARD KAOLIN MINE
 (vertical scale 1 cm. \approx 3 meters)

ITINERARY

- 5 miles Turn left on Ga. Highway 24 west.
- 6 miles Turn left onto 4-lane Ga. 24 west, which is a short segment of the partly completed new Fall Line Freeway.
- 7 miles Start down the gentle slope of the Washington Co. Escarpment. The rather flat plateau we are leaving is the Sandersville Upland, which is underlain by 150+ feet of impermeable Twiggs Clay and other Barnwell/Jackson overburden units. The escarpment marks the edge of the area where ground water recharge has been able to penetrate erosional breaches through these overburden units to favorably oxidize the kaolins beneath. Therefore, the escarpment marks the practical eastern edge of the kaolin mining district.
- 9 miles Cross Buffalo Creek, type area of the Buffalo Creek Formation.
- 13 miles Turn right onto Tucker unpaved mine road, about 1 mile past Jackson Construction Co., a large mine earthmoving contractor.
- 14 miles **STOP 1:** Turn left into IMERY'S Sheppard and Huber's Brown kaolin mines. They mine almost exclusively coarse soft clay from the Buffalo Creek Fm., but do stockpile some hard fine kaolin from the Jeffersonville Fm. where it occurs in sufficient quality in the overburden. The Buffalo Creek Fm. kaolin is the very lowest clay exposed in the mine; everything above is overburden that must be removed before mining can begin. Note the typical smooth conchoidal fracture of this coarse kaolin. We may also see good examples of pisolites in the kaolin. In this area the pisolites are generally filled with smectite. There is an impure split within the main commercial kaolin stratum here, which is quite sandy and smectitic (Jones, 1988).
For safety reasons please be sure to stay well back from the highwalls in this and all mines!
- In this area we will see a clay blunger, which mixes and disperses the kaolin into a water-based liquid to be pumped through pipelines to the processing plant some 20 miles distant. We will also stop briefly where IMERY'S has placed a pile of marine Clinchfield Sand and Twiggs Clay from one of their downdip mines, so those interested can collect Late Eocene fossils (perhaps shark, ray, barracuda, etc. teeth and mollusks).
- 16 miles Return to Ga. 24 east, turn left back toward Sandersville.
- 19 miles **STOP 2:** Turn right just after crossing Buffalo Creek, go about 2 miles to



<p>Name: TABERNACLE Date: 9/19/100 Scale: 1 inch equals 2000 feet</p>	<p>Location: 032° 57' 01.5" N 082° 57' 02.4" W Caption: STOP 2, THIELE KAOLIN GRAY HARD CLAY MINE AT THE BASE OF WASHINGTON CO. ESCARPMENT</p>
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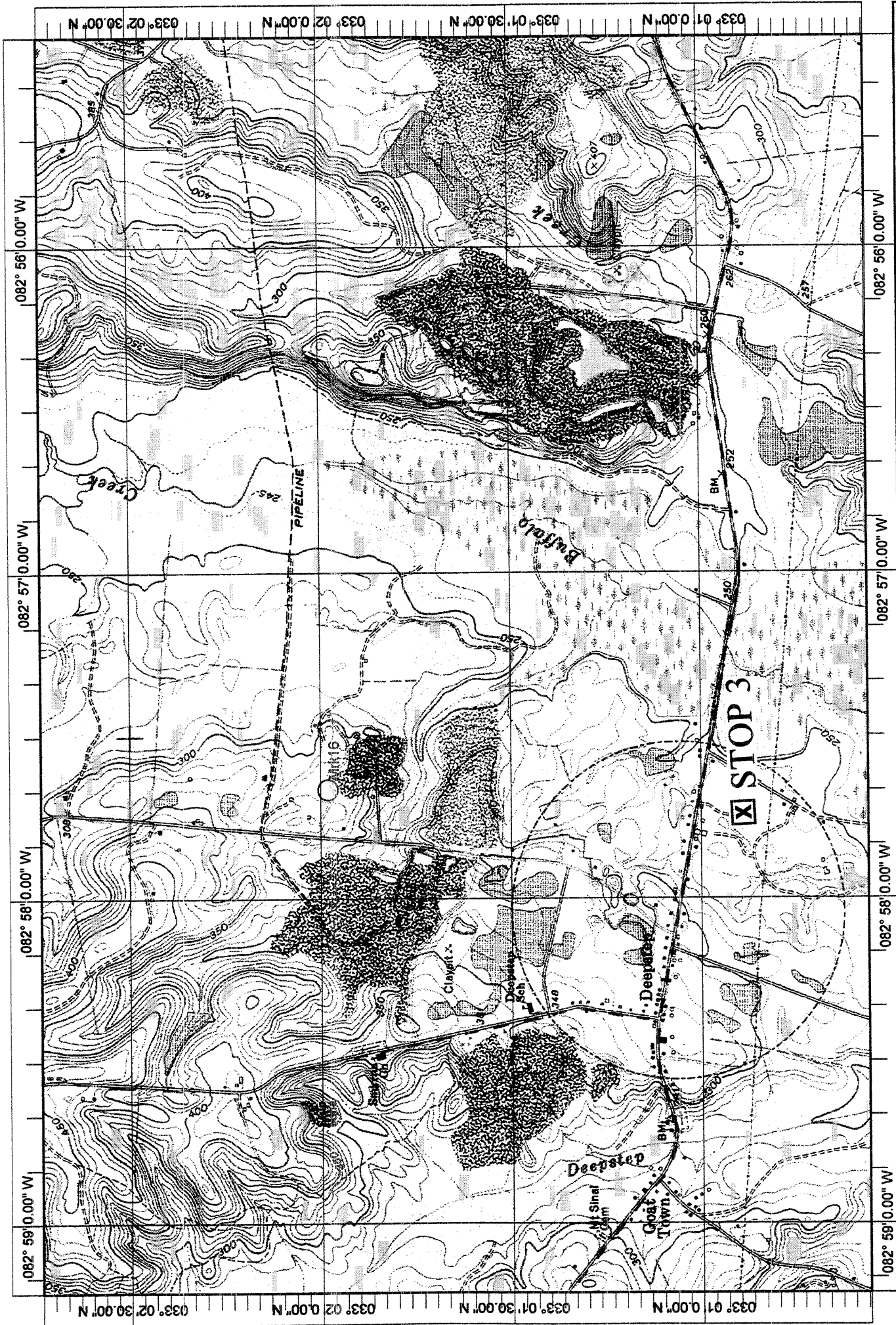


Name: DEEPSTEP
 Date: 9/14/100
 Scale: 1 inch equals 1000 feet

Location: 033° 01' 36.8" N 082° 57' 36.7" W
 Caption: DAY 1 LUNCH STOP AT IMERY'S RECLAIMED FRANKLIN MINE, NOW A RECREATION FACILITY.

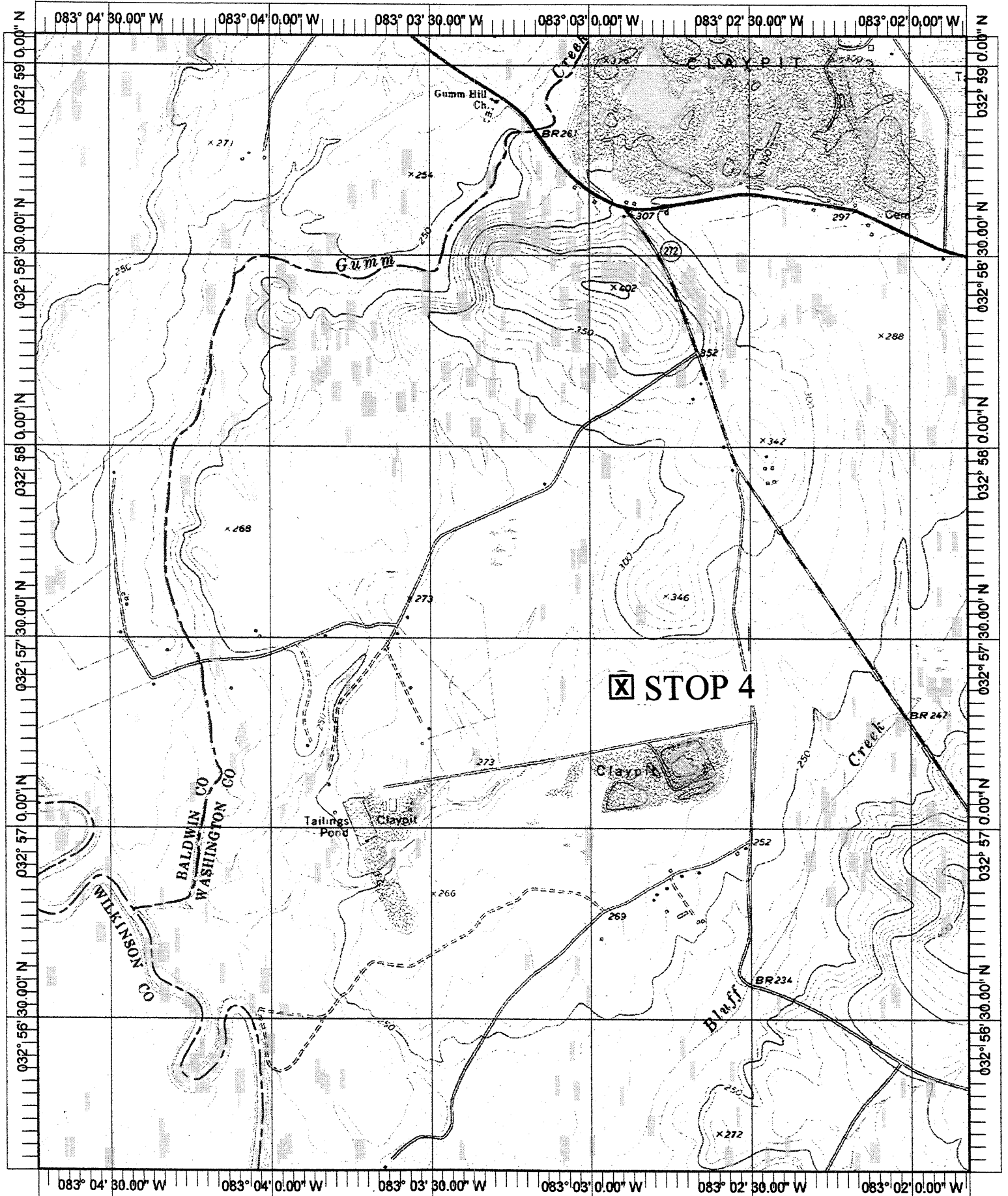
Thiele's General Refractories (Dukes) mine. Here a reduced and pyritic gray kaolin is mined from the Jeffersonville Mbr. of the Huber Fm. The kaolin is gray because it is still under the edge of the escarpment, covered by impermeable Twiggs Clay, and not yet flushed by oxidizing ground water. This type of kaolin is used for calcination where the organic matter is driven off as CO₂ during 900° to 1050° C. heating in the kiln. It could also be whitened by oxidation and bleaching with concentrated ozone gas. Note the typical rough earthy or hackly fracture of this hard fine kaolin, in comparison to the smooth conchoidal fracture of the Buffalo Creek Fm. clays. This is due to the tight face-to-face crystal particle packing of the Jeffersonville Mbr. kaolins.

- 20 miles Return to Ga. 24 west, turn left and re-cross Buffalo Creek.
- 22 miles Turn right on Old Eighty-five Road north, proceed to town of Deepstep.
- 24 miles Go through Engelhard's Everett Mine. Notice the large dragline that is still sometimes used for removal of overburden in areas where there is little artesian water pressure on the base of the mined kaolin stratum.
- 28 miles **LUNCH STOP:** In Deepstep, go straight one more mile to entrance to IMERY'S Lake Franklin. Turn into Lake Franklin and park for lunch. This entire area was mined in the 1950's to the 1970's, and has been reclaimed to make an excellent fishing lake, swimming beach, and employees recreation area. This is a good example of the results of the 1968 Georgia Mined Land Use Law, which was the first state mine reclamation law in the U.S. When lunch is finished, return to Deepstep. Note the C.T. Harris operation on the left; another of the large mine earthmoving and kaolin truck-hauling contractors in the district.
- 33 miles Turn left on Deepstep county road east.
- 34 miles **STOP 3:** Turn right on unpaved road into Thiele Kaolin Co. Boatright Mine. Here soft kaolin and lignitic clay of Late Cretaceous age are exposed. Fossil pollen from this lignite has established the age and shown that the clay was deposited in a dominantly non-marine back-delta environment. Interestingly, there is another organic clay higher in the section that palynology has shown to be an elevated terrace sediment from the nearby creek. This dark upper clay is probably Pleistocene in age, and contains fossil wood from a paleo-beaver dam or lodge (Rich, *et al*, 2000). Return to Ga. 24, turn left to return to Deepstep.
- 35 miles Turn left on Old Eighty-five Road south, go to end at Ga. 24.



Location: 033° 01' 38.9" N 082° 57' 16.9" W
 Caption: STOP NO. 3, THIELE'S BOATRIGT MINE, WITH CRETACEOUS AND PLEISTOCENE LIGNITES.

Name: DEEPSTEP
 Date: 9/14/100
 Scale: 1 inch equals 2000 feet



STOP 4

Name: GUMM POND
 Date: 9/14/100
 Scale: 1 inch equals 2000 feet

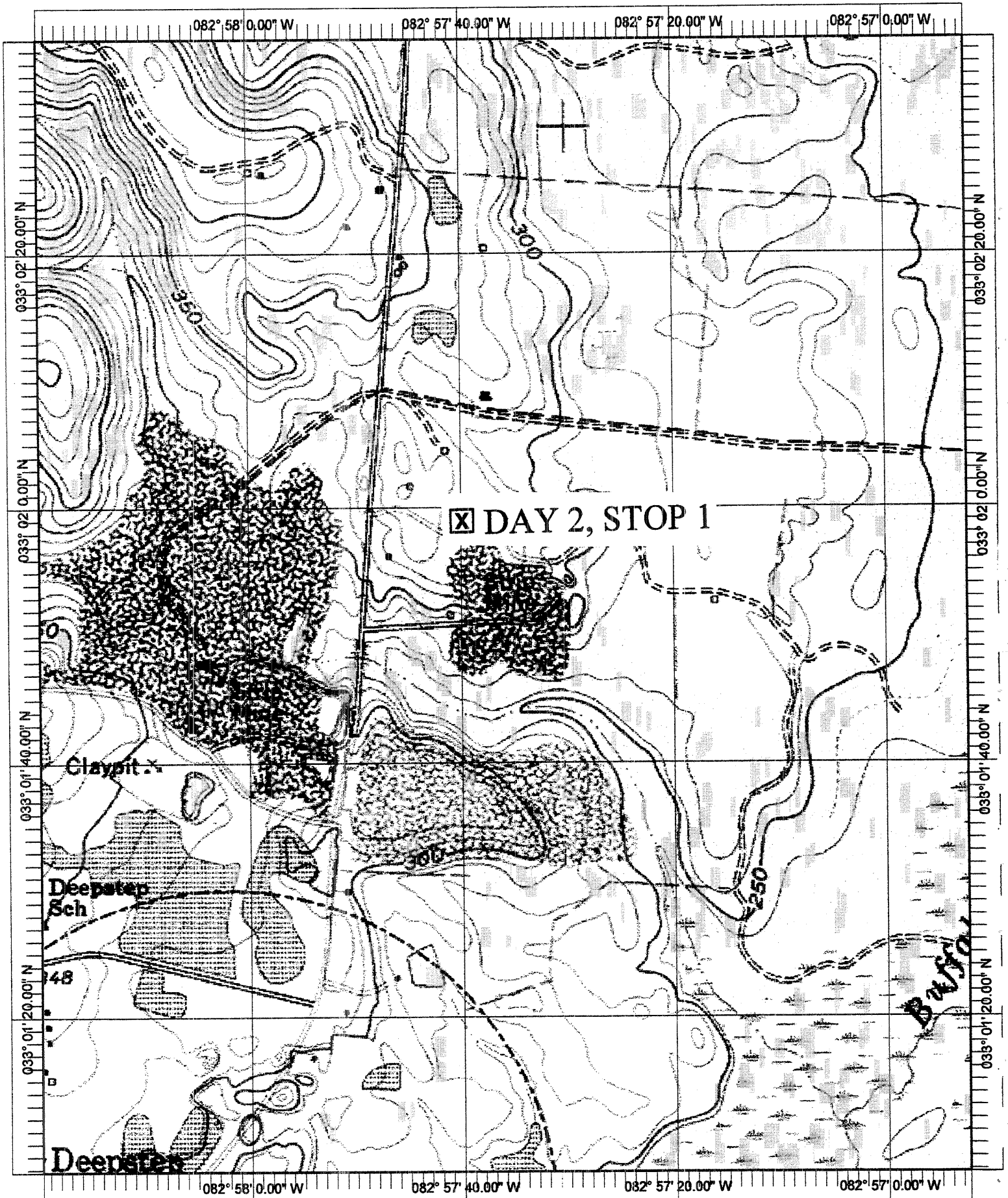
Location: 032° 57' 35.4" N 083° 03' 16.6" W
 Caption: STOP 4, THIELE'S AVANT MINE IN TYPE AREA OF THE
 OCONEE GROUP AT THE OCONEE RIVER.

ITINERARY

- 36 miles Turn right on Ga. 24, go west toward Milledgeville. This is the route of the new Fall Line Freeway (although the Fall Line is some 20 miles to the north here). Two new lanes will be built on the north side of the present highway, making a 4 lane east-west cross-state expressway. Note that kaolin is being mined in advance of construction to avoid loss.
- 39 miles Turn left on Ga. 272 south.
- 41 miles **STOP 4:** Turn right into Thiele's Avant Mine area. This is the present downdip limit of minable, coarse Buffalo Creek Fm. kaolin in the area, and if mining progress allows, we may see the contact between the well oxidized, cream colored clays and gray kaolins that are still in a reduced state (see illustration in text). The cream kaolins are much easier to process by standard magnetic and reduction leaching methods to attain commercial brightness and whiteness specifications. This mine may also provide a good viewpoint to see several superimposed fining-upward sequences in the Huber Fm., each capped by a lens of kaolin. End of first day, return to Ga. 272.
- 43 miles Turn left, return to Ga. 24 east, Sandersville, and the Villa South Motel.

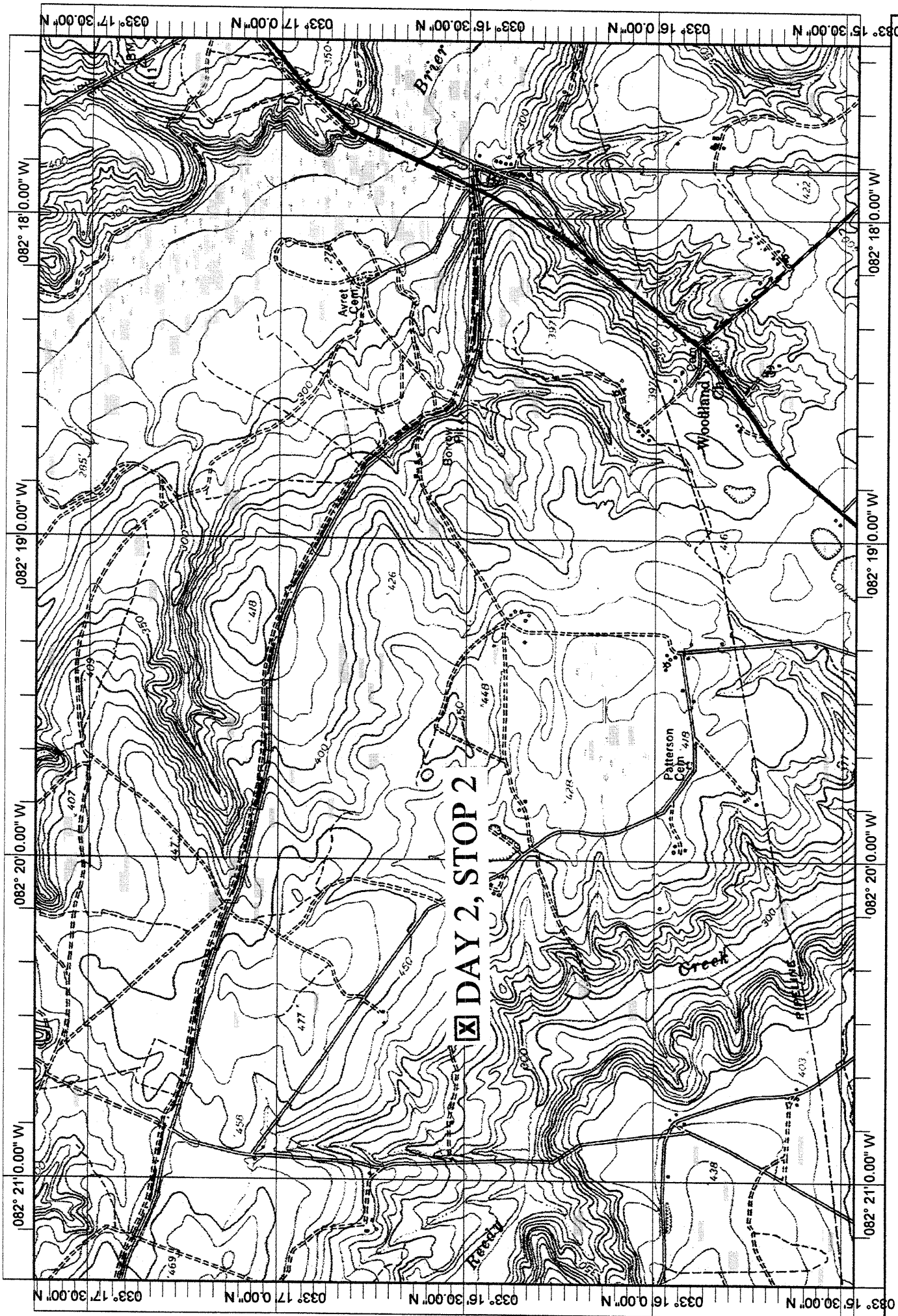
SECOND DAY

- 0 miles Leave Villa South Motel, turn right on Ga. 15 north. Note the Kaolin Plaza shopping center on left (elsewhere, shopping malls are seldom named for minerals!).
- 2 miles Turn left at Sandersville courthouse on Deepstep Road, go west to Deepstep.
- 17 miles Turn right in Deepstep on the first paved road, go by entrance to IMERY'S Lake Franklin.
- 18 miles **STOP 1:** Turn right on unpaved road into Georgia Industrial Minerals' mica and sand plant. Meet David Avant, geologist, GGS member, and facility owner/operator. Discuss how various commercial grades of muscovite mica and silica sand are separated and processed here, and the mineralogy and genesis of the muscovite. Examine several examples of the mineral products produced here, and see how David's new venture has developed and grown since he began in 1995. Go into his two nearby micaceous kaolin mines to discuss how selective mining is planned and accomplished.
- 18 miles Return to Deepstep, turn left on Deepstep Road and go east.
- 32 miles Turn left onto Fall Line Freeway, Sandersville bypass. Go north around Sandersville and merge onto Ga. 88 east. Continue east to Wrens.
- 66 miles Turn left in Wrens on Ga. 17 north.
- 78 miles **STOP 2:** Turn right on Huber mine road, and go to Huber's Bracewell Mine. Here they mine a hard, fine kaolin from the Jeffersonville Mbr. of the Huber Fm., which is used for hydrous paper coating pigment products. The overburden units are also extremely interesting. The prominent unconformity at the top of the Huber Fm. kaolin is overlain by a siliceous unit that Carver (1980) called the Albion Member. Here the Albion consists of a siliceous "flint kaolin" lens in a silica-cemented sandstone. There is a zone of exceptionally abundant small fossil clam shells that resembles the Clinchfield Sand of central Georgia. Indeed, the Albion may well turn out to be an eastern facies of the basal Late Eocene Clinchfield Sand.
- 79 miles Drive to Huber's employees' meeting area for a box lunch, overlooking the water supply lake.



Name: DEEPSTEP
 Date: 9/14/100
 Scale: 1 inch equals 1000 feet

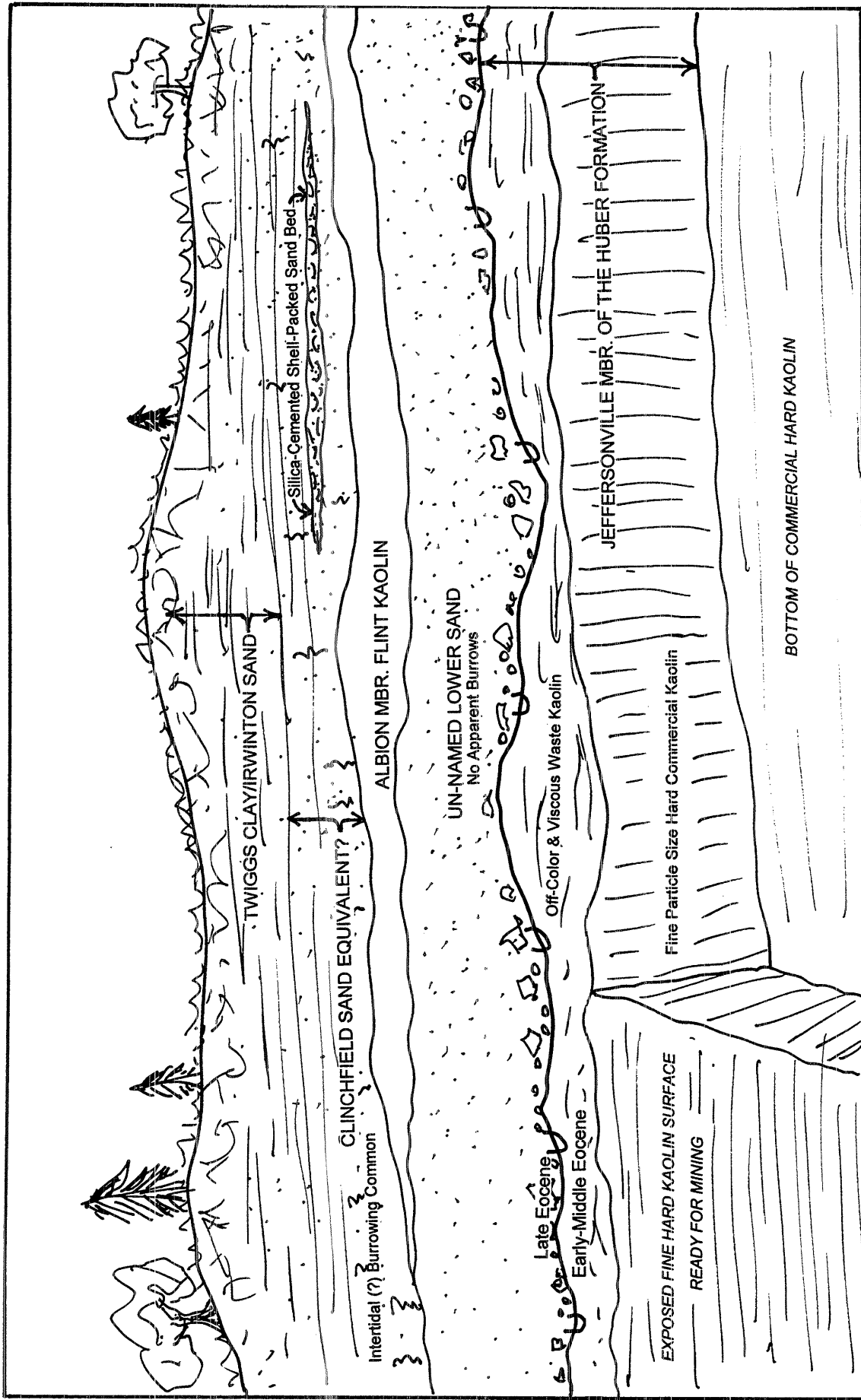
Location: 033° 01' 52.3" N 082° 57' 36.0" W
 Caption: DAY 2, FIRST STOP, GA. INDUSTRIAL MINERALS SAND
 PLANT AND AVANT MICA MINES



DAY 2, STOP 2

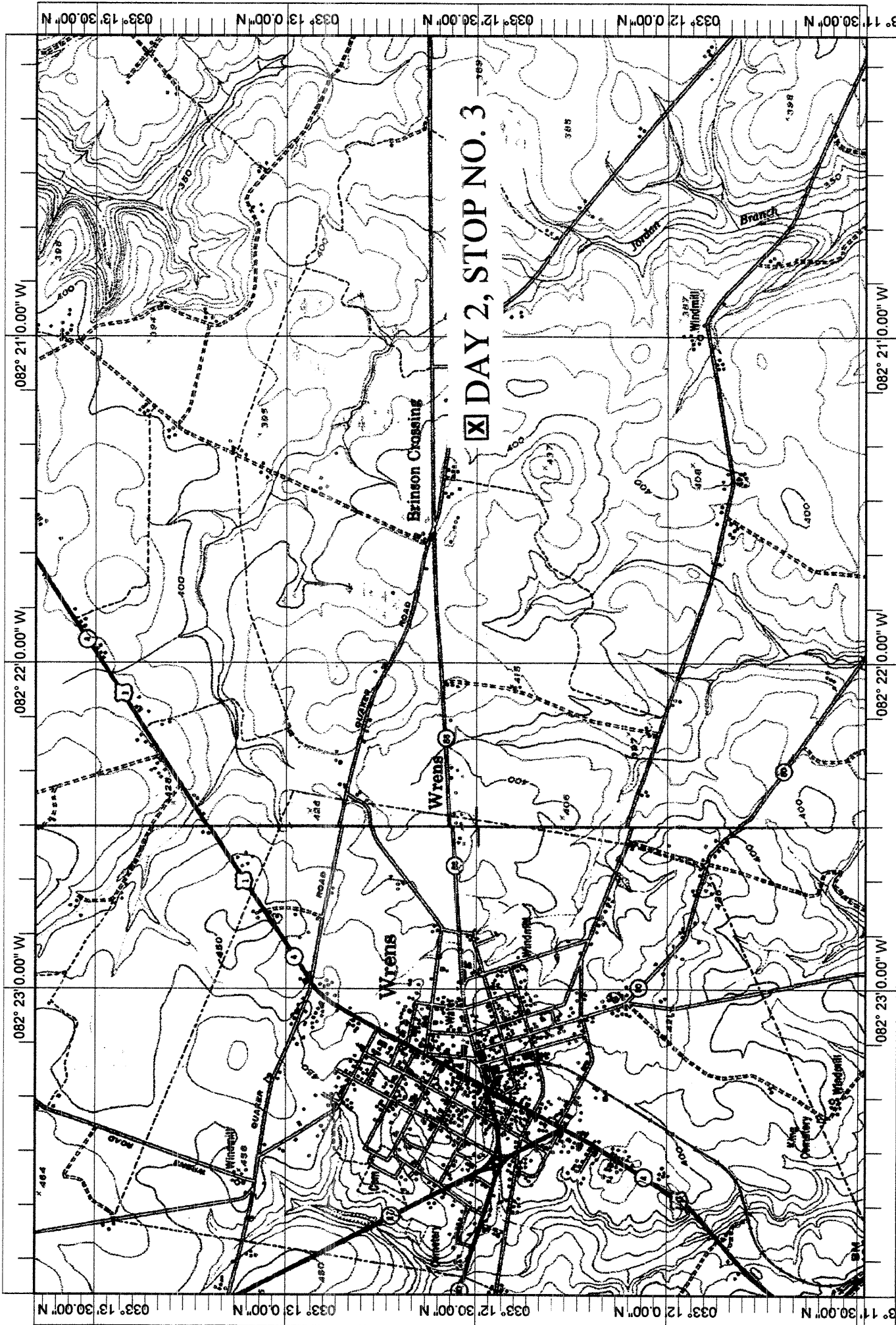
Name: AVONDALE
 Date: 9/14/100
 Scale: 1 inch equals 2000 feet

Location: 033° 16' 33.3" N 082° 19' 23.2" W
 Caption: DAY 2, STOP NO. 2, HUBER'S BRACEWELL MINE WITH BOTH HARD AND FLINT KAOLIN EXPOSED.



STOP 2, 2nd DAY: HUBER KAOLIN CORP. BRACEWELL MINE
 (Vertical Scale 1 cm. \approx 1.5 meters)

- 80 miles Return to Ga. 17 south, turn left and return to Wrens. In the center of town, turn left on Ga. 88 east, toward the town of Matthews.
- 81 miles **STOP 3:** Fork right on a paved road, following the signs to A&M Products' fuller's earth processing plant and mines. A&M is a subsidiary of the Clorox Company. Here we will learn how Twiggs Clay fuller's earth (slightly opaline smectite) is semi-calcined to the point of incipient fusion, crushed, sized, packaged, and marketed as adsorptive pet granules (kitty litter). The production and quality of this material is quite interesting. The fuller's earth is mined carefully in three distinct layers, each with particular specifications for key quality items such as friability, density, adsorptivity, and dusting losses. The overburden is a mottled soil zone and red hematitic fuller's earth. Below is the 'Upper Boundary Layer' which has low-adsorption and is dense, but highly friable and yields little wasteful dust. The 'Middle Boundary Layer' is moderately adsorptive, but only passably dense and has high dusting losses. The 'Lower Boundary Layer' is highly adsorbent, with low density, but dusty. Crude clay from the three layers is blended to make a consistent, properly sized product with high absorbency, and low density (so the package will not be too heavy). It must also create a minimum of dust when poured and used in the home. This is an excellent example of how a raw mineral commodity can be selectively mined, blended, and processed to produce a competitive product for a demanding market.
- 82 miles End of field trip. Return to Sandersville and Villa South Motel.



X DAY 2, STOP NO. 3

Name: MATTHEWS
 Date: 9/14/100
 Scale: 1 inch equals 2000 feet

Location: 033° 12' 34.1" N 082° 22' 00.5" W
 Caption: DAY 2, STOP NO. 3, A and M CLOROX CAT LITTER PLANT AND ABSORBENT
 FULLERS EARTH MINE.

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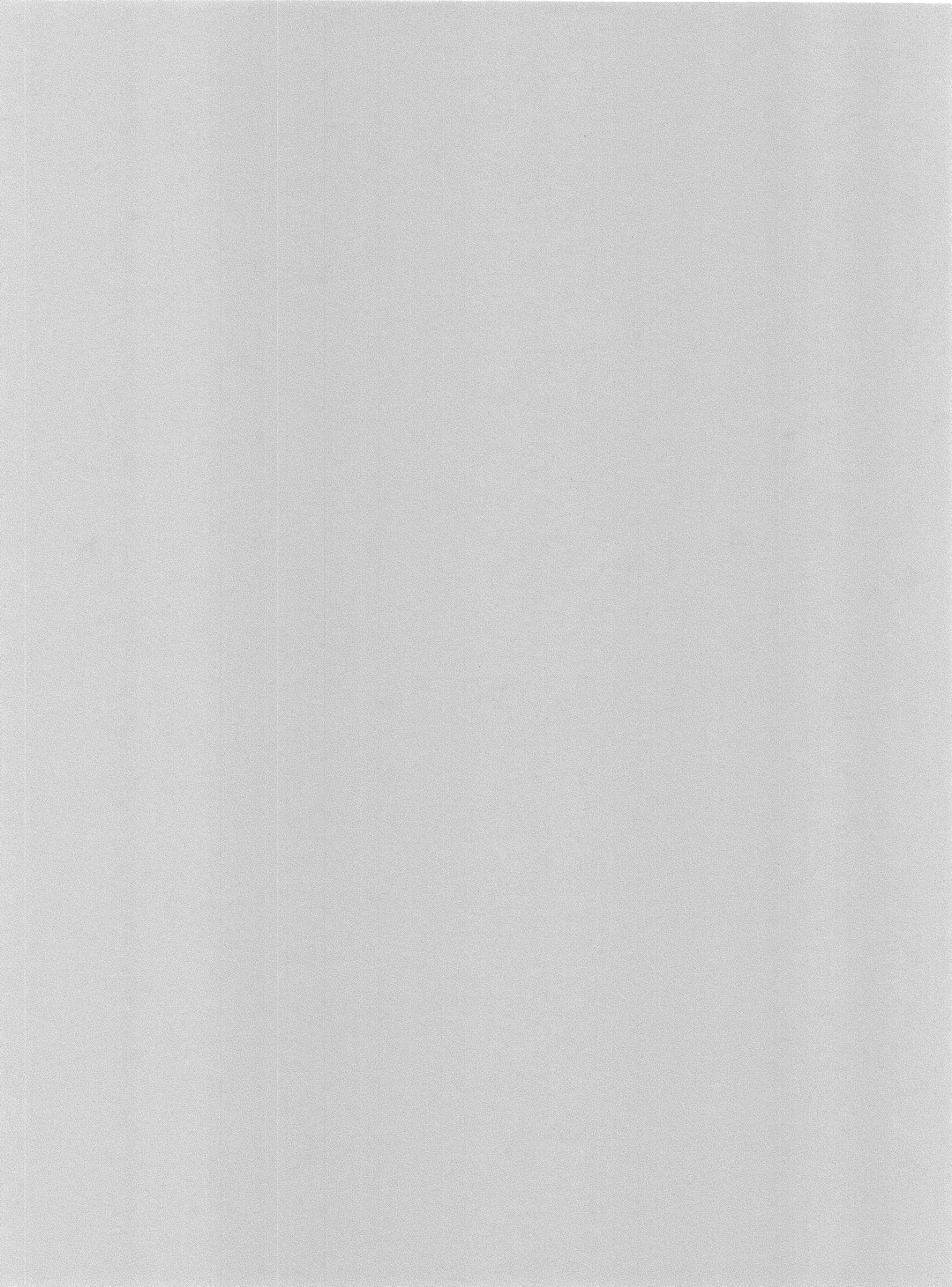
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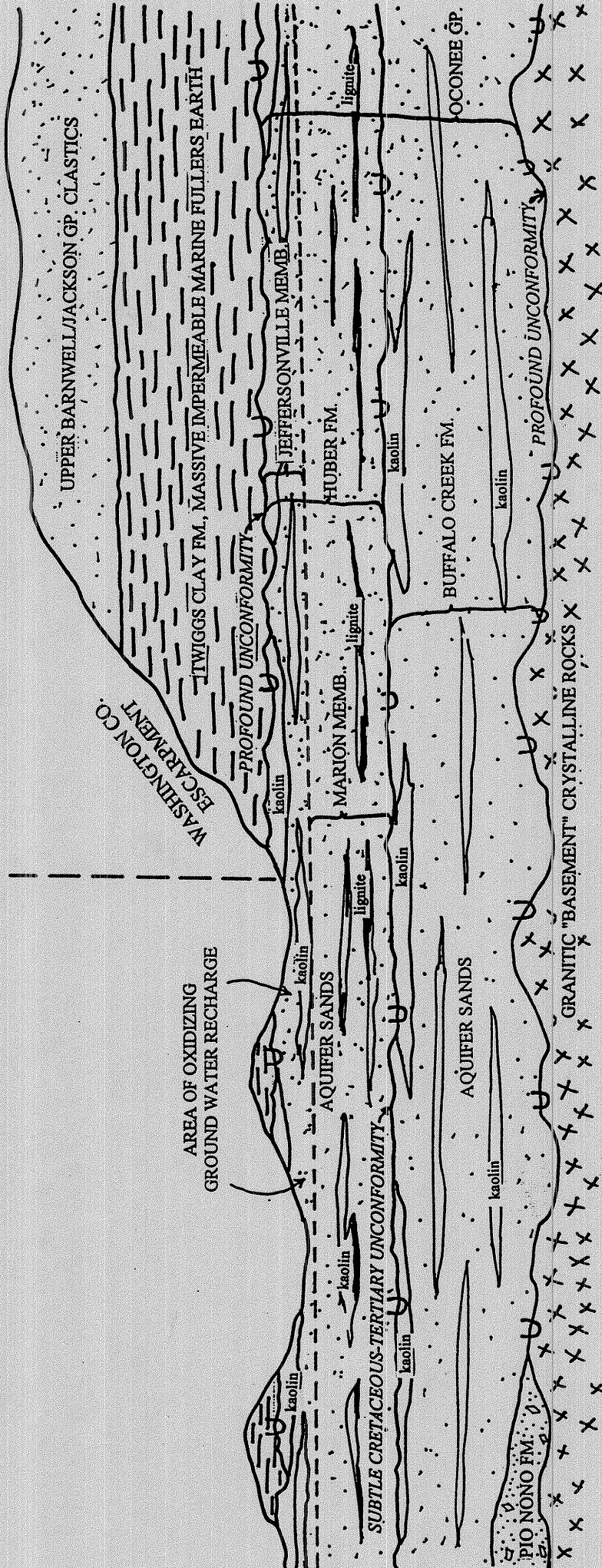


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