

Michael E. Lyle. CLAY MINERALOGY OF THE PUNGO RIVER FORMATION, ONSLOW BAY, NORTH CAROLINA CONTINENTAL SHELF. (Under the direction of Dr. Stanley R. Riggs) Department of Geology, May 1984.

ABSTRACT

The Pungo River Formation in Onslow Bay, North Carolina consists of the Burdigalian (late early Miocene), Langhian (early middle Miocene), and the Serravallian (middle Miocene) depositional sequences as defined by seismic stratigraphy and biostratigraphy. X-ray diffraction analyses have defined the clay mineral composition of these sequences as follows:

Serravallian (BBF Depositional Sequence)	Montmorillonite	50 to 70%
	Illite	25 to 40%
	Chamosite	1 to 10%
	Sepiolite	not detectable
Langhian (AF Depositional Sequence)	Montmorillonite	6 to 45%
	Illite	41 to 89%
	Sepiolite	3 to 18%
	Chamosite	not detectable
Burdigalian (FPF Depositional Sequence)	Montmorillonite	25 to 70%
	Illite	27 to 70%
	Chamosite	0 to 24%
	Sepiolite	3 to 18%

Clinoptilolite, a zeolite mineral, is present infrequently in the Burdigalian, not detectable in the Langhian, and present throughout the Serravallian. Well crystallized, mica-derived montmorillonite and a poorly crystallized illite are interpreted to be of terrigenous origin. Sepiolite, chamosite, and a glauconitic illite, are interpreted to be of authigenic origin. Clinoptilolite is

interpreted to be authigenic in the Burdigallian sediments and detrital in the Serravallian. The diagenetic alteration of clays and formation of zeolite is thought to be related to variations in availability of Fe, Mg, and silica in response to changing climatic conditions, weathering processes, and sea-level fluctuations.

CLAY MINERALOGY OF THE PUNGO RIVER FORMATION,
ONSLOW BAY, NORTH CAROLINA CONTINENTAL SHELF

A Thesis

Presented to
the Graduate Faculty of the Department of Geology
East Carolina University

In Partial Fulfillment
of the Requirements for the Degree
Master of Science in Geology

by

Michael E. Lyle

May, 1984

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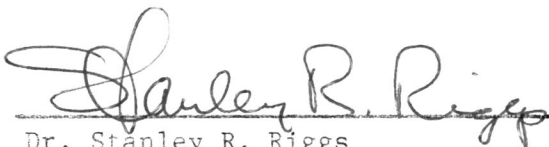
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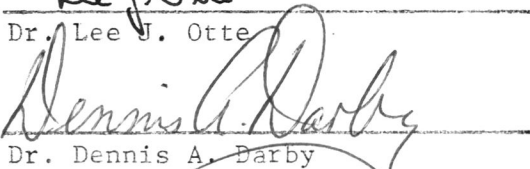
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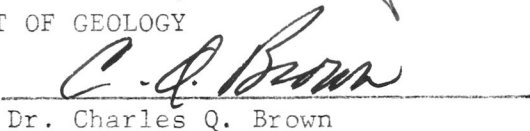
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INTRODUCTION

The Miocene of the southeastern United States is characterized by high concentrations of a whole series of anomalous authigenic minerals, including vast concentrations of phosphate (Riggs, 1980). These minerals are found in two contemporaneous units in the southeast: the Hawthorn Formation of Florida, Georgia, and South Carolina, and the Pungo River Formation of North Carolina.

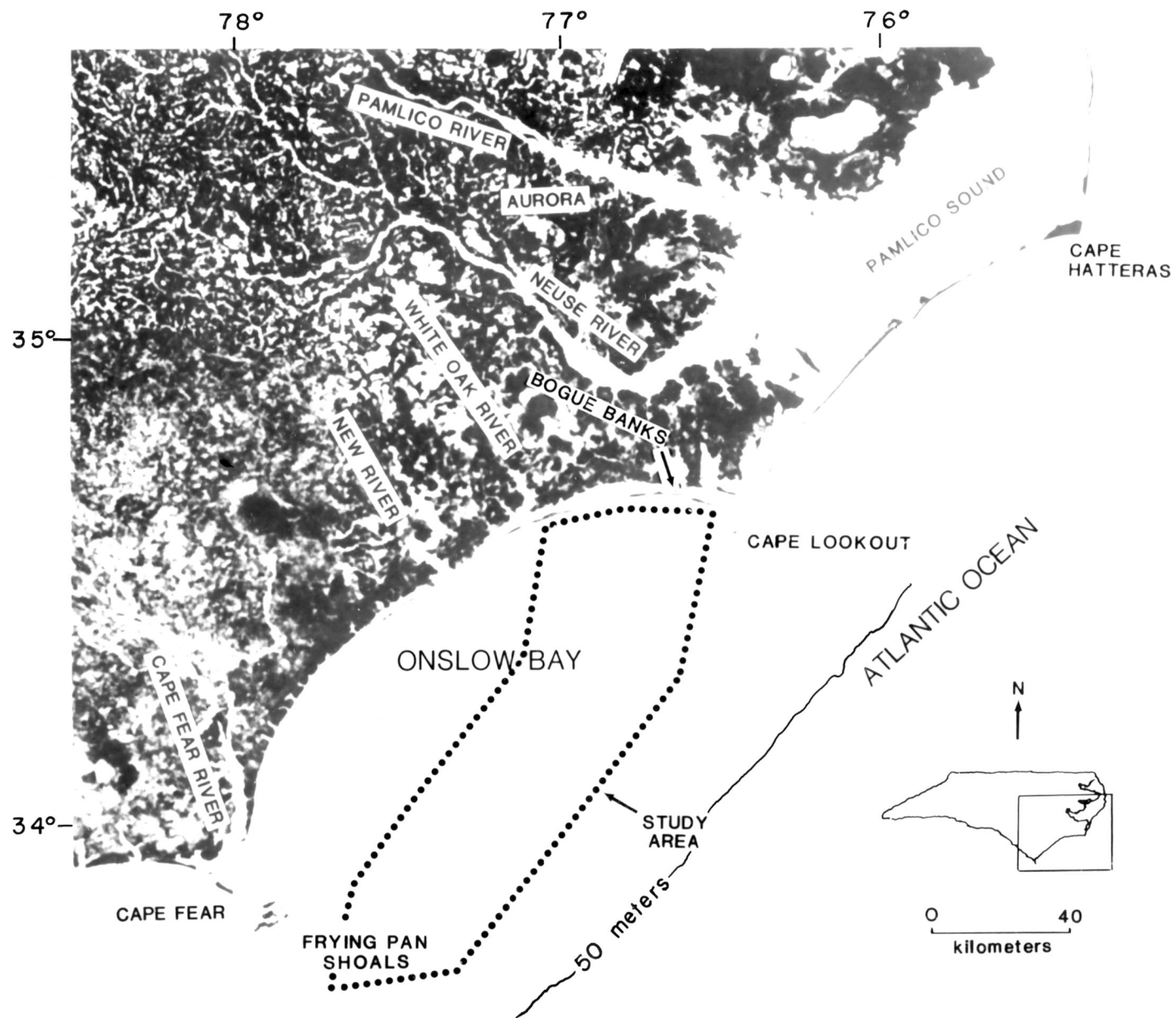
The sedimentary units of these formations consist of complex and interbedded sequences of phosphatic sands, silts, clays, limestones, and dolomites (Weaver and Beck, 1977; Scarborough 1981; Riggs and others, 1982a). The clays include abundant palygorskite, montmorillonite, and sepiolite in the Hawthorn Formation (Heron and Johnson, 1966; Weaver and Beck, 1977) and smectite and illite in the Pungo River Formation of North Carolina (Rooney and Kerr, 1964).

The Miocene phosphatic formations in the southeastern United States formed in response to oceanographic events of global extent (Riggs, 1984). Riggs believes that these highly cyclical deposits with regional patterns of terrigenous, phosphate, and carbonate deposition were primarily responses to the interaction of glacial eustatic sea-level fluctuations, climatic changes, and Gulf Stream dynamics.

Regional Setting

Onslow Bay (Plate 1) is an arcuate bay situated on the

Plate 1. Location map of the southeastern North Carolina coastal plain and continental shelf including Onslow Bay. This map is based upon ERTS NASA/USDA SAT-L 1973, meter band .8 - 1.1.



southeastern Atlantic continental shelf. It is bordered by Bogue Banks and Cape Lookout to the north, by the barrier islands along the outer edge of the North Carolina coastal plain to the west, by Cape Fear and Frying Pan Shoals to the south. The eastern boundary is the shelf edge, which occurs at a depth of approximately 50 meters. Water depths in Onslow Bay average 20 to 30 meters and grade from 6 meters at the base of the lower forebeach to about 50 meters at the shelf edge. The study area is the zone within Onslow Bay where the Pungo River Formation crops out; this area extends from the northeastern portion of the bay, southwestward into the Frying Pan area in southern Onslow Bay and encompasses approximately 9800 km².

Previous Work

Numerous studies of the Pungo River Formation have been conducted since it was first described by Brown (1958) and named by Kimrey (1964; 1965). The most important studies include those of Gibson (1967), Miller (1971; 1982), Brown and others (1972), Scarborough (1981), Katrosh and Snyder (1982), Riggs and others (1982a), Scarborough and others (1982), and Snyder and others (1982a). Pilkey and others (1967) first described phosphatic sands in the Holocene sediments of Onslow Bay. Meisberger (1979) described Miocene phosphatic sands in vibracores taken immediately offshore of

Bogue Banks and Steele (1980) described Miocene phosphatic sands in auger samples drilled on Bogue banks. Subsequent studies of the Pungo River Formation in Onslow Bay include Lewis (1981), Lewis and others (1982), Blackwelder and others (1982), Snyder, S. W. P. (1982), Snyder S. W. P., and others (1982), Riggs and others (1982b, in press), and Waters (1983).

Clay mineralogy of the Pungo River Formation was first described by Rooney (1965) in Aurora, NC. He found montmorillonite and a glauconite illite to be the dominant clay minerals. The presence of a zeolite, clinoptilolite, led to the suggestion that there were volcanic associations present at the time of Pungo River Formation deposition (Rooney and Kerr, 1964; 1967). Potluri (1966) found glauconite present as silt-sized grains in phosphate pellets from the Pungo River Formation in Beaufort County. He related the presence of glauconite and pyrite formation in phosphate pellets to reducing conditions in the environment of deposition. Miller (1971) listed mixed-layer montmorillonite-illite and 1 M illite as the predominant clays along with trace amounts of chlorite in the Pungo River Formation of the North Carolina coastal plain. He noted that clinoptilolite is more abundant in phosphate-rich beds than in clay-rich beds. Meisberger (1979) found glauconite present and in greater abundance than other material within the Miocene phosphorite pellets in northeastern Onslow Bay. Siedlicki (1983) reported smectite and halloysite in the silt

and clay fraction of the Pungo River Formation in Aurora.

Objectives

The clay mineral studies mentioned in the preceding section provide minimal quantitative information concerning the types of clay in the Pungo River Formation. Of the studies mentioned, only Rooney (1965) presents a complete breakdown of clay type with some diagenetic changes. Detailed studies of the clay mineralogy of Miocene sediments in Onslow Bay have not been done.

Clay mineral studies can provide insight on 1) recent and ancient climatic conditions (Biscaye, 1965; Griffin and others, 1968; Grim, 1968; Chamley, 1979; Kennet, 1982); 2) environment of deposition (Grim, 1968; Keller, 1970; Carroll, 1970a; Wilson and Pitman, 1977; Weaver and Beck, 1977); and 3) diagenesis (Keller, 1964; Lucas and Ataman, 1968; Grim, 1968; Carroll, 1970b; Reynolds, 1970; Drever, 1971; Gibbs, 1977; Paton, 1978).

The purpose of this study is to determine the clay mineralogy of the Pungo River Formation in Onslow Bay. More specifically, the objectives are:

- 1) to identify the major and minor clay minerals;
- 2) to determine the lateral and vertical distribution of the clay minerals in the Miocene sediments;

- 3) to establish authigenic/diagenetic alteration of the clay fraction; and
- 4) to interpret paleoclimatic conditions and depositional environment at the time of sediment formation.

GEOLOGIC SETTING

Structure

Onslow Bay is situated on the northern flank of the Carolina Platform (Snyder, S. W. P., 1982). The platform is a major first-order, large-scale feature consisting of pre-Jurassic continental crust that has affected sedimentation throughout the Cretaceous and Tertiary in this region (Snyder, S. W. P., 1982). Snyder described various smaller scale structures which occur on the platform and in the Onslow Bay area (Fig. 1) and have controlled Neogene sedimentation, including the following:

1) An Oligocene deltaic depositional series of prograding clinoforms occurs in western Onslow Bay and the adjacent coastal plain (Lawrence, 1975; Meisberger, 1979; Lewis and others, 1982).

2) The White Oak Lineament, a north to south trending monoclinical erosional scarp in northern and central Onslow Bay. The scarp might have been initially associated with a tensional fault system in the Carolina Platform (Snyder, S.W.P., 1982), however, recent seismic evidence suggests that it is entirely an erosional feature. Snyder believes that the scarp was cut by the Gulf Stream.

3) The Cape Lookout High lies north of Onslow Bay. This second-order topographic high, trending almost east to west, separates the adjacent Aurora and Northeastern Onslow Bay embayments (Scarborough, 1981; Snyder, S.W.P., 1982).

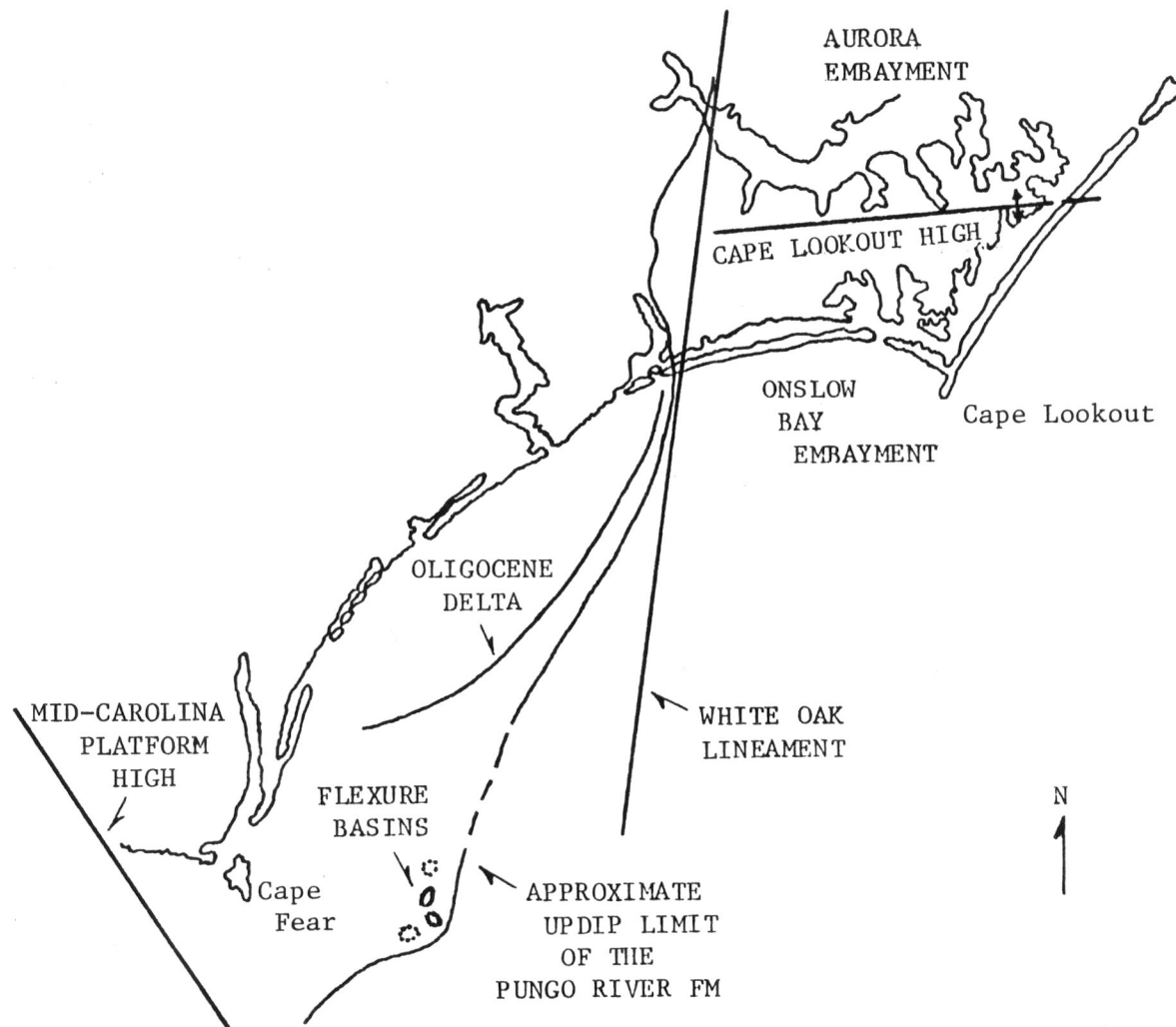


Figure 1 - Location map of structural and topographic features in the Onslow Bay area (From Snyder, S.W.P., 1982).

4) A series of flexure basins occur near Frying Pan Shoals. Snyder (S.W.P., 1982) believes that they may represent the surficial expression of differential subsidence in the crystalline basement.

5) The Mid-Carolina Platform High is a broad structural feature extending from Cape Romain, South Carolina, to central Onslow Bay, North Carolina. It is analagous to the Cape Fear Arch and is now interpreted to be the shallowest portion of continental crust on top of the Carolina Platform (Snyder, S. W. P., 1982).

Stratigraphy

The lowermost units identified in the Onslow Bay sedimentary sequences are moldic biomicrites with interbedded calcarenite sand and grayish green, slightly clayey, carbonate rich, quartz sands. These sands are tentatively assigned to the Oligocene Belgrade Formation and the lower Miocene Silverdale Formation, respectively (Baum, and others, 1979; Riggs and others, 1982b, in press). These units are unconformably overlain by the Miocene Pungo River Formation.

Three depositional sequences, separated by unconformities and consisting of at least eighteen depositional units each composed of interbedded lithofacies, have been identified in the Pungo River Formation of Onslow Bay using high resolution seismic profiling (Snyder, S. W. P., 1982) (Figs. 2 and 3). The three depositional sequences form a broad northeast to southwest outcrop belt of the Pungo

GEOCHRONOMETRIC SCALE IN M.Y.		EPOCHS		STAGE	MIOCENE DEPOSITIONAL SEQUENCES OF SNYDER (S. W. P., 1982)	PUNGO RIVER Fm. UNITS OF LEWIS (1981)	PUNGO RIVER Fm. UNITS OF RIGGS AND OTHERS (1982)	PUNGO RIVER Fm. UNITS OF SNYDER (S. W. P., 1982)	PUNGO RIVER Fm. UNITS OF THIS STUDY	FACIES DESCRIPTION														
10	LATE		MESSINIAN																					
			TORTONIAN								D	NO3	BBF-5	S5	DOLOSILTY QUARTZ SAND									
													BBF-4	S4										
													BBF-3	S3										
			SERRAVALLIAN								NO1/ NO2	BBF-2	S2	PHOSPHATIC, SILTY QUARTZ SAND										
	BBF-1	S1		PHOSPHATIC, MUDDY QUARTZ SAND																				
	15	MIDDLE		SERRAVALLIAN	BBF	SERRAVALLIAN																		
												LANGHIAN	AF	LANGHIAN										
																					BURDIGALIAN	FPF	BURDIGALIAN	
												G	FP5	FPF-6	B6	FORAMINIFERAL, QUARTZ MUDDY SAND								
FPF-5														B5	SILTY QUARTZ SAND									
EARLY		BURDIGALIAN	FPF-4	B4																				
			FPF-3	B3																				
			H	FP4		FPF-2	B2	PHOSPHATIC, QUARTZ SANDY MUD																
			I	FP3		FPF-1	B1	MUDDY, PHOSPHORITE QUARTZ SAND																
			J	FP2	MUDDY, FORAMINIFERAL, PHOSPHORITE QUARTZ SAND																			
	K		FP1	MUDDY, FORAMINIFERAL, PHOSPHORITE SAND																				
	AQUITANIAN																							

Figure 2. Miocene seismic units of Onslow Bay and their lithology (Lewis, 1981; Riggs and others, 1982b; Snyder, S. W. P., 1982). Shaded areas designate sampled units.

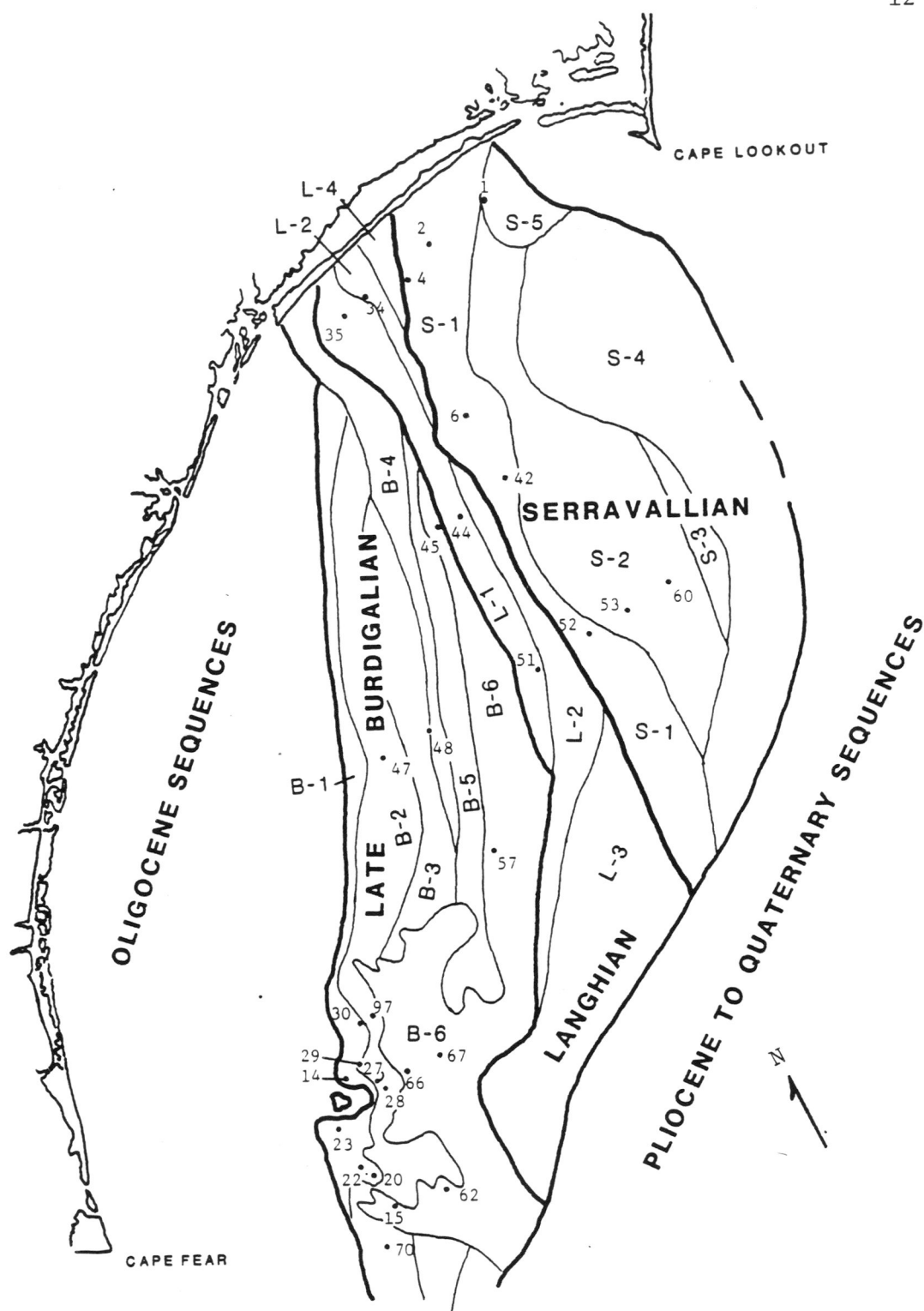


Figure 3. Location map showing 1) the outcrop belt of the Pungo River Formation across Onslow Bay; 2) the 3 depositional sequences of the Pungo River Formation defined by seismic stratigraphy and biostratigraphy; 3) 15 of the 18+ depositional units defined by seismic stratigraphy; and 4) the location of vibracores used in this study. The seismic sequences and units are from Snyder (S. W. P., 1982) and the nomenclature of the units are for this study only. • = vibracore hole.

River Formation across Onslow Bay. The sequences, deposited along the eastern flank and around the nose of the Mid-Carolinian Platform High, dip east and southeast off of the High (Lewis, 1981; Snyder, S. W. P., 1982; Riggs, 1984).

The depositional sequences, consisting of the Burdigalian (6 depositional units), the Langhian (4 depositional units), and the Serravallian (5+ depositional units) were probably formed in response to 1-10 million year duration third-order sea level cycles (see p. 67) (Snyder, S. W. P., 1982). Each depositional unit is characterized by vertical and lateral sediment patterns defined by the terrigenous, phosphatic, and calcareous components, and deposited in response to the transgressive portion of fourth-order sea-level cycles of relatively short (< 1 million years) duration (Riggs, 1984). The cycles also have a regressive stage which is characterized by non-deposition, erosional scouring and channeling, and diagenetic alteration (Riggs, 1984).

The Pungo River Formation in Onslow Bay is unconformably overlain by 1) various Pliocene and Pleistocene carbonate sequences and 2) thin and variable thicknesses of Holocene sands.

PROCEDURES

Sampling

Samples were obtained from vibracores taken in Onslow Bay in May and October of 1980 from the R/V Eastward (cruise #E-3-80) and the R/V Endeavor (cruise #EN-057), respectively, under the direction of Dr. S. R. Riggs. Lewis (1981) described the acquisition and subsequent processing of the cores, as well as preparing core descriptions. Core locations within the study area are shown in Figure 3. The vibracores and samples used in this study are listed in Table 1.

The original purpose of the study was to describe the mineralogy and texture of the terrigenous component of the Pungo River Formation. Preliminary examination of Lewis' data, the vibracores, and whole rock analyses by x-ray diffraction showed quartz to be the primary terrigenous mineral. Since terrigenous clays were not considered at that time, quartz content in Lewis' lithofacies formed the basis for sample selection. An arbitrary value of >20% quartz was used to select units for study.

Riggs and others (1982b) developed an economic classification of the sediment units in the Frying Pan and northeast Onslow Bay phosphate districts (Fig. 3). Subsequently, (Snyder, S. W. P., 1982) produced a detailed seismic-stratigraphic classification for the entire Miocene section in Onslow Bay (Fig. 2). This latter work indicated gaps where individual units had been either sparsely sampled

UNIT	CORE	SAMPLE No.	DEPTH BELOW SEDIMENT SURFACE (meters)
S-5	1	1	5.00-5.25
S-2	53	1	1.25-1.50
S-2	53	2	3.75-4.00
S-2	53	3	5.25-5.50
S-2	60	1	5.50-5.75
S-1	2	1	4.50-4.75
S-1	4	1	5.50-5.75
S-1	6	1	0.50-0.75
S-1	6	2	3.00-3.25
S-1	6	3	7.25-7.50
S-1	42	1	2.50-2.75
L-2	34	1	2.00-2.25
L-2	52	1	3.50-3.75
L-1	35	1	3.75-4.00
L-1	44	1	1.75-2.00
L-1	44	2	3.00-3.25
L-1	44	3	5.50-5.75
L-1	51	1	4.00-4.25
B-6	15	1*	1.50-1.75
B-6	45	1	1.75-2.00
B-6	45	2	3.50-3.75
B-6	45	3	5.00-5.25
B-6	62	1*	3.50-3.75
B-6	62	2	4.25-4.50
B-6	62	3*	5.00-5.25
B-6	66	1	3.00-3.25
B-6	67	1	3.50-3.75
B-6	67	2*	5.00-5.25
B-6	67	3*	7.00-7.25
B-6	70	1*	2.00-2.25
B-5	48	1	4.00-4.25
B-5	57	1	4.75-5.00
B-2	27	1*	1.50-1.75
B-2	27	2*	3.00-3.25
B-2	27	3*	5.00-5.25
B-2	28	1*	2.00-2.25
B-2	47	1	5.00-5.25
B-2	63	1	2.25-2.50
B-2	97	1*	3.25-3.50
B-1	20	1	1.00-1.25
B-1	20	2	3.50-3.75
B-1	20	3	5.50-5.75
B-1	23	1	2.00-2.25
B-1	29	1	2.75-3.00
B-1	14	1	4.75-5.00
B-1	22	1	4.75-5.00
B-1	30	1	1.00-1.25
B-1	30	2	1.75-2.00
B-1	30	3	2.50-2.75
B-1	30	4	5.00-5.25

Table 1. Vibracores and the sediment samples used in this study along with their depth below the sediment surface. *= analyzed for clay mineralogy only.

or not sampled at all for the present study, and caused some units to be oversampled. When Snyder's work was completed, the largest portion of the laboratory work had been finished and time limitations precluded examining new samples from the gaps in the same detail as the previously sampled units.

Laboratory Analyses

The general laboratory procedures are outlined in Figure 4. Samples were split using the quartering method (Carver, 1971). Separate splits were made for each sieve and pipette analysis. According to Folk (1980), the two analyses can be conducted in this manner if the mud content is relatively high and the sample is thoroughly mixed before splitting. He also said that one must assume that both splits have the same proportion of constituents.

Each split to be sieved or pipetted for grain size analysis was dispersed (Folk, 1980) using Calgon and placed in a shaker for 30 minutes. The dispersed sample was wet sieved in a U.S. Standard ASTM 8", 4 phi ($\emptyset$) (0.0625mm) sieve to separate the coarser than 4 phi fraction from the finer than 4 phi fraction.

Sieve Analysis. The coarse fraction was oven dried at 60° C overnight then sieved through a nest of 0.5 phi intervals of U. S. Standard ASTM 8" sieves using a Tyler Rotap Sieve Shaker. Each size fraction was weighed on a Mettler H10T Balance. Individual and cumulative percentages (Appendix A) were calculated for each size interval using the

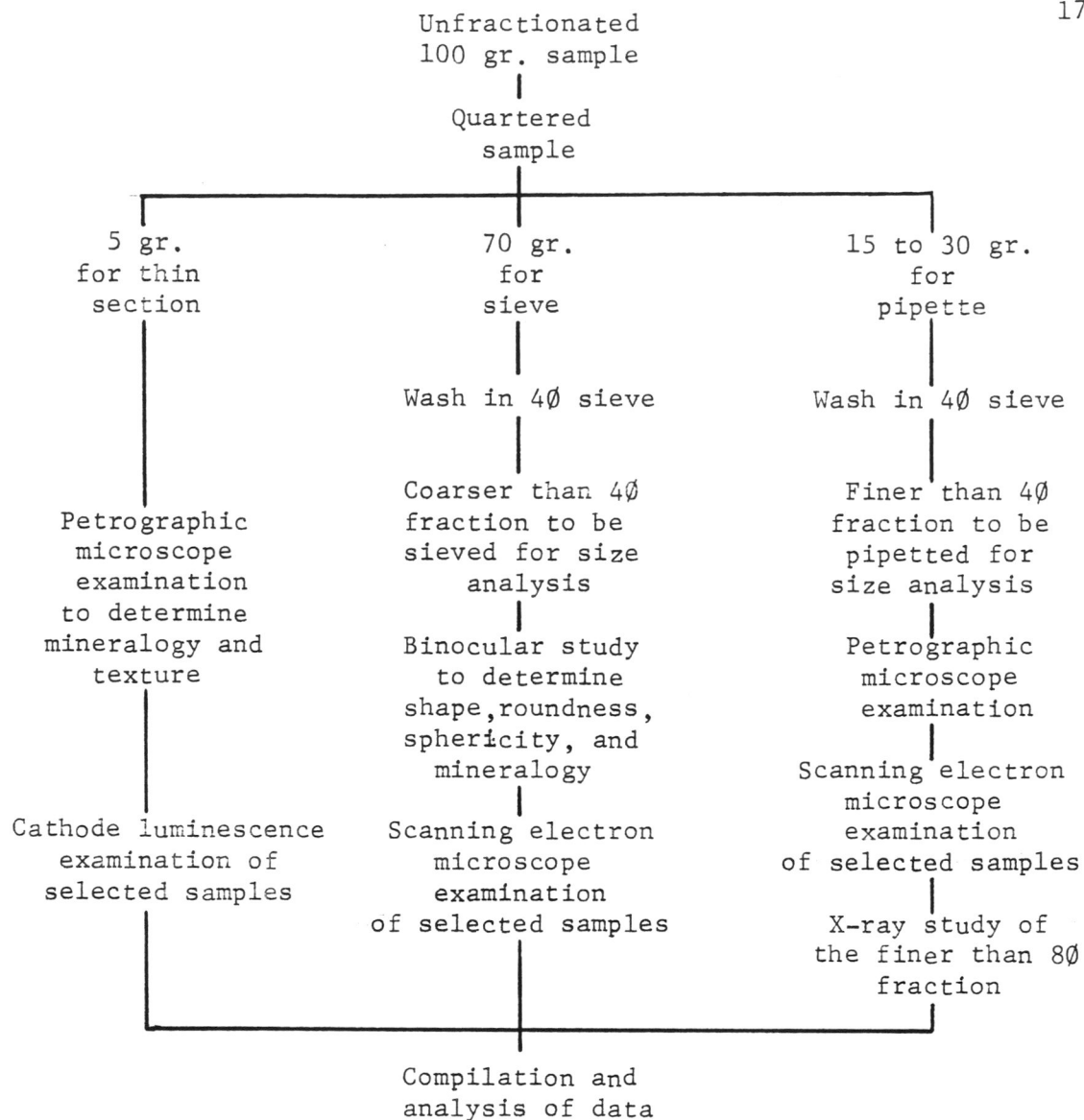


Figure 4. Flowchart of procedures used to accomplish the laboratory analysis.

following formulas (Folk, 1980):

$$(1) \text{ Cumulative percent} = \frac{\text{Cumulative weight}}{\text{Total sample weight}} \times 100\%$$

$$(2) \text{ Individual percent} = \frac{\text{Individual weight}}{\text{Total sample weight}} \times 100\%$$

Pipette Analysis. The fine fraction from each 15 to 30 gram split was pipetted from 1000 ml cylinders in 1 phi intervals. Withdrawal times for the pipette analyses and individual and cumulative percents were computed using the following formulas (Folk, 1980):

$$(3) \quad T = \frac{D}{1500 \times A \times d^2} \quad \text{where: } T = \text{time in min}$$

$D = \text{depth in in}$
centimeters
 $A = \text{density of clay and quartz dependent on temperature}$
 $d = \text{particle diameter}$

$$(4) \text{ Cumulative percent} = \frac{100(S + F - P)}{S + F}$$

where: $S = \text{weight of sand on the } 4 \phi \text{ sieve}$
 $F = \text{amount of mud in the cylinder}$
 $P = \text{quantity of each pipette sample times } 50$

$$(5) \text{ Individual percent} = \quad CW$$

where: CW is the difference in cumulative weight %

Thin Section Analysis. The split samples for thin sections were placed in 40ml paper cups, mixed with epoxy, and slabbed for thin sections. The thin sections were stained with sodium cobaltinitrite and amaranth red to aid in

the identification of potassium and plagioclase feldspars, respectively (Carver, 1971). Preparation and staining techniques of the thin sections are listed in Appendix B. Cover slips were not used in order to allow for study by cathodoluminescence.

Percentages of the minerals present in each thin section are based on a 300 grain point count using the line method (Carver, 1971) with a 0.5 mm interval on the mechanical stage. This technique yielded a counting error of 0.7% to 3% (Folk, 1980).

Sediment characteristics. Color determinations of the total sediment were based on wetted samples in sunlight utilizing the color chart by Goddard and others (1975). Characteristics of the sand and silt grains, including degree of rounding and sphericity, were based on charts from Scholle (1979) and Payne (1974). Sphericity of sand and silt sized grains in thin section were measured along the long and short axis with a calibrated micrometer ocular scale. In order to insure randomness, the first 100 grains encountered in the point count were used to determine average sphericity and roundness.

Clay Analysis. Clay samples were prepared for x-ray diffraction analysis utilizing a procedure from Carroll (1970a) (Fig. 5). However, the clay was separated from the silt by pipette instead of centrifuge. After pipetting, the samples were centrifuged at 2500 RPM for 5 minutes to separate the water and the clay. The water was decanted, and

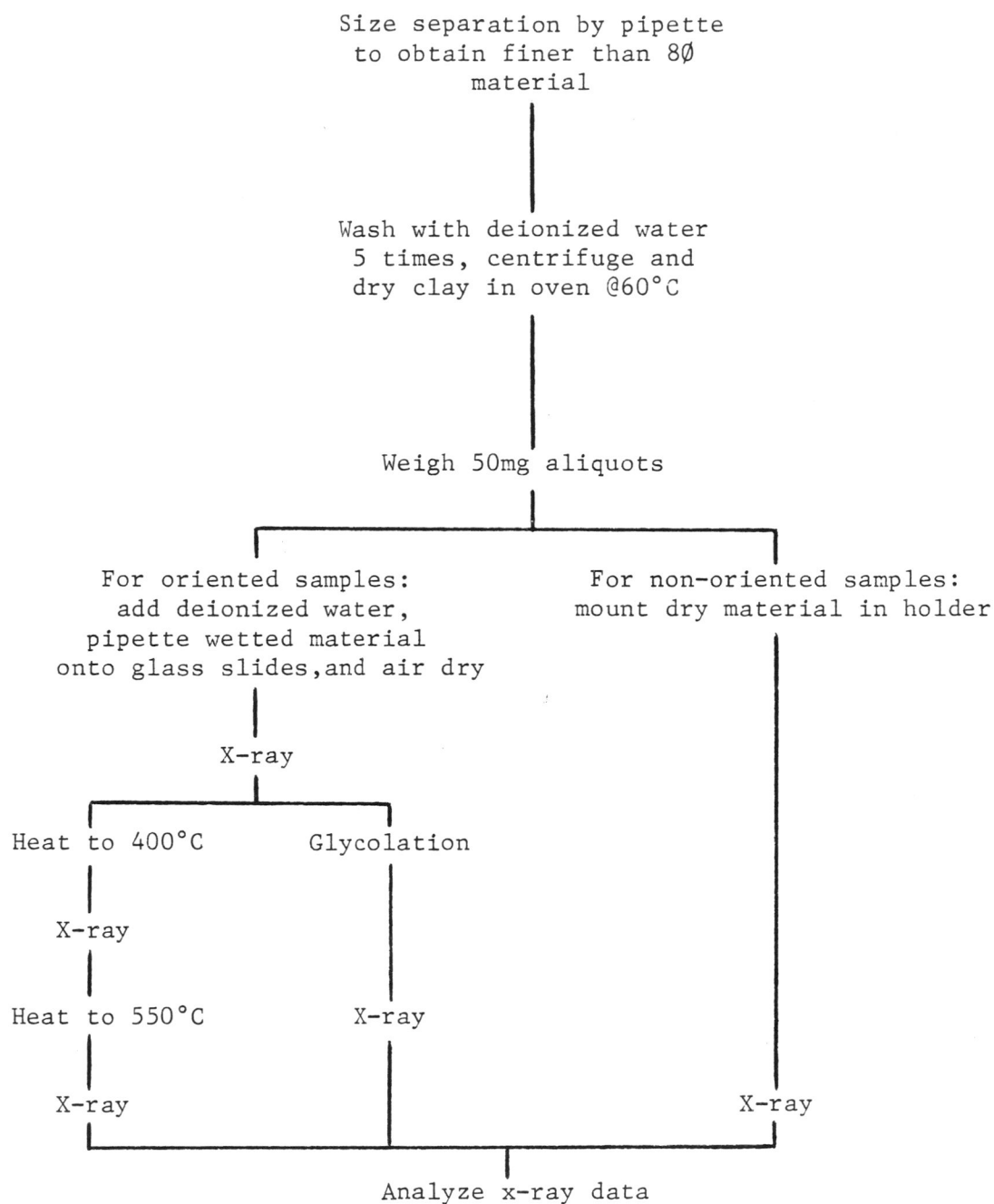


Figure 5. Flowchart of routine treatments to the finer than 8 phi material of all samples.

the clay was washed by stirring in deionized water for 5 minutes and recentrifuging at 2500 RPM for 5 minutes. All samples were washed five times, then placed in an oven at 60° C until dry. Deionized water was added to the clay to make a slurry, which was pipetted onto a glass slide and allowed to air dry, producing a preferred basal orientation of the clay particles on the slide. Powdered material of the finer than 8 phi fraction was packed into fiberglass sample holders and lightly pressed with a spatula to obtain relatively unoriented mounts. Oriented slides enabled identification and quantification of the clay groups while unoriented slides were utilized for more detailed identification of the clay types (Thorez, 1976).

Ethylene glycol treatments were used to identify expandable clay groups (Thorez, 1976). Ethylene glycol, $C_2H_6O_2$, is an organic compound that will cause some clay, such as smectite, to expand by adsorbing the compound onto interlayer surfaces. The procedure, which was routinely done for all oriented samples, consisted of suspending the slides over glycol heated to 60° C until they were moist from the vapor, followed by x-ray analysis. Heat treatments to all oriented slides consisted of 1) heating to 400° C for one hour to test for phillipsite, a zeolite, and to collapse expandable clays; and 2) heating to 550° C for one hour to test for kaolinite structural collapse.

Thorez (1976) listed two techniques to identify the smectite species: K and Mg saturations followed by treatment

with glycerol. The procedures from each of five samples (52-1, 44-2, 23-1, 22-1, and 6-3) involved obtaining two aliquots of finer than 8 phi material. One aliquot (50 mg) was saturated in a 1N solution of K acetate and the other aliquot (50 mg) was saturated in a 1N solution of Mg-acetate. The saturations were accomplished by: 1) washing the samples with the ionic compounds; 2) centrifuging to remove excess fluid; 3) sedimenting the remainder onto glass slides; and 4) allowing them to air dry. The treated samples were first x-rayed, then treated with glycerol (glycerolation), and x-rayed again. Glycerol ($C_3H_8O_3$), an organic compound, was applied in the same manner as ethylene glycol.

In order to differentiate between $7\text{\AA}$ chamosite and $7\text{\AA}$ kaolinite, a procedure by Abdel-Kader and others (1978) was used. According to the procedure, 50 mg of clay is 1) washed twice with 5 ml 1 N lithium chloride (LiCl) solution for 5 minutes; 2) washed once with 4 ml .1N LiCl and allowed to stand for 2 hours at 50°C ; 3) washed with 9 ml of dimethylsulfoxide (DMSO) for 5 minutes; 4) washed with 90% DMSO, < 10% water, and < .01N LiCl and allowed to stand overnight at 90°C ; 5) centrifuged to separate the supernatant liquid; 6) mounted on glass slides in routine manner described in the procedures and x-rayed. The procedure causes the $7\text{\AA}$ kaolinite peak to shift to $11.2\text{\AA}$ while the chamosite peak remains at $7\text{\AA}$ (see p. 49). Three samples (1-1, 6-1, and 30-3) were treated with the procedure.

Samples were x-rayed using a General Electric (Diano)(XRD-6) X-ray Diffractometer with a Model 700 Detector. Routine instrument settings are given in Table 2. Pulse height analyses were conducted periodically to achieve and maintain optimum machine performance. Clay mineral standards from the University of Missouri were analyzed to insure accurate clay mineral identification and relative crystallinity of the illite.

Determinations of clay mineral percentages are close approximations at best (Biscaye, 1965). The method for calculating clay mineral percentages of montmorillonite, illite, kaolinite, and chlorite was adapted from Biscaye. I included the calculation of a $12\overset{\circ}{\text{\AA}}$ clay component which is interpreted to be sepiolite. The calculation used in this study consisted of: 1) identifying the basal (001) peaks from the glycolated runs, 2) determining the area under the peaks, and 3) using these values in the following formula:

$$(6) \% \text{ of clay mineral in sample} = \frac{100 \times \text{basal peak area of mineral}}{17\overset{\circ}{\text{\AA}} + 12\overset{\circ}{\text{\AA}} + 10\overset{\circ}{\text{\AA}} + 7\overset{\circ}{\text{\AA}}}$$

where: $17\overset{\circ}{\text{\AA}}$ = peak area of the $17\overset{\circ}{\text{\AA}}$ component times 1
 $12\overset{\circ}{\text{\AA}}$ = peak area of the $12\overset{\circ}{\text{\AA}}$ component times 1
 $10\overset{\circ}{\text{\AA}}$ = peak area of the $10\overset{\circ}{\text{\AA}}$ component times 4
 $7\overset{\circ}{\text{\AA}}$ = peak area of the $7\overset{\circ}{\text{\AA}}$ component times 2

To evaluate precision of the clay sample preparation technique, x-ray diffractometer, and data quantification, sixteen replicate analyses were run on two samples. Both samples were divided into 4 subsamples each. All subsamples

Console

Milliamps	7
Kvp	45
Meter Range	High-A

Diffractometer

Radiation	CuK α $\lambda=1.5418$
Filter	Ni
Slits	1° mr and $.2^\circ$
Scan rate	$1^\circ/30\text{sec}$; $1^\circ/\text{min.}$

Detector

Range	250
Time constant	2.5
Amp gain	16
Potentiometer	140 kv
PHS	$E_L-280; E_u-441$
Rate meter	25 seconds

Table 2. Routine instrument settings for the x-ray analysis conducted on a General Electric (Diano) XRD-6 Diffractometer.

were prepared, mounted on glass slides, and glycolated in the same manner. Each slide was subjected to four runs on the x-ray goniometer. On the first two runs, a slide was x-rayed from 2° to 13° (2θ). The slide was removed from the sample holder in the goniometer and replaced again for runs three and four.

The clay mineral percentages were then calculated for each x-ray run. Statistical parameters of mean ($\bar{x}$) and standard deviation (s) were calculated for each clay mineral in each sample. Precision, or the coefficient of variation (c), was calculated (Till, 1974):

$$(7) \quad c = \frac{100s}{\bar{x}}$$

A plot of means versus coefficients of variation (Fig. 6) shows a range in precision error of 3 to 24% with precision improving as mean clay percent increases.

Crystallinity index is a factor used to express 1) the degree of mineral crystallinity and 2) the degree of degradation of the crystal lattice of the clay. It may also reflect trends of weathering or diagenetic factors present either during or after deposition (Thorez, 1976). Crystallinity indices were determined for all illite and smectite minerals present in the samples. Crystallinity of the $17\text{\AA}$ (smectite) component was determined by the valley/peak ratio method (Biscaye, 1965; Thorez, 1976 (Fig. 7a). Crystallinity of the $10\text{\AA}$ (illite) component was determined by peak characteristics such as height and width

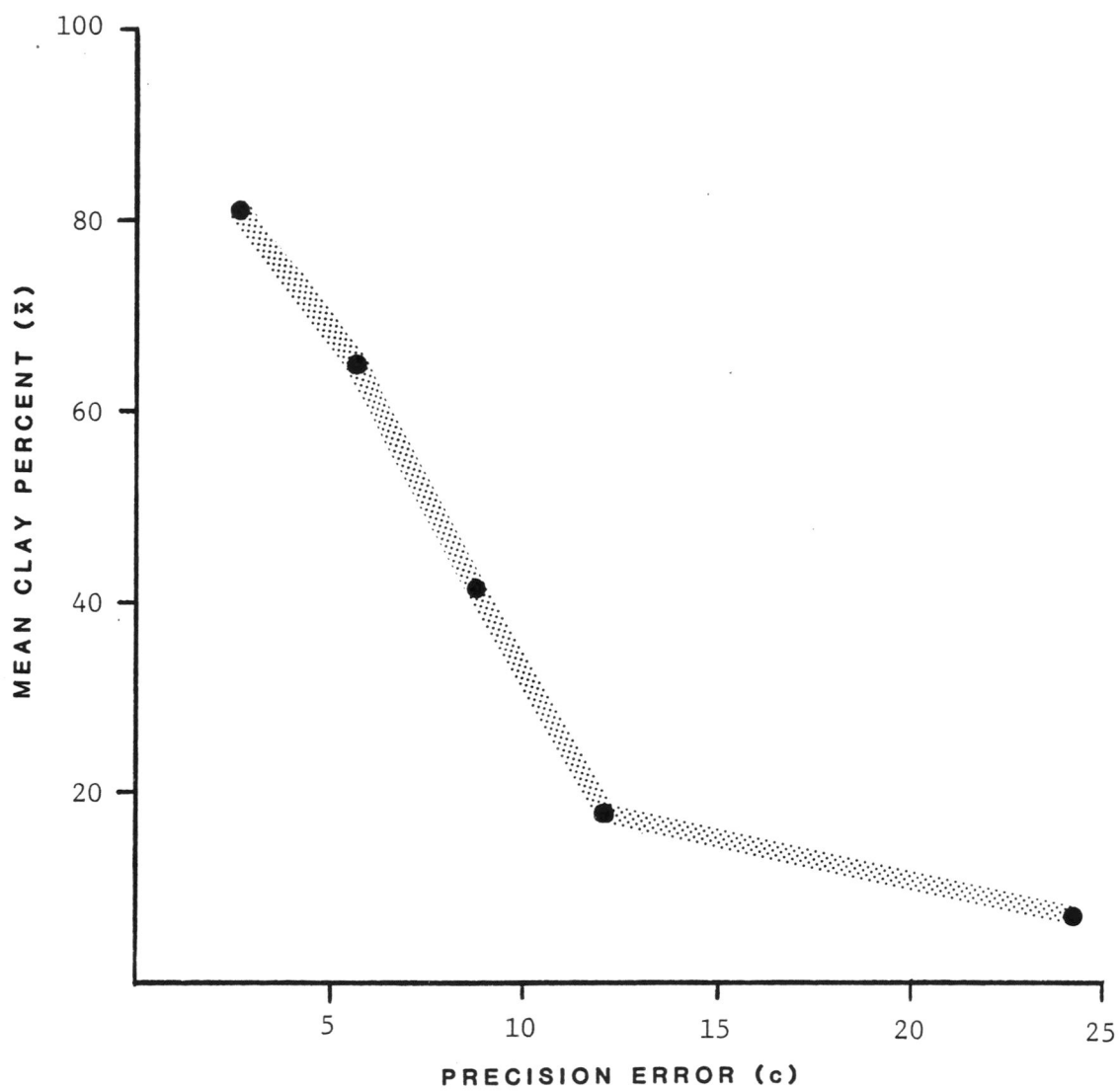


Figure 6. Plot of coefficient of variation (c = precision error) vs. mean clay percent.

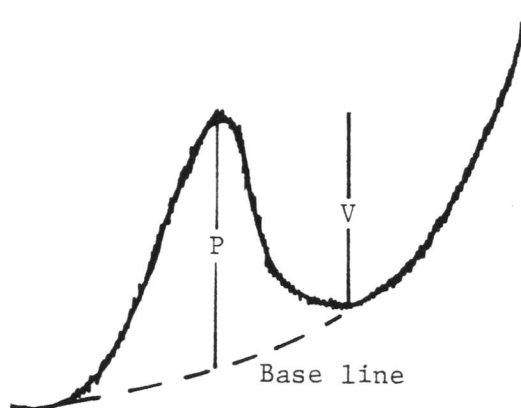


Figure 7a. Method used by Biscaye (1965) and Thorez (1976) to determine crystallinity of the basal smectite peak using the formula, $C_s = V/P$. C_s = smectite crystallinity; V = height of valley from apex to base line; P = height of peak from apex to base line.

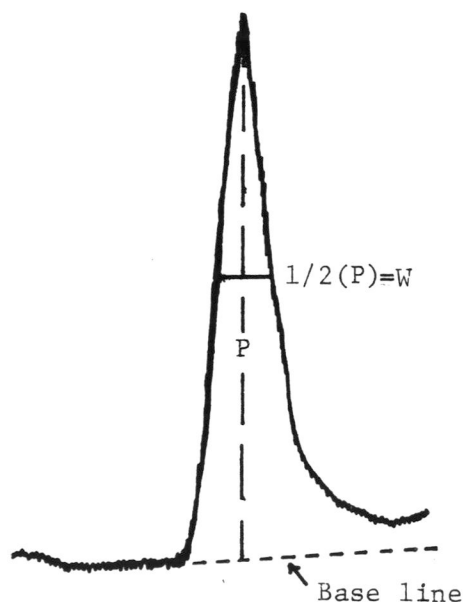


Figure 7b. Method used by Thorez (1976) to determine crystallinity of the basal illite peak using the formula, $C_I = P/W$. C_I = illite crystallinity; P = height of peak from apex to base line; W = width of peak at $1/2$ peak height. Diffractogram is a well crystallized illite standard where $C_I = 10$. Crystallinities of Onslow Bay illites are compared to the standard where '0' is most poorly crystallized and '10' is most well crystallized.

(Fig. 7b).

Cathodoluminescence. A Nuclide Model ELM 2A Luminoscope was used for cathodoluminescence examinations of ten thin sections to detect authigenic overgrowths on quartz grains. Samples were selected (1-1, 2-1, 4-1, 6-1, 6-2, 20-3, 30-2, 44-2, 62-2, and 63-1) which contained many large (4 phi or coarser) quartz grains which allowed for easier examination. The thin sections were cleaned with alcohol to remove any oils that might contaminate the helium atmosphere in the luminoscope sample chamber.

Scanning Electron Microscopy (SEM). Scanning electron microscopic analyses were performed on sand and silt grains from samples using an ISI-40 instrument. The purpose of this analysis was to detect any crystal terminations on quartz grains or any cleavage present in feldspars to determine their relative 'freshness'. Crystal terminations or cleavage might go unnoticed with lower magnification of optical microscopes.

Approximately 30 milligrams of material from the sieve and pipette analysis of each sample were combined in a test tube with a 10% HCL solution, centrifuged at 2500 RPM for 5 minutes to separate the supernatant, washed twice with deionized water, and recentrifuged after each washing. After each washing the washed samples were dried, mounted on SEM stubs, and sputter coated with gold/palladium.

Statistics. The statistical parameters used for the textural analysis included: 1) graphic mean phi size; 2)

inclusive graphic standard deviation (sorting); 3) inclusive graphic skewness and kurtosis; and 4) mode (Folk, 1980). Values obtained from percentiles in cumulative probability curves (Appendix C) were used in statistical parameter formulas (Appendix D). The mode was determined using the graphic procedure of Folk (1980) which is also described in Appendix D. Maturity was determined by: 1) using the clay matrix and sorting values from the petrographic study; 2) inserting those values into the flow chart (Appendix E); and 3) assigning a classification to the sample of immature, submature, mature, or supermature.

RESULTS

Textural Analysis

Textural analyses of the total, unfractionated samples were performed to characterize the sediment with respect to sand, silt, and clay components and to determine any inter-relationship of the clay and non-clay components. Textural parameters of the samples (Appendix F) are summarized in Table 3, while sand, silt, and clay concentrations (Appendix G) are summarized in Figure 8. Textural parameters and sand-silt-clay concentrations show the Burdigalian and Serravallian depositional sequences have similar grain size characteristics and both sequences are different from the Langhian.

Sediments in the Burdigalian, Langhian, and Serravallian sequences are poorly sorted with mean phi sizes in the fine sand to coarse silt ranges. Twenty-six out of 39 samples are bimodal or trimodal which may be indicative of reworking, multiple sediment sources, or sea-level fluctuations. Studies on shelf sediments have shown that relict sediments may be in disequilibrium with processes currently acting on them, particularly during transgressive/regressive sea-level fluctuations (Emery 1968; Swift and others, 1971; Reineck and Singh, 1973). Thus, the modality of the sediments may be the combined results of 4th-order sea-level cycles of the Pungo River Formation (Riggs, 1984) and the multiplicity of origins of terrigenous, authigenic, and biogenic components of the sediments.

	N.A.	Terr. (%)	Sand (%)	Silt (%)	Clay (%)	Mean Size (ϕ)	Sorting	Skewness	Kurtosis
Serravallian	11	58	64	24	12	3.5 vf sand	4.1 x poor	1.4 sf skewed	2.2 v leptokurtic
Langhian	7	43	45	39	16	4.8 c silt	4.2 x poor	.20 f skewed	1.5 leptokurtic
Burdigalian	21	43	62	27	11	3.9 vf sand	3.5 v poor	.41 sf skewed	1.7 v leptokurtic

Table 3. Summary of textural data for the 3 depositional sequences in the Pungo River Formation, Onslow Bay. Terrigenous percentages are taken from point counts of 300 points in the petrographic analysis. All other percentages were derived from seive and pipette analysis. N.A. = number of samples analyzed; Terr = terrigenous.

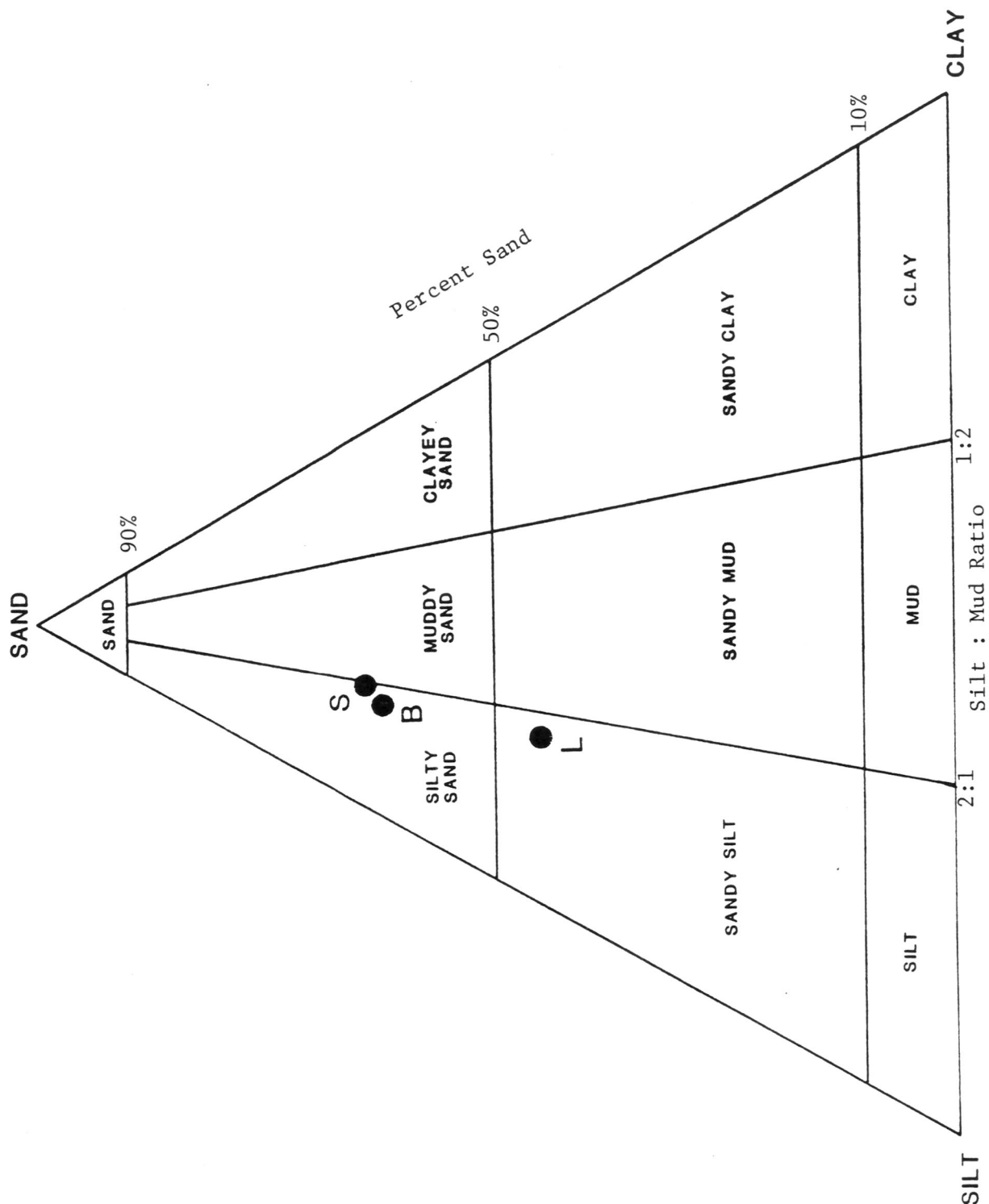


Figure 8. Ternary diagram summarizing sand-silt-clay percentages for the Burdigalian (B), Langhian (L), and Serravallian (S) depositional sequences. Classification is based on Folk (1980).

The dispersion technique used to break down the clay fractions may be a problem with respect to the textural characterization of the samples. The technique uses Calgon to disperse the finer than 8 ϕ sediment size fraction (Folk, 1980). Clay minerals (e.g. kaolinite) in the finer than 8 ϕ size fraction can flocculate upon entering marine waters and settle out with silts, as demonstrated by Gibbs (1977). Filter feeders may also aggregate fine particles and deposit them as larger (coarser than 8 ϕ) fecal pellets (Pryor, 1975; Potter and others, 1980). Consequently, disaggregation procedures using Calgon would tend to cause the grain size distribution to be skewed to the finer side, producing a distortion from the grain sizes actually deposited. The fine to strongly fine skewness of the samples (Table 3; Appendix F) might reflect this laboratory disaggregation.

Petrographic Analysis

Thin sections of the Pungo River sediments of Onslow Bay were examined in order to determine the types and distribution of terrigenous minerals to supplement the x-ray analysis. Percentages of minerals present in the samples are shown in Appendix H. Grain size and roundness values for the minerals are shown in Table 4. Matrix material, consisting of quartz, carbonate minerals, and clays, is ubiquitous in all samples. Quartz is the most abundant terrigenous mineral in the sand and silt fraction of all samples and is subdivided into monocrystalline and polycrystalline types. Potassium and plagioclase feldspars, muscovite mica, and zircon are present as accessory minerals. Small amounts of glauconite, chert, and opaque minerals are also present in the Pungo River Formation sediments.

Percentages of terrigenous component in the sand and silt size range are generally higher in northern Onslow Bay samples than in central and southern samples. Carbonate materials are present in all units, with calcium carbonate shell being the dominant form in southern Onslow Bay samples and dolomite rhombs in the northern Onslow Bay samples (T. L. Stewart, pers. comm., 1984). Phosphate is present in most samples, having its highest concentration in the southern Onslow Bay samples.

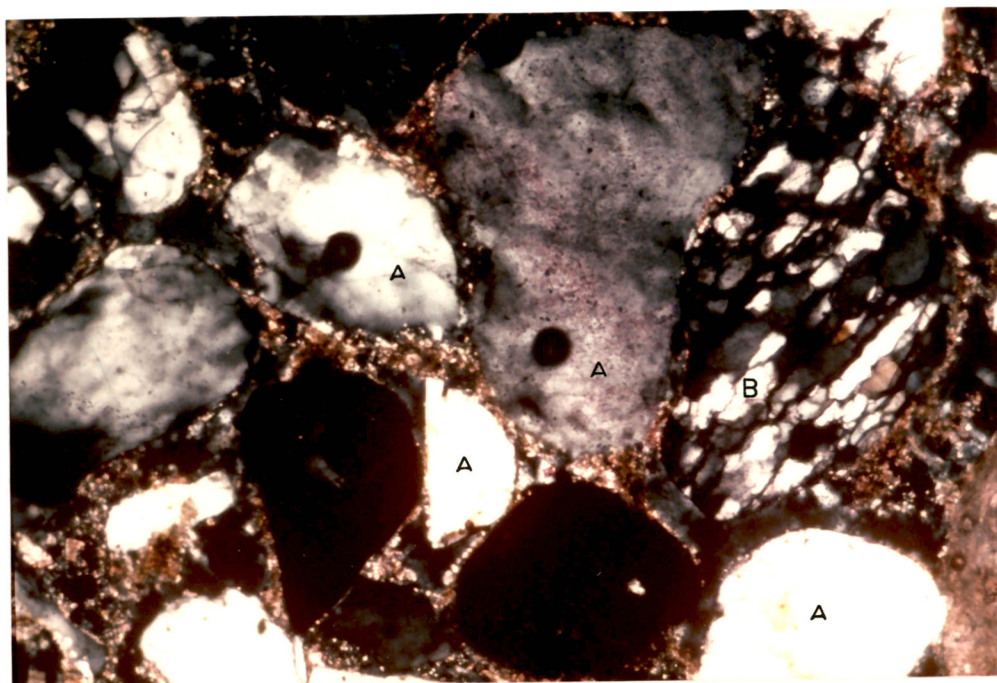
Monocrystalline quartz. This category comprises 95% to 100% of the quartz in the Pungo River Formation sediments (Plate 2a). Grain surfaces are generally smooth with minor

	Distribution in total sediment (%)	Size Range	Roundness	Sphericity
Monocrystalline quartz	10 - 79	0.005mm (47-1) - 0.80mm (4-1)	Subangular - subround	Moderate
Polycrystalline quartz	T - 1	0.10mm (20-3) - 2.30mm (4-1)	Subround - round	High
Chert	0 - 2	0.02mm (30-1) - 0.90mm (2-1)	Subround	Moderate
Potassium feldspar	0 - 6	0.05mm (6-3) - 0.65mm (6-1)	Subround	Moderate
Twinned feldspar	0 - 2	0.01mm (14-1) - 0.14mm (6-1)	Subround	Moderate
Untwinned feldspar	0 - 3	0.01mm (14-1) - 0.25mm (20-3)	Subround	Moderate
Muscovite mica	0 - 2	0.05mm (4-1) - 0.25mm (67-1)	-	Low
Zircon	0 - T	0.06mm (6-2) - 0.13mm (30-2)	Subround	Moderate
Shell	0 - 37	0.07mm (23-1) - 4.00mm (67-1)	-	-
Shell fragments	0 - 13	0.07mm (20-1) - 3.00mm (67-1)	-	-
Dolomite rhombs	0 - 8	0.03mm (1-1) - 0.05mm (1-1)	-	-
Sparry calcite	0 - 6	0.01mm (30-1) - 0.70mm (60-1)	-	-
Pelletal phosphate	T - 34	0.10mm (23-1) - 2.70mm (4-1)	Round	High
Skeletal phosphate		0.14mm (22-1) - 0.50mm (4-1)	-	Low
Intraclastic phosphate		0.11mm (30-4) - 1.20mm (20-3)	Subangular - subround	Moderate
Glaucanite	0 - 2	0.03mm (20-1) - 0.12mm (30-1)	Subround - round	High
Opaque grains	T	0.04mm (30-2) - 0.15mm (45-1)	Angular - subround	Moderate

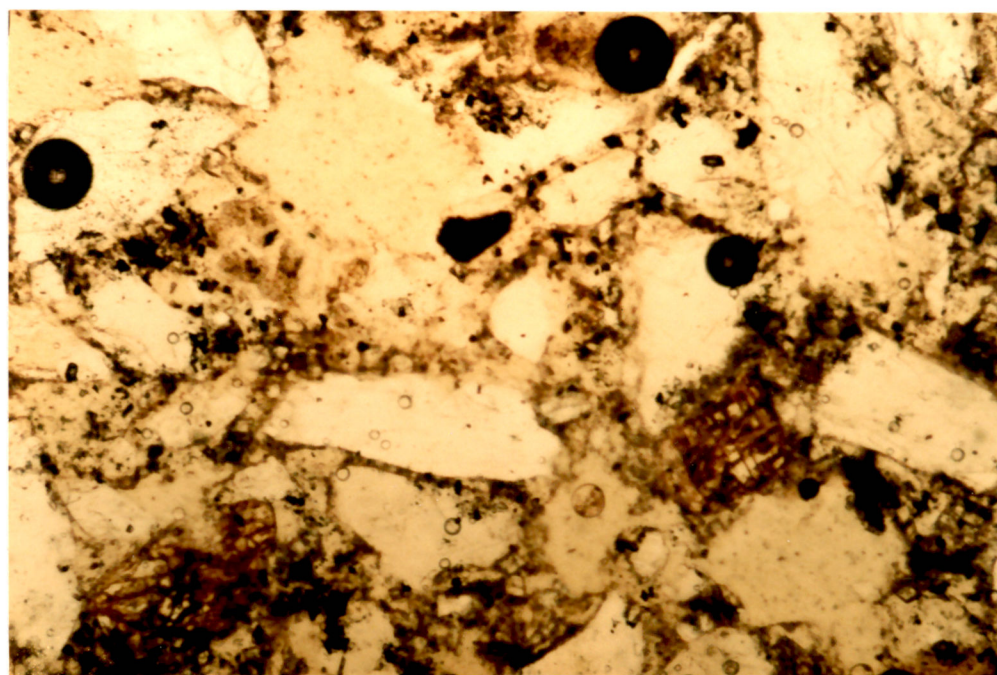
Table 4. Summary characteristics of mineral grain types found in the thin section study. Sample numbers are in parentheses. The data is based on 300 grain point and comparison with Payne (1974) and Scholle (1979). T= trace or <1%.

Plate 2a. Photomicrograph of monocrystalline quartz (A) and polycrystalline quartz (B) in sample 20-3. (crossed nicols, 65x)

Plate 2b. Photomicrograph of orthoclase feldspar (in yellow) in sample 1-1. White grains are quartz. (plane light, 65x)



0.15
mm



0.15
mm

pitting. Extinction of the monocrystalline quartz ranges from 35% undulatory (65% straight extinction) in sample 35-1 to 97% undulatory (3% straight extinction) in sample 45-2. Inclusions consist of rods (apatite?) and needles (rutile?) present in less than 1% of the grains. Vacuoles are present in most grains. Monocrystalline quartz in the Pungo River Formation is classified as "plutonic" or "common", according to Folk's (1980) classification, suggesting a probable igneous source. Cathodoluminescence study revealed no overgrowths on the quartz grain and the SEM study revealed no crystal terminations.

Polycrystalline quartz. This category comprises a small portion (<1%) of the quartz in the Pungo River Formation sediments. The individual crystals within the whole grain are lenticular in shape (Plate 2a). The polycrystalline grains fit the "stretched metamorphic" category of Folk's (1980) classification which indicates they might have undergone shear or strain without recrystallization.

Feldspars. Feldspars are second in abundance in the terrigenous sand and silt fraction. Three types of feldspars occur in the Pungo River Formation sediments: 1) potassium feldspars: 2) untwinned feldspars, and 3) twinned plagioclase feldspars.

Potassium feldspars, represented by orthoclase and microcline, are recognized in thin section (Plate 2b) by their cleavage and yellow stain resulting from treatment with sodium cobaltinitrite. Grains having polysynthetic twinning

in 2 directions at right angles (Kerr, 1959), were classified as microcline. Due to the low amount present in the samples (<1%), the microcline is included with potassium feldspars in Appendix H.

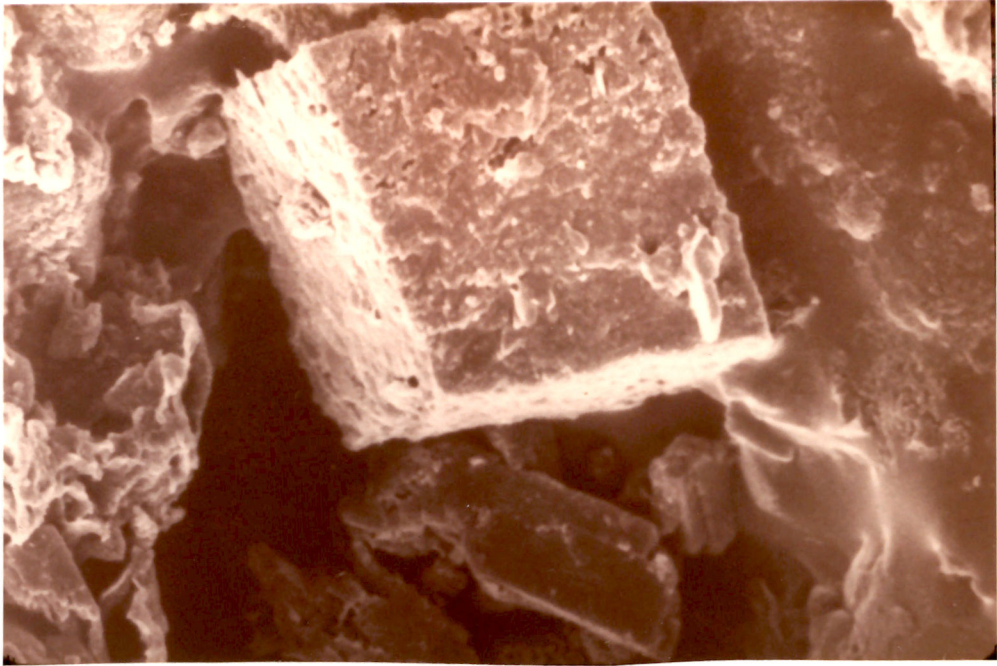
Untwinned plagioclase feldspars are recognized by their cleavage, positive (+) biaxial figures, and the pink stain resulting from amaranth red. I was not able to determine plagioclase feldspar mineral(s) that comprise this category, but the stain will not work for pure albite. However, the stain will work on more calcic varieties (Carver, 1971). Pink stained, fine silt-sized grains may once have been part of larger twinned grains that have since been weathered, leaving individual grains with uniform extinction (Van der Plas, 1975).

Twinned feldspars, other than microcline, are interpreted to be plagioclase. Albite and oligoclase comprise this category as determined by the Michel-Levy method for optical determination (Kerr, 1959).

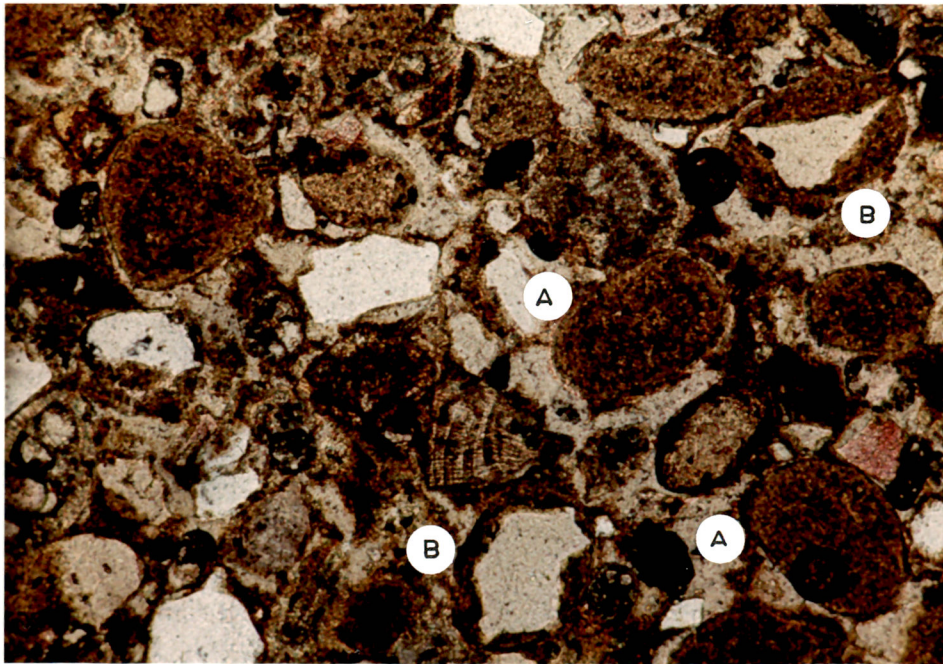
Carbonates. Four types of carbonate materials occur in the Pungo River Formation samples including: 1) whole shells; 2) shell fragments; 3) dolomite rhombs; and 4) sparry calcite. Whole shells, fragments, and rhombs (Plate 3a) are pitted, indicating possible solution activity. Dolomite rhombs show zonation in plane light which might be due to iron content (Kerr, 1959). Sparry calcite occurs as void filling material. Authigenic pyrite and sparry calcite coat and fill the micro-shell material. The pyrite occurs as thin

Plate 3a. SEM photograph of a dolomite rhomb in sample 6-1. The pitted nature of the rhomb surfaces suggest solution activity or etching.

Plate 3b. Photomicrograph of pelletal phosphate (A) and intraclastic phosphate (B) grains in sample 22-1. White angular grains are quartz. (plane light, 65x)



$\frac{5}{\mu}$



$\frac{0.15}{\text{mm}}$

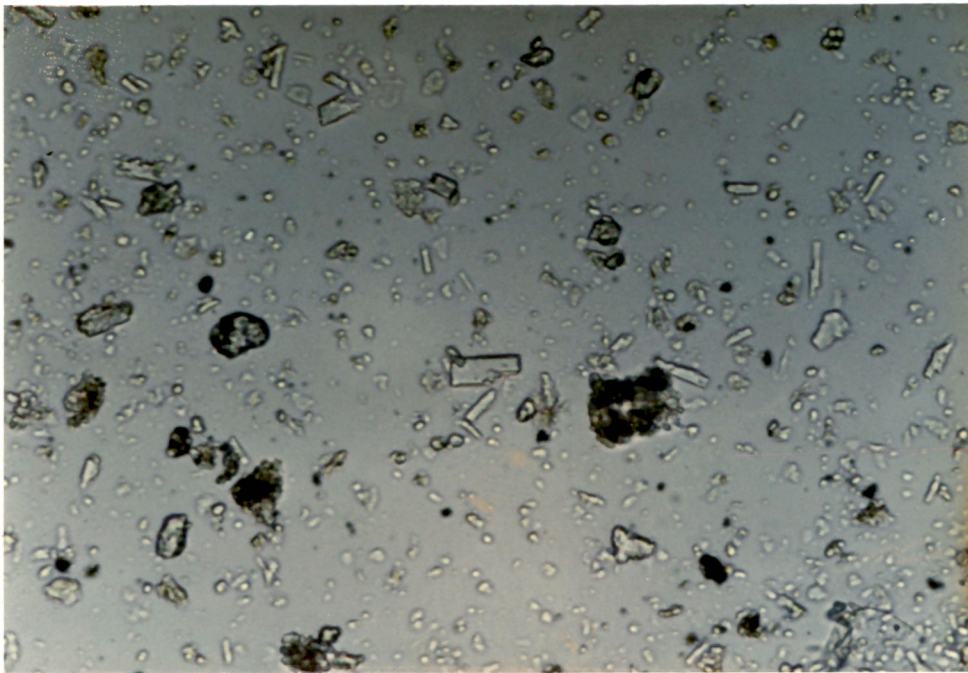
covering on the surfaces of shell fragments, whereas calcite occurs as anhedral particles attached to inner surface of foraminiferal tests. In sample 60-1, the calcite infilling of tests is so complete as to be almost indistinguishable from sparry calcite.

Phosphate. Phosphate is present in most Pungo River Formation samples. Three varieties of phosphate grains were observed in thin section: 1) pelletal phosphate, round to oval-shaped grains which often have rims, are most common (Plate 3b); 2) skeletal material consisting primarily of bone, teeth, and shell fragments; and 3) intracrystalline phosphate, are irregular shaped grains with quartz and feldspar inclusions (Plate 3b). More detailed information on phosphate types can be found in Riggs (1979) and Scarborough (1980).

Clinoptilolite. Lath-shaped crystals were first observed in small amounts in the silt fraction. The laths are not easily observed in whole sample thin sections since they are relatively small ($< .04\text{mm}$) and are probably masked by clay- and silt-sized material and because of their very low birefringence. The crystals are transparent in plane light (Plate 4a) with an index of refraction in blue light of approximately 1.490. Under crossed nicols, the crystals are only slightly anisotropic. Cleavage is perfect in one direction (Plate 4b). Rooney and Kerr (1964) described clinoptilolite in the Pungo River Formation at Aurora. These lath-shaped grains are interpreted to be clinoptilolite on

Plate 4a. Photomicrograph of clinoptilolite laths in sample 6-1. The laths are similar to those described by Rooney and Kerr (1964) for the Pungo River Formation in the Aurora area. (plane light, 40x)

Plate 4b. SEM photograph of the same crystals in Plate 4a above.



0.15
mm



5
 μ

the basis of their optical characteristics (Deer and others, 1963).

Matrix. The ubiquitous very fine silt- and clay- sized material consists of quartz, feldspars, dolomite, calcite, and clay minerals. The remainder of this section will consider the clay mineral fraction of the matrix material.

Clay Mineral Analysis

Clay mineral percentages (Table 5) were determined for all 39 samples selected for mineralogical and textural study. An additional eleven samples were selected from the Frying Pan Area to give a more complete picture of the clay mineralogy. Four principal clay mineral types, smectite, illite, chamosite, and sepiolite, as well as a zeolite, clinoptilolite, were found in the Pungo River Formation samples. Average clay mineral percentages of the 3 depositional sequences indicate that Burdigalian and Serravallian clay suites are generally similar to each other and different from the Langhian.

Smectite. Smectite is defined as $14\text{\AA}$ to $16\text{\AA}$ expandible phyllosilicate in which the basal (001) peak shifts to a higher d-spacing ($17\text{\AA}$) after treatment with ethylene glycol (glycolation) (Thorez, 1976). All samples were treated with ethylene glycol as a test for smectite.

Responses of the basal (001) smectite peak to the treatments are shown in Table 6. Untreated samples have

	UNIT	CORE	SAMPLE	CLAY	Smec		Ill		Cham	Sep	Clin	001/002 for illite
					%	CI	%	CI	%	%		
SERRAVALLIAN	S-5	1	1	14	27	.53	63	7	10	-	P	5
	S-2	53	1	2	50	.60	45	1	4	-	P	8
	S-2	53	2	11	61	.46	38	3	-	-	P	12
	S-2	53	3	17	66	.57	33	1	-	-	P	8
	S-2	60	1	40	58	.61	41	1	-	-	-	8
	S-1	2	1	14	57	.83	29	4	13	-	P	4
	S-1	4	1	10	59	.69	37	5	4	-	P	5
	S-1	6	1	12	71	.48	25	2	4	-	P	5
	S-1	6	2	5	56	.63	41	3	3	-	P	3
	S-1	6	3	11	70	.58	29	5	1	-	P	4
	S-1	42	1	5	59	.51	40	7	1	-	P	6
	avg.	7+	11+	12	58	.59	38	4	4	-	P	6
LANGHIAN	L-2	34	1	23	45	.98	41	1	-	14	-	25
	L-2	52	1	16	4	.42	89	3	-	7	-	20
	L-1	35	1	7	14	.55	86	4	-	-	-	9
	L-1	44	1	16	17	.47	81	3	-	2	-	8
	L-1	44	2	7	16	.41	79	7	-	5	-	24
	L-1	44	3	32	27	.78	66	3	-	7	-	14
	L-1	51	1	8	65	.73	26	1	-	9	-	5
	avg.	5+	7+	16	24	.62	70	3	-	6	-	15
BURDIGALIAN	B-6	15	1	-	-	-	100	1	-	-	-	5
	B-6	45	1	5	30	.50	64	2	-	6	-	21
	B-6	45	2	1	83	.57	16	1	-	1	-	4
	B-6	45	3	6	48	.47	52	2	-	-	-	17
	B-6	62	1	-	67	.15	9	2	24	-	-	2
	B-6	62	2	1	51	.72	23	2	26	-	P	6
	B-6	62	3	-	64	.74	33	2	-	3	-	15
	B-6	66	1	25	61	.79	26	2	-	13	P	10
	B-6	67	1	-	12	.55	59	3	29	-	-	12
	B-6	67	2	13	56	.60	41	2	-	3	P	14
	B-6	67	3	-	-	-	54	3	6	40	P	7
	B-6	70	1	-	16	.38	84	4	-	-	-	5
	B-5	57	1	7	62	.45	38	1	-	-	P	8
	B-3	48	1	2	68	.62	24	1	-	8	P	8
	B-2	27	1	-	57	.69	39	2	4	-	P	9
	B-2	27	2	-	60	.68	32	2	8	-	-	7
	B-2	27	3	-	64	.62	29	2	7	-	-	6
	B-2	28	1	-	41	.68	59	2	-	-	P	2
	B-2	47	1	41	-	-	100	2	-	-	-	8
	B-2	63	1	9	46	.66	52	3	2	-	P	5
	B-2	97	1	-	59	.15	38	1	-	3	-	8
	B-1	20	1	12	64	.64	18	2	-	18	P	3
	B-1	20	2	7	57	.81	40	2	-	3	-	12
	B-1	20	3	6	57	.58	39	2	-	4	-	8
	B-1	23	1	13	60	.76	34	1	-	6	-	3
	B-1	29	1	11	53	.42	42	2	5	-	-	6
	B-1	14	1	5	70	.71	28	2	1	-	P	11
	B-1	22	1	6	25	.54	70	2	-	5	-	36
	B-1	30	1	15	34	.45	59	2	7	-	-	8
	B-1	30	2	4	56	.51	33	3	11	-	-	4
	B-1	30	3	6	46	.61	36	2	18	-	-	5
	B-1	30	4	14	52	.62	28	4	20	-	-	5
	avg.	19+	32+	11	49	.52	42	2	5	4	P	9

Table 5. Total clay percentages of specific clay minerals and crystallinity indices (CI) for the two major clay minerals. The table also denotes the presence (P) of clinoptilolite (Clin) in the samples. Smec= smectite; Ill= illite; Cham= chamosite; Sep= sepiolite. + = total cores and samples analyzed in each unit.

Sample Treatment	Burdigalian		Langhian		Serravallian
	22-1	23-1	44-2	52-1	6-3
Untreated	14.0Å	14.0Å	15.0Å	15.0Å	15.0Å
Ethylene glycol	17.0Å	17.0Å	17.0Å	17.0Å	17.0Å
Magnesium saturation	18.0Å	16.0Å	16.0Å	15.0Å	13.0Å
Magnesium saturation/ glycerol	18.0Å	17.0Å	17.0Å	17.0Å	18.7Å
Potassium saturation	10.0Å	10.0Å	10.0Å	10.0Å	10.0Å
Potassium saturation/ glycerol	14.0Å	13.0Å	13.0Å	13.0Å	13.0Å
400°C heating	10.0Å	10.0Å	10.0Å	10.0Å	10.0Å
550°C heating	10.0Å	10.0Å	10.0Å	10.0Å	10.0Å

Table 6. D-spacing response (in angstroms) of the basal (001) smectite peaks to various treatments of clay samples from the Pungo River Formation in Onslow Bay.

peaks with a $14\text{\AA}$ or $15\text{\AA}$ d-spacing. Treatment with ethylene glycol causes an expansion of the peak to $17\text{\AA}$, identifying the clay mineral as an expanding type (Fig.9). The LiCl-DMSO procedure of Abdel-Kader and others (1978) expands the peak to $18\text{\AA}$ which collapses, upon air drying, to $14\text{\AA}$ (Fig. 9). Magnesium saturation followed by glycerolation identifies the clay mineral as a montmorillonite rather than a vermiculite clay because vermiculite will not expand after this treatment (Thorez, 1976). According to Harward and others (1969), the expansion of the peak following Mg-saturation/glycerolation also rules out beidellite, an aluminum and silica rich smectite, because the beidellite peak remains at $14\text{\AA}$. Rooney (1965) determined the smectite present in the Pungo River Formation in Aurora to be a high K-montmorillonite.

All samples were subjected to heat treatments, which collapsed the smectite basal peak to $10\text{\AA}$ (Fig. 9). Thorez (1976) believes that heat treatments may help determine whether smectite was formed 1) authigenically from alteration of volcanic material, augite, hornblende, feldspars, or hydrothermal solutions; or 2) transformed from mica due to weathering. Mica-derived smectite will collapse to $10\text{\AA}$, while authigenic smectite collapses to $9.5\text{\AA}$ (Thorez, 1976). He believes the higher angstrom collapse of the mica-derived variety is due to the presence of K^+ ions in the smectite layers inherited from the parental mica structure.

Paragenesis of the smectite is also indicated by the K-acetate and glycerol saturations. Potassium saturated, mica-

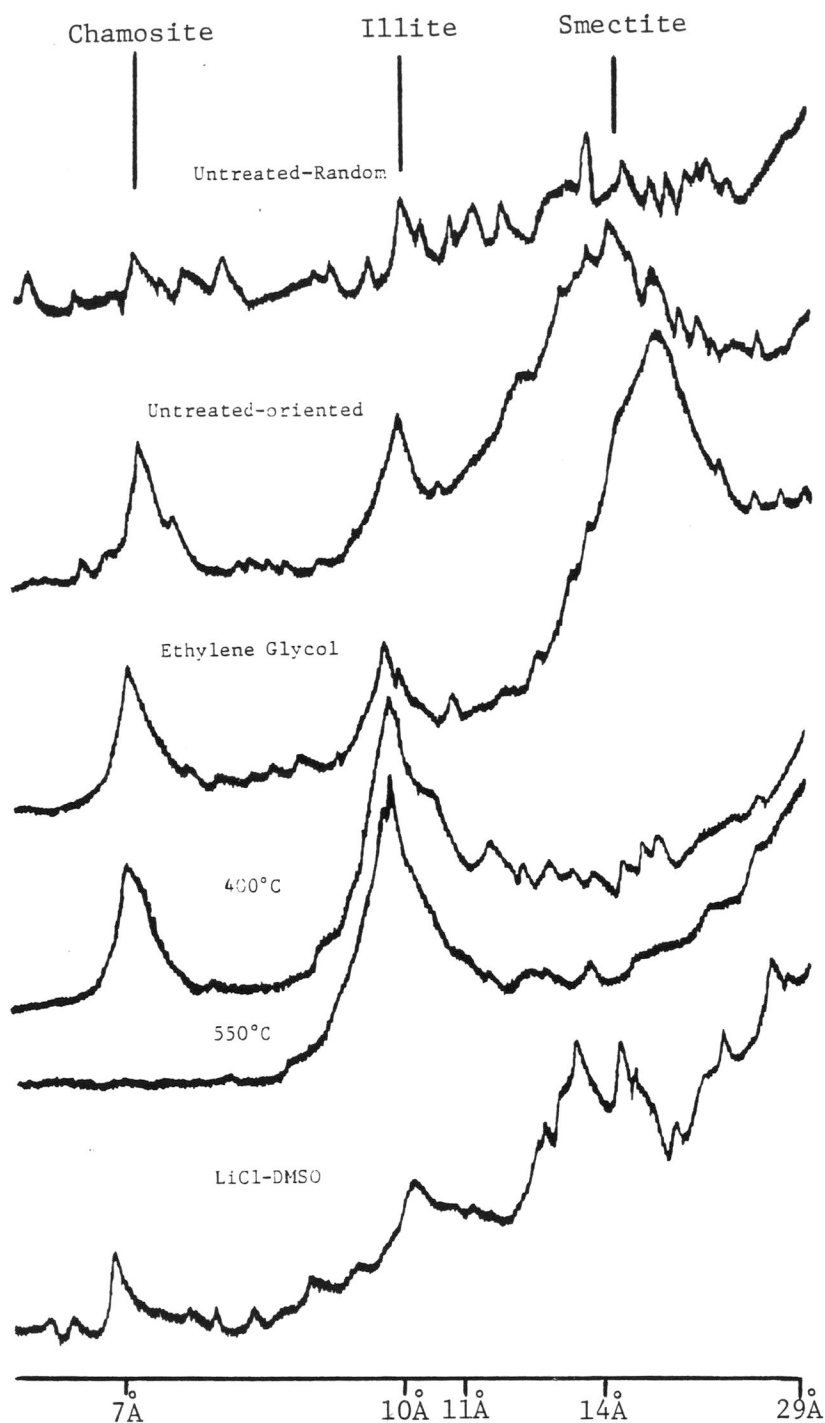


Figure 9. X-ray diffractograms of sample 30-3 showing basal peak responses to listed routine treatments as well as LiCl-DMSO treatment.

derived smectite collapses to $10\text{\AA}$ while authigenic smectite would give a $12\text{\AA}$ spacing (Weaver, 1958). Potassium saturation followed by glycerolation allows for an expansion of the basal peak up to $14\text{\AA}$ for mica derived smectite and $\sim 18\text{\AA}$ for authigenic smectite (Table 6) (Thorez, 1976).

Table 5 contains the crystallinity ratios for smectite in the Pungo River Formation samples. These data indicate that smectite is well crystallized (Biscaye, 1965; Thorez, 1976), with crystallinity values slightly higher in the Langhian and Serravallian sequences than in the Burdigalian.

Illite. Illite is defined as a $10\text{\AA}$ phyllosilicate whose basal (001) peak is not affected by glycolation (Gaudette and others, 1964). LiCl-DMSO saturation (Abdel-Kader and others, 1978) produced no change in the $10\text{\AA}$ peak (Fig. 9). Three illite species were identified on the basis of their 060 (hkl) peaks, if present, on the diffractogram. Illite varieties included dioctahedral 1M and 1MD polymorphs and a trioctahedral variety, glauconite. Dioctahedral clays have trivalent (+3) charge cations (e.g. Al^{+3} , Fe^{+3}) and trioctahedral clays have a divalent (+2) charge (e.g. Fe^{+2} , Mg^{+2}) in the octahedral sites. According to Grim and others (1951) glauconite fits the trioctahedral classification on the basis of x-ray analysis, even though it is dioctahedral on the basis of chemical analysis. Due to the poor quality of the 060 peaks, no attempt was made to quantify the illite varieties.

The ratio of 001 to 002 (001/002) peaks in the same

sample is a significant indicator of Fe content in the octahedral layers (Grim and others 1951; Thorez, 1976). Ratios greater than three indicate Fe-rich illites and ratios less than two indicate Mg-rich illites (Thorez, 1976). On this basis, all but two of the samples are Fe-rich (Table 5) (Thorez, 1976).

Crystallinities of the illite in the Onslow Bay samples (Table 5) generally rank low when compared to a crystallinity scale in which 10 is maximum crystallinity (Fig. 7b). Three samples are exceptions to this; samples 1-1, 42-1, and 44-2 have high crystallinities (~ 7). Warshaw and Roy (1961) interpret well crystallized Fe-rich illite to be celadonite and poorly crystallized Fe-rich illite to be glauconite.

Chamosite. Two types of chamosite have been described in the literature. First is a kaolinite-type chamosite having a $7\text{\AA}$ basal (001) peak that does not expand upon glycolation and collapses upon heating to 550°C . Second is a chlorite-type clay mineral having a $14\text{\AA}$ basal (001) peak that does not expand upon glycolation and does not collapse upon heating to 550°C (Carroll, 1970a). No $14\text{\AA}$ non-expandable peaks were found in the Pungo River Formation samples. A $7\text{\AA}$ non-expandable peak was found in 22 samples.

Thorez (1976) said that a poorly crystallized kaolinite may be difficult to differentiate from a chamosite clay mineral. The procedure by Abdel-Kader and others (1978) causes the $7\text{\AA}$ kaolinite peak to shift to $11.2\text{\AA}$ while the chamosite peak remains at $7\text{\AA}$ (Fig. 9). Three samples (1-1,

6-1, and 30-3) were treated with the procedure. The $7\text{\AA}$ peak after treatment indicates chamosite, but the overall quality of diffractograms is poor.

Due to the lack of an available chamosite standard, no crystallinities were determined. It is possible, however, to get a relative crystallinity by examining peak symmetry (Thorez, 1976). A poorly crystallized peak (Fig. 10a) is assymetrical, broad, and blunt, while a well crystallized (Fig. 10b) peak is more symmetrical, narrow, and sharp. Crystallinity of chamosite in the Pungo River Formation samples is poor to moderate.

Sepiolite. Sepiolite is a clay mineral whose structure is similar to that of amphiboles with amphibole-like silica chains parallel to the mineral fibers (Carroll, 1970a). "Zeolitic water" (water loosely held in the lattice and lost at low temperatures) is present in interstices between amphibole chains. This clay mineral is not affected by glycolation or heating to approximately 300°C . An incremental increase in heating to 420°C causes the $12\text{\AA}$ (110) peak to collapse to approximately $10\text{\AA}$ (Fig. 11). This collapse results from driving off 'bound water' (OH_2) or crystalline water within the sepiolite structure (Caillere and Henin, 1972).

Due to the lack of sepiolite standards, no crystallinities were determined. Shape of the $12\text{\AA}$ peaks are all degraded and assymmetric to the high angstrom side (Fig. 11) indicating a relatively poor sepiolite crystallinity.

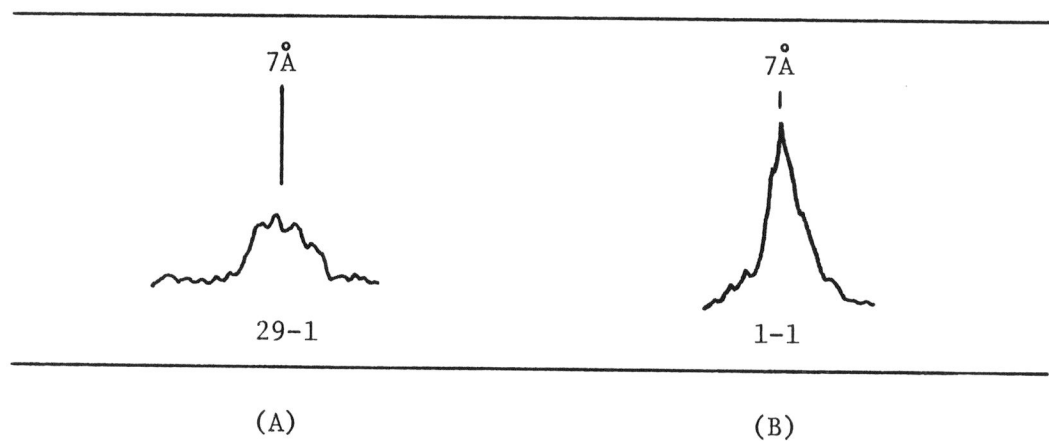


Figure 10. $7\text{\AA}$ d-spacing of two samples. (A) shows poorly crystallized assymetrical peak in sample 29-1 and (B) shows a moderately well crystallized, more symmetrical peak.

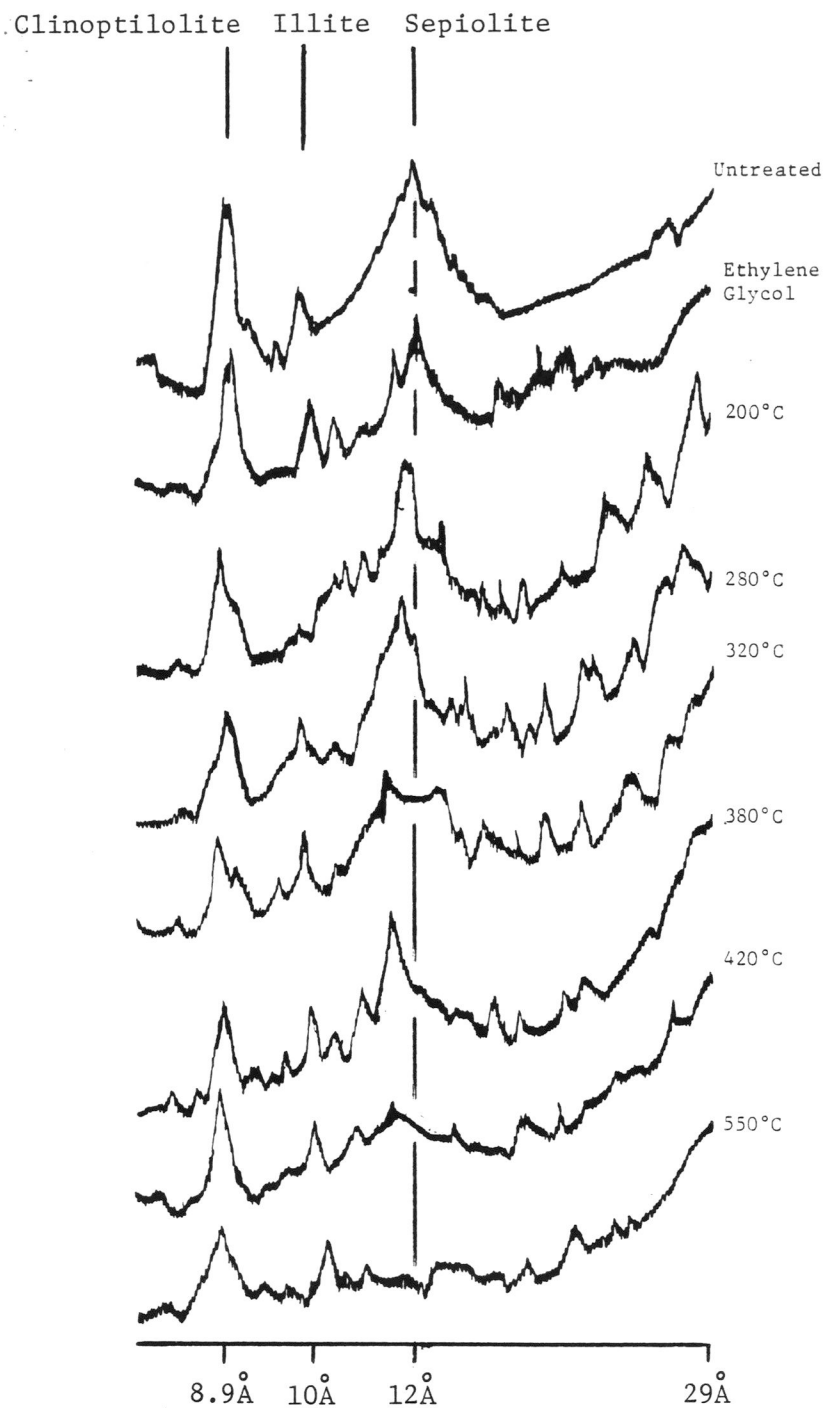


Figure 11. X-ray diffractograms showing heat treatments to sample 67-3 and the corresponding leftward shift of the 12 Å sepiolite peak towards the 10 Å position.

Clinoptilolite. Clinoptilolite is defined as a potassium- and sodium-rich member of the heulandite structural group of the zeolites (Hay, 1966). While not a clay mineral, it did show up in the x-ray analysis of the clay fraction. The relative stability of the $9\text{\AA}$ 020 peak throughout the heat treatments (Fig. 11) indicates clinoptilolite rather than heulandite (Rooney and Kerr, 1964). Due to the lack of an adequate quantifiable procedure, no percentages were determined for this mineral. Clinoptilolite is present throughout the Serravallian, not detectable in the Langhian, and present infrequently in the Burdigalian sediment units.

X-ray data for clinoptilolite is shown in Table 7. Onslow Bay samples and a published standard of Chen and others (1978) are based on unoriented mounts. Rooney and Kerr (1964) used oriented mounts for their analysis of Pungo River Formation samples from Aurora.

Due to lack of data concerning clinoptilolite crystallinities, no crystallinities were determined for the mineral in the Onslow Bay samples. However, all samples containing clinoptilolite have a slightly asymmetric to symmetric, sharp peak indicating fair to good crystallinity.

D-spacing (Å)	Peak intensities		
	(1)	(2)	(3)
8.93	100	100	100
7.94	86	70	42
6.81	26	-	22
5.14	20	-	24
4.65	26	-	18
3.97	93	100	98
3.92	53	57	57
3.41	46	-	44

Table 7. Peak intensity data based on x-ray diffraction studies of clinoptilolite from (1) the Pungo River Formation in Onslow Bay; (2) Pungo River Formation in Aurora, N.C. (Rooney and Kerr, 1964); and (3) a published standard (Chen and others (1978)).

DISCUSSION

Smectite and illite are the principal clay minerals in the Pungo River Formation sediments of Onslow Bay and sepiolite and chamosite are accessory clays. A zeolite, clinoptilolite, is also present in minor concentrations. X-ray analysis suggests that smectite and clinoptilolite are well crystallized, while the illite, chamosite, and sepiolite are moderate to poorly crystallized.

Rooney (1965) speculated on the paragenetic sequence that lead to the presence of montmorillonite, illite, and clinoptilolite being present in the Pungo River Formation in the Aurora area (Fig. 12). He believed that some volcanic glass altered to glauconite and later altered to montmorillonite. The remaining portion of unaltered glass produced the zeolite. According to Rooney, the first stage of this transformation, glass to glauconite, would take place in an environment of low Eh. As conditions became more oxidizing, zeolite would form from the remaining glass and glauconite would alter to montmorillonite. The glauconite to montmorillonite transformation is structurally feasible since both clays are dioctahedral with trivalent cations in their octahedral sites. Rooney believes the transformation from glauconite to montmorillonite would require a loss of K, Na, and Ca from interlayer positions of the glauconite and oxidation of divalent Fe. The zeolite transformation might happen as Si and Al from decomposing glass combines with the K, Na, and Ca.

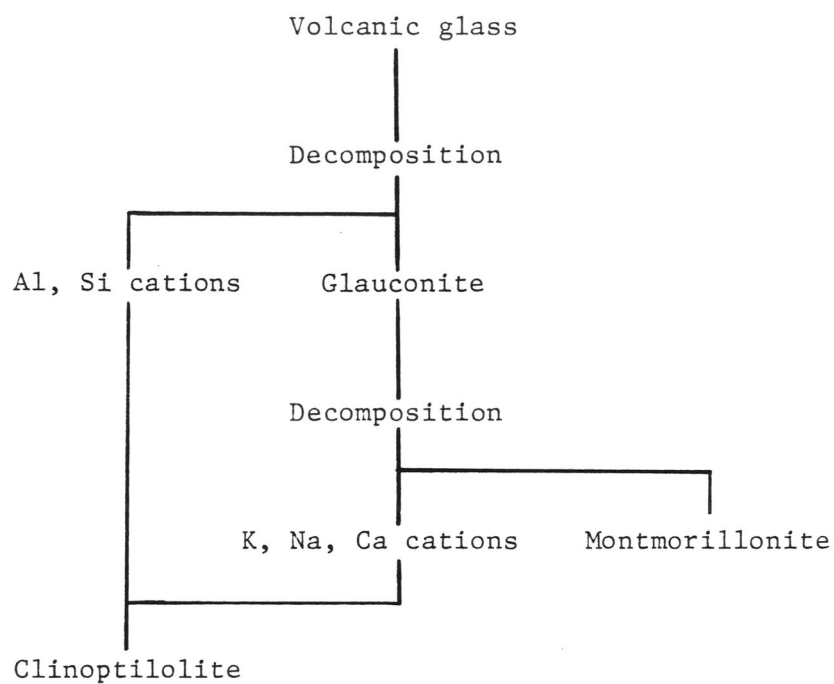


Figure 12. Flow chart showing the paragenetic sequence of the clay-zeolite suite in the Pungo River Formation of Aurora according to Rooney (1965).

A problem with Rooney's hypothesis is that no glass structures or shards have been found in either the Pungo River Formation at Aurora (Rooney and Kerr, 1964) or in the Pungo River Formation sediments of Onslow Bay. However, it is probable that if the glass was present, it was subsequently altered or transformed, leaving no direct evidence of its presence. Another problem with Rooney's glass-to-glaucinite-to-montmorillonite transformation is the alteration process itself. If glass is altering to illite in the high Na, K, and Ca environment that he requires to build zeolites, what would cause the illite to degrade to a montmorillonite? Bonding between adjacent sheets of illites is stronger than in smectites because there are more interlayer cations and less water (Warshaw and Roy, 1961). Interlayer cations, such as K, hold the layers together with stronger ionic bonds, whereas interlayer water is bonded by weaker hydrogen and Van der Waals bonds. Rooney's ideas, though admittedly speculative, illustrate the problems associated with interpreting the paragenetic sequence of clays and their diagenesis in the Pungo River Formation sediments.

Another approach to understanding the genesis of clay minerals is to consider the role of regional environment in clay mineral formation. Biscaye (1965) and Griffin and others (1968) found that the clay mineral component of Recent Atlantic Ocean sediments is primarily detrital and reflects continental weathering environments. The studies have

demonstrated latitudinal trends of clay minerals which formed on land and were transported to and deposited in the oceans. The latitudinal trend shows increasing amounts of illite and chlorite toward higher latitudes and smectite and kaolinite toward the lower latitudes. Kennet (1982) carried the idea of continental weathering patterns and clay mineral formation one step further. If the type of clay in a soil strongly reflects climatic control, there should be a relationship between clay mineral distribution in depositional basins to climatic patterns on adjacent landmasses.

Some clay formation in soils is the result of decomposing rock-forming minerals (e.g. feldspars, micas, amphiboles, etc.) and other clays due to chemical weathering by groundwater. The more water that is flushed through the pedogenic environment, the more complete the decomposition. Since rainfall and temperature generally increase with decreasing latitude, simpler 3 and 2 layer phyllosilicates form in low latitude regions. Conversely, drier and colder climates of higher latitudes tends to favor the formation of more complex 3 and 4 layer phyllosilicates.

Paton (1978) cited an example of weathering a dioctahedral mica in a pedogenic environment. As K ions are removed by hydrolysis, exfoliation occurs, causing thinner phyllosilicate plates and formation of illite. As the process continues, water begins to occupy interlayer sites forming montmorillonite. If the process were to continue under severe leaching conditions, the structure would

breakdown to kaolinite, due to loss of Al in the octahedral layer and complete removal of one tetrahedral layer. Paton believes that the transition from illite to montmorillonite is mainly superficial, in that alteration is confined to removal of non-framework cations (i.e. K) while leaving the phyllosilicate structure intact. Silicon and Al, the two principal cations of the framework structure, maintain the same ratio of $\text{SiO}_2/\text{Al}_2\text{O}_3$ throughout the transition. According to Grim (1968), the $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio increases as the transition proceeds from illite to montmorillonite. This results in a decreased charge imbalance allowing K to be stripped away and water to enter between layers.

Cation deficient water plays a key role in the leaching process in two ways (Keller, 1964). First, in a semi-arid environment where evaporation exceeds rainfall, leaching occurs initially. Then as the water evaporates, cation availability increases, decomposition is terminated and montmorillonite is produced. Second, if rainfall exceeds evaporation and there is good drainage to flush out cations, alteration continues to kaolinization. In areas where rainfall exceeds evaporation and drainage is poor, montmorillonite is produced; initial leaching occurs but cations cannot be transported out of the system and the transition is terminated producing montmorillonite as the end product.

Riggs (1984) proposed a model for deposition of the phosphorite sediment sequence on the southeastern United

States continental margin. The sedimentation model (Table 8) is a direct response to major climatic events which resulted in cyclical glaciation and deglaciation and associated sea-level fluctuations. This idealized cycle model corresponds to the depositional units of Snyder (S. W. P., 1982) (Fig. 2). In his model, changing paleoclimates affected the weathering processes and determined types and volumes of terrigenous sedimentation from adjacent land areas; these changing patterns should be reflected in the type of terrigenous clay minerals formed (Riggs, pers. comm., 1984. For example, Grim (1968) noted that glacial deposits in North America have higher concentrations of illite while warmer climate deposits have higher amounts of montmorillonite and kaolinite.

Chamley (1976) (Fig. 13) proposed a model for clay mineral formation on land in response to warm and cold climatic regimes. The subarctic to boreal climate on the Chamley model should equate to the maximum regression stage of Riggs' cycle model (Table 8). The temperate climate on the Chamley model should equate to the maximum transgression stage of the cycle model. Illite and chlorite form in response to cooler and drier climates, while pedogenic smectite and kaolinite form in warmer and wetter climates. Colder climate and lower sea level equates to higher relief and reduced vegetative cover, allowing faster runoff of sediment particles and cations (Copeland and others, 1983). Consequently, clay minerals are more rapidly eroded and

- | | |
|---|---|
| (1) Sea level at early- to mid-stage transgression | Moderating climate; westward migration of Gulf Stream; fine grained terrigenous sediment backfills fluvial channels and estuaries; interbeds of phosphate and carbonate; fine grained terrigenous mud and sand dominate inside of embayed shelf system. |
| (2) Sea level at mid- to late-stage transgression | Transgression continues; warming of shelf waters; continued westward migration of Gulf Stream; decreasing terrigenous sedimentation and increasing phosphate deposition. |
| (3) Sea level at maximum during interglacial stage | Warm climatic conditions; minimal terrigenous sedimentation; sub-tropical marine fauna, local phosphate pavements and bypass surfaces; erosion and channels caused by Gulf Stream current. |
| (4) Regression with sea level at a minimum during a glacial maximum | Lowering of sea level allowing for eroding, truncating, and channeling of previously deposited sediments; eastward migration of Gulf Stream; colder and arid climatic conditions; increased terrigenous sedimentation on shelf; subaerial or submarine non-depositional exposure. |

Table 8. Model for the deposition of an idealized Miocene lithologic cycle in response to glaciation and deglaciation on the S. E. United States continental margin (from Riggs, 1984).

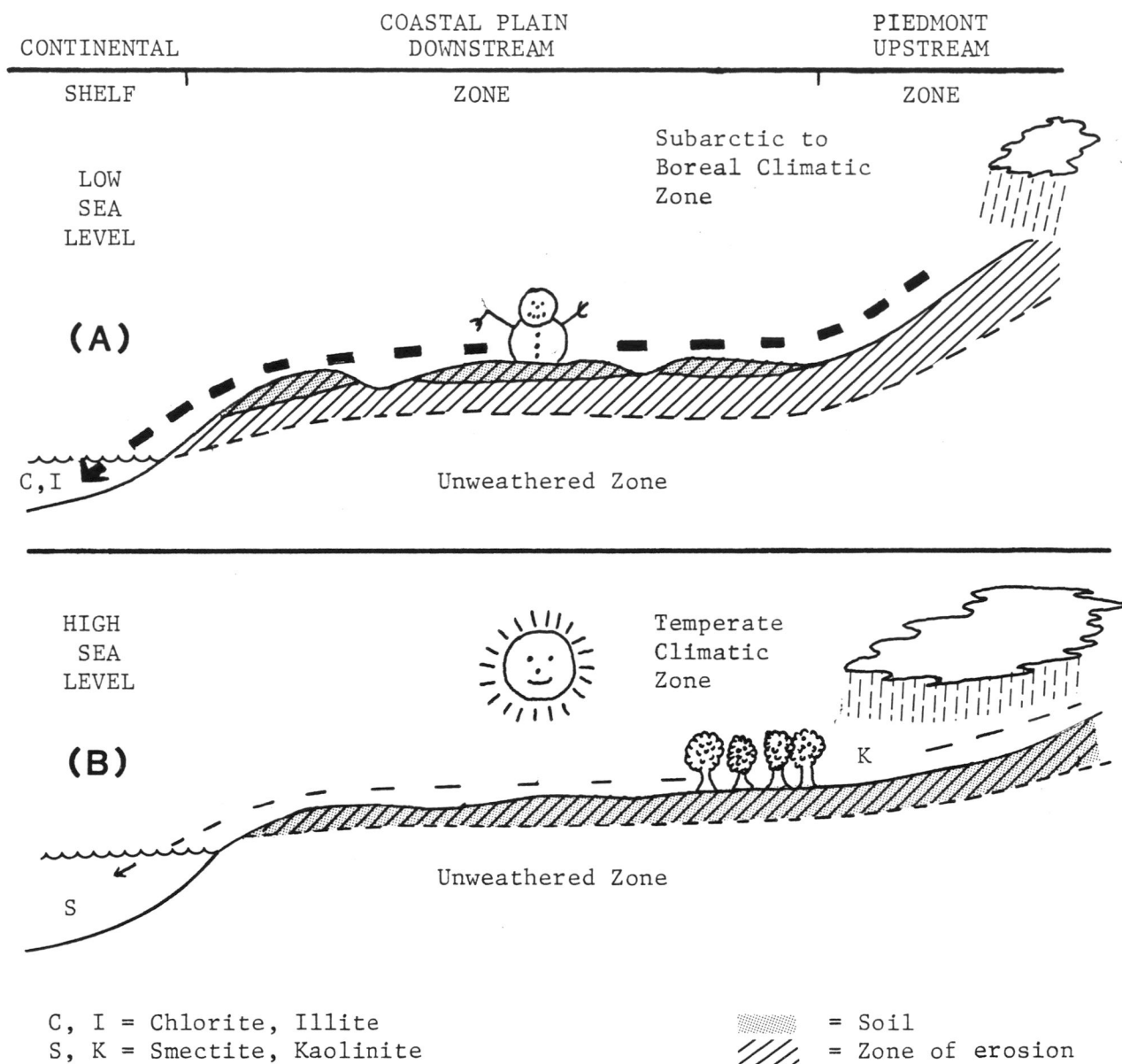


Figure 13. A generalized model for continental clay mineral formation in (A) subarctic to boreal and (B) temperate climatic regimes (modified from Chamley, 1976). The subarctic to boreal climatic zone would be characterized by decreased temperature, rainfall, and vegetation and increased terrigenous input to the adjacent shelf. The temperate climatic zone would be characterized by increased temperature, rainfall, and vegetation and decreased terrigenous input to the adjacent shelf.

transported eastward during the initial phase of a glacial eustatic low sea-level. Later, when the climate warms, these less weathered deposits are drowned and reworked by shelf processes. At this time, coastal rivers are drowned forming estuaries. Erosion decreases and deep soils are favored. This allows illites and chlorites to alter to smectite and kaolinite minerals.

Smectite is the dominant clay in the Serravallian sediments analyzed. According to Chamley's model (1976), a warm moist climatic condition should have prevailed during the Serravallian with a corresponding high sea level. Illite is the predominant clay in the Langhian sediments analyzed. Consequently, cooler and drier climates should have prevailed with a correspondingly lower sea level during Langhian deposition. Clay suites in the Burdigalian sediments analyzed appear more complex, fluctuating between dominantly smectite and illite.

A plot of average smectite and illite percentages for the ten depositional units sampled in this study shows smectite decreasing and illite increasing toward the top of each depositional sequence (Fig. 14). A strict interpretation of the data with respect to Chamley's model conflicts with the sea-level data of Vail and others (1979). A major second-order cycle of relative sea level rise (Fig. 15) occurred from about 30 mya, in the late Oligocene, to about 6 mya, in the late Miocene. This overall transgressive event, during which the Pungo River Formation was deposited, is

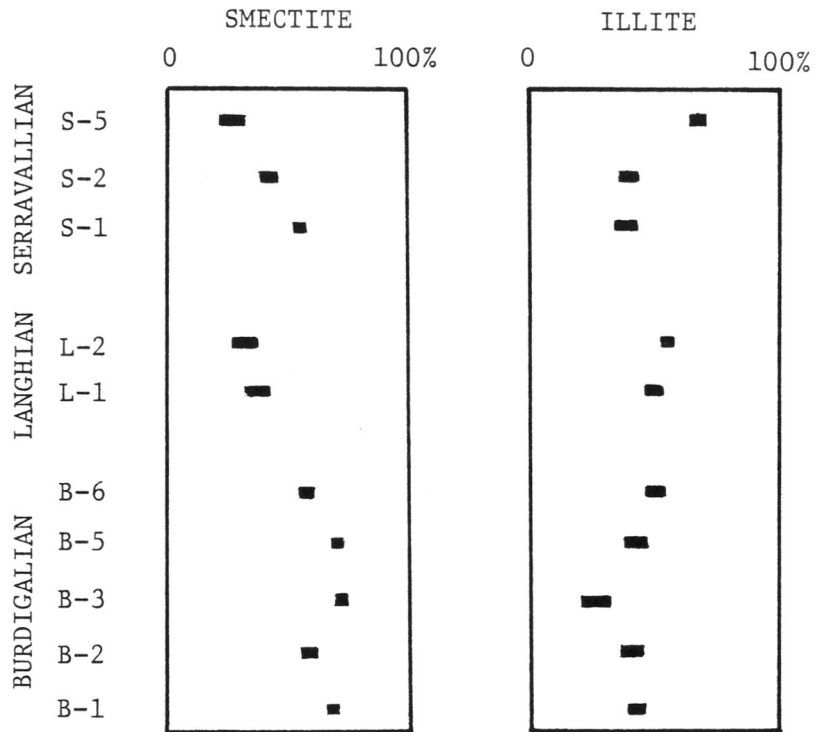


Figure 14. Plot of average smectite and illite percentages in each of the sampled Pungo River Formation units. Dark bars indicate range based on the precision error in Figure 6.

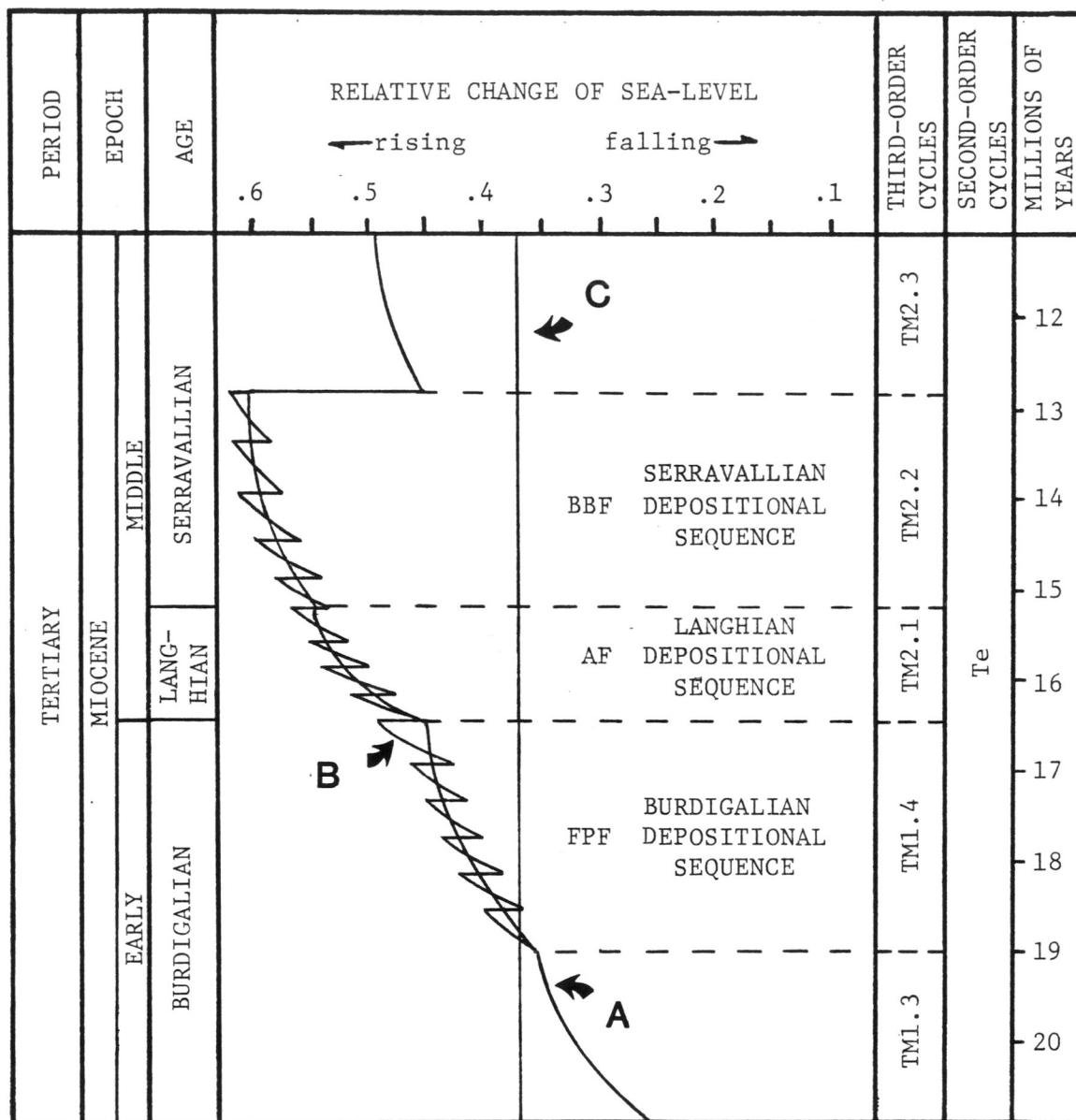


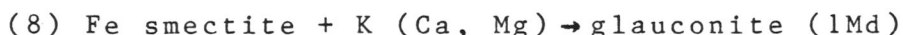
Figure 15. Global cycles of relative sea-level change during the early to middle Miocene. A= third-order sea-level cycles of Vail and others (1979); B= fourth-order sea-level cycles of Snyder (S. W. P., 1982) and Riggs (1984); and C= present sea-level.

punctuated by smaller scale third-order cycles of transgression and regression suggesting alternating climatic conditions superimposed on the larger scale warming trend. In addition, Snyder (S.W.P., 1982), and Snyder, S.W.P., and others (1982) Riggs and others (1982b) and Riggs (1984) have demonstrated that at least 18 still smaller scale, fourth-order sea-level fluctuations occur superimposed upon the second- and third- order cycles. An interpretation of the Vail curves with respect to Chamley's model predicts increasing abundances of smectite during deposition of the Pungo River Formation. There are at least two possible explanations for the apparent discrepancy between the Onslow Bay data to that of Vail and others (1979) interpreted with respect to Chamley's model (1976).

First, the illite clay at the tops of depositional sequences could be glauconite, which is an authigenic clay formed in marine environments. Glauconite has been reported in the clay fraction in the Pungo River Formation (Rooney, 1965; Meisberger, 1979) as well as in the sand and silt fraction (Appendix H) (Potluri, 1966; Meisberger, 1979). Due to diluent effects of clays in a mixture, the 060 peaks are not adequately discernable and percentages of glauconite in the samples could not be determined. Relatively small amounts of K in the interlayer structure causes glauconite to have a symmetric peak to the low angle side of x-ray diffractograms. Asymmetry of the $10\text{\AA}$ peak indicates a degraded condition which is easily confused with 1Md illite (Carrol, 1970a). Confusion may be further compounded because glauconite in unconsolidated sediments not subjected to pressure does not develop hkl (e.g. 060) reflections (Carroll 1970a).

Glauconite can form when there is: a) clay (e.g. smectite) present which can be

built into an illitic three layer clay; b) a local reducing environment exists; and c) sufficient cations, including trivalent Fe are present to build the material into an illitic clay (Burst, 1958). Carroll (1970a) found that illite formed in reducing conditions does not develop the characteristic green-colored glauconite, that develops from a high Fe smectite which is altered to illite. The reaction she described proceeds as follows:



Smectite from the adjacent landmass could have been a likely source material for the illitic glauconite in the Pungo River Formation samples in Onslow Bay.

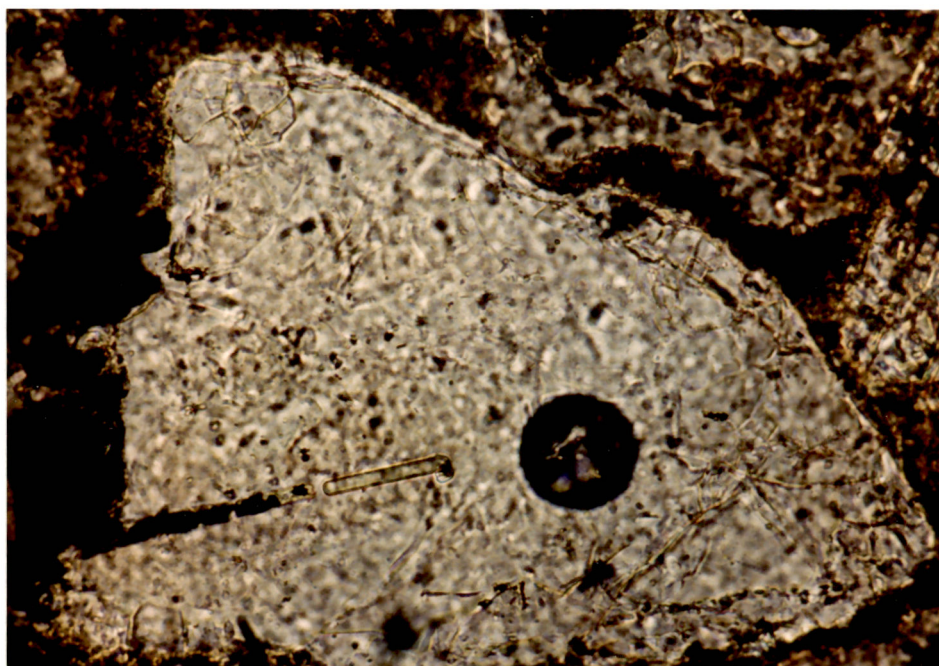
Second, the sampling pattern used for this study did not take into consideration the cyclic sedimentation in the Pungo River Formation. Samples high in illite may merely reflect a point in the section which was deposited during sea-level regression. The sampling pattern used in this study may include the integrated effects of second-order, third-order, and fourth-order cycles. However, there is a slight increase in average smectite percentages from the Burdigalian to the Serravallian (Table 5). The increase might indicate a partial correlation of the data to the Vail curves during third order cycles.

Chamosite occurs in 18 of the 22 samples in the Serravallian and in some samples of the Burdigalian. Chamosite is usually the predominant accessory clay when smectite dominates the clay mineral fraction (Table 5). Chamosite is an Fe-rich phyllosilicate with a kaolinite type, 2 layered, $7\text{\AA}$ structure. Like glauconite, chamosite requires a high Fe source, generally reducing conditions, and a material from which to form. If Chamley's model is correct, then degraded clay from terrestrial weathering processes may supply a source material for chamosite.

Abundant sources of Fe are available on the marine continental shelf for formation of chamosite and glauconite. In non-clay components, Fe occurs 1) as oxide/hydroxide grain coatings (Plate 5); 2) as dissolved divalent Fe; 3) in suspension as colloidal particles; 4) as a constituent of clastic particles (Appendix H); and 5) as chelated organic complexes (Mehra and Jackson, 1960; James, 1966; Carroll, 1970a; Gibbs, 1977). Iron-stained sands occur over extensive portions of the shelf south of Cape Hatteras; these sediments may have originated in subaerial environments of the Piedmont (Judd and others, 1970; Milliman and others, 1972). Doyle (1967) found that lack of Fe staining in shelf sediments suggests an oxygen-poor depositional environment in which the staining was removed by iron sulfide formation. Iron stained grains constitute less than 10% of the sediment in all samples. Iron occurs in average concentrations of 670ppb in streams and 10ppb in seawater (Turekian, 1969; Anikouchine and Sternberg, 1981). Lower values of dissolved Fe in ocean water are due to the higher alkaline pH's of sea water than river water; this causes Fe to precipitate (White and others, 1963) enabling it to be remobilized and concentrated in authigenic sediments by chemical reactions on the sea floor (James, 1966).

Degraded kaolinite, stripped of some of its Al and Si and deposited on the shelf, could serve as the initial clay material for producing chamosite. James (1966) described a mixed layer kaolinite-chamosite suggesting such a

Plate 5. Photomicrograph of iron coating on quartz grain and infilling a dissolved inclusion in sample 20-3.
(plane light, 250x)



0.018

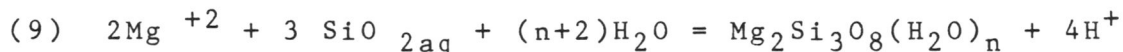
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transformation is possible. Chamosite, which has much more magnesium than kaolinite, could obtain the Mg required for the transformation from sea water. Magnesium, the fifth most abundant element in the ocean has an average concentration of 1,350ppm in sea water (Horne, 1969; Anikouchine and Sternberg, 1981). Drever (1971) found that, in highly reducing conditions, divalent Mg from sea water can replace Fe in exchangeable sites in the montmorillonite structure. Free Fe liberated from this exchange is then available for transformation of kaolinite to chamosite and smectite to glauconite under reducing conditions.

Sepiolite occurs most commonly in highly alkaline, evaporitic environments, where silica and Mg concentrations are high and Al is low (Weaver and Beck, 1977). Grim (1968) and Weaver and Beck (1977) believe that sepiolite forms authigenically in transitional sediment environments such as lakes, lagoons, bays, and soils, as opposed to more open marine conditions. Supplies of necessary ions (e.g. Mg and Si) are derived from upstream hydrolysis which are trapped in downstream zones and are available for crystallization into sepiolite.

In contrast, Isfording (1973) found that sepiolite can form as a direct precipitate in alkaline (pH~8) marine environments where silica concentrations are high. According to Isfording, silica leached by subaerial weathering from phyllosilicates during warm, moist climatic conditions is transported to the shelf by fluvial processes. When proper

pH conditons and silica and Mg concentrations are high enough, the following reaction occurs:



If more arid conditions lead to sepiolite formation as suggested by Grim (1968) and Weaver and Beck (1977) other contemporaneous evaporite-related sediments might occur in association with the sepiolite. Since none have been documented in the Pungo River Formation, Isfording's hypothesis for the formation of sepiolite may fit Chamley's climatic model more closely.

Clinoptilolite is a Na and K zeolite that forms under conditions of high silica concentration and high pH. Most clinoptilolite crystallizes from aqueous solutions where chemical activities of base cations, Si, and water influence the type of zeolite that will precipitate (Hay, 1966; Boles and Wise, 1978). According to Hay, H ions compete with cations for the aluminosilicate framework. Therefore, high ratios of cations to H ions tend to cause a high pH which is essential for zeolite formation. Hay specified that the permeability must be relatively low in order to allow cations to stay in place long enough for the reactions to occur.

The present study found that clinoptilolite occurs as individual crystals in the silt and clay fraction (finer than 4 ϕ). It was not clear whether the individual euhedral crystals (Plate 4) were authigenic or detrital. Rooney and Kerr (1964) found clusters of zeolite crystals in the Pungo

River Formation sediments in Aurora. Lack of clusters and broken individual crystals scattered throughout the matrix suggest that the grains have been transported. Waters (1983) and Hale and Spruill (pers. comm., 1983) found clinoptilolite crystals growing as clusters inside foraminifera tests in some southern Onslow Bay cores, suggesting that clinoptilolite in certain cores is authigenic. Foraminifera tests range from fine to very fine sand size and the clinoptilolite crystals within the foraminifera tests range from medium silt down to clay size. The crystals in the mud fraction are of similar size as those in the foraminifera. Reworking of older sediments may leach away the surrounding shell, exposing the clinoptilolite clusters which are broken up into individual crystals, and redispersing them throughout the sediment. Irregular edges on one side of clinoptilolite crystals in Plate 4 may be where individual crystals were broken from the clusters.

High silica concentration in pore waters is required to form sepiolite and clinoptilolite (Isfording, 1973). In the world ocean silica comes from rivers, pore water refluxes, and volcanic and biogenic sources (Heath, 1974) (Fig. 16). On continental shelves, the sources of silica are from weathering of onshore silicate rocks (Reynolds, 1970), upwelling of dissolved biogenic silica with a minor contribution from volcanic sources (Kennet, 1982). Clinoptilolite found in deep sea sediments apparently forms from silicious organisms (Iijima, 1978; Riech and von Rad, 1979).

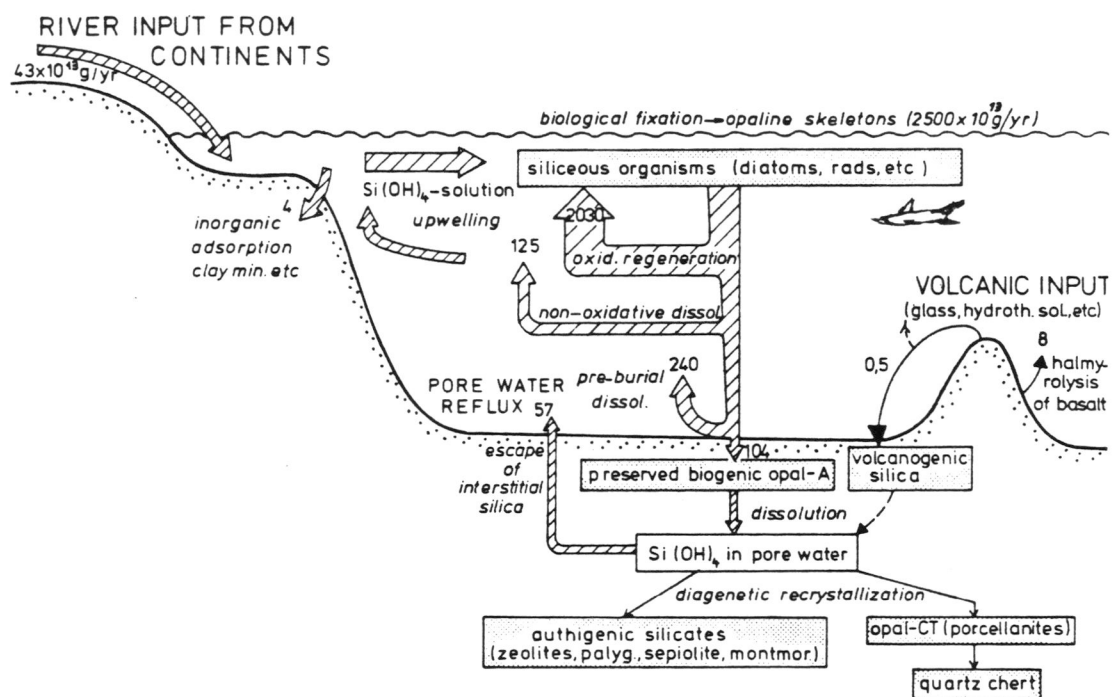


Figure 16. Cycle of dissolved silica in the oceans. All numbers represent magnitudes of dissolved silica in 10^{13} grams SiO_2 /year. Silica sources are in capitals; transformations (cycling) are in italics; solid phases are stipled (from Heath, 1974).

In Riggs' (1984) continental margin model for phosphorite sedimentation (Table 8), the main silica sources could be dramatically different. During low to intermediate sea-level stands and cooler, drier climates, upwelling should play a major role in moving deep, silica-rich water onto the continental margins. Also, leaching of terrestrial silicate rocks would be at a minimum with relatively low input of dissolved silica onto the shelves. During the transgressive event, silica- and P-rich waters would move further across the shelf. Since transgression is in response to the development of warmer and more humid climatic conditions, leaching of silica from terrestrial silicate rocks should increase as weathering conditions become more lateritic. During high sea-level stands, the Si content in shelf waters should be at a maximum, allowing for optimum formation of authigenic clinoptilolite and sepiolite. Miller (1971) noted that clinoptilolite is more prominent in phosphate-rich beds than clay-rich beds. Miller's trend suggests a link between silica and P which lends itself to the idea of upwelling.

Examination of clay suites reported in the literatures in the Hawthorn Formation of Florida, Georgia, and South Carolina and the Pungo River Formation of Onslow and Aurora embayments, points to some interesting trends. The Hawthorn and Pungo River Formations are contemporaneous and continuous units which formed in response to a major Miocene phosphogenic event (Riggs, 1984). These units contain an anomalous suite of clay minerals which consist dominantly of

1) attapulgite, sepiolite, and montmorillonite in Florida and Georgia; 2) attapulgite, sepiolite, and montmorillonite, with traces of illite and clinoptilolite in South Carolina; and 3) montmorillonite, illite, and clinoptilolite, with traces of sepiolite and chamosite in North Carolina (Fig. 17) (Rooney, 1965; Heron and Johnson, 1966; Weaver and Beck, 1977). If the Pungo River and Hawthorn Formations are contemporaneous and continuous, then the changing north to south pattern of clay distributions indicate a general latitudinal zonation from sub-tropical climates in the south to more temperate climates in the north. Sepiolite, which requires warm climates to form, should decrease as climatic conditions become more temperate with increasing latitude. Likewise, increasing amounts of illite with increasing latitude indicate more temperate climatic conditions.

Weaver and Beck (1977) noted an inverse relationship between the presence of attapulgite and sepiolite and that of clinoptilolite in the Hawthorn Formation. No attapulgite occurs in the Onslow Bay samples; however, with the exception of two units, the same general inverse relationship occurs between sepiolite and clinoptilolite (Fig. 18). Hay (1978) found that the presence of divalent Mg required for sepiolite formation, restricts the formation of clinoptilolite. If Mg is the controlling factor, then there might have been some cyclicity in Mg concentrations during deposition of the Pungo River Formation sequences.

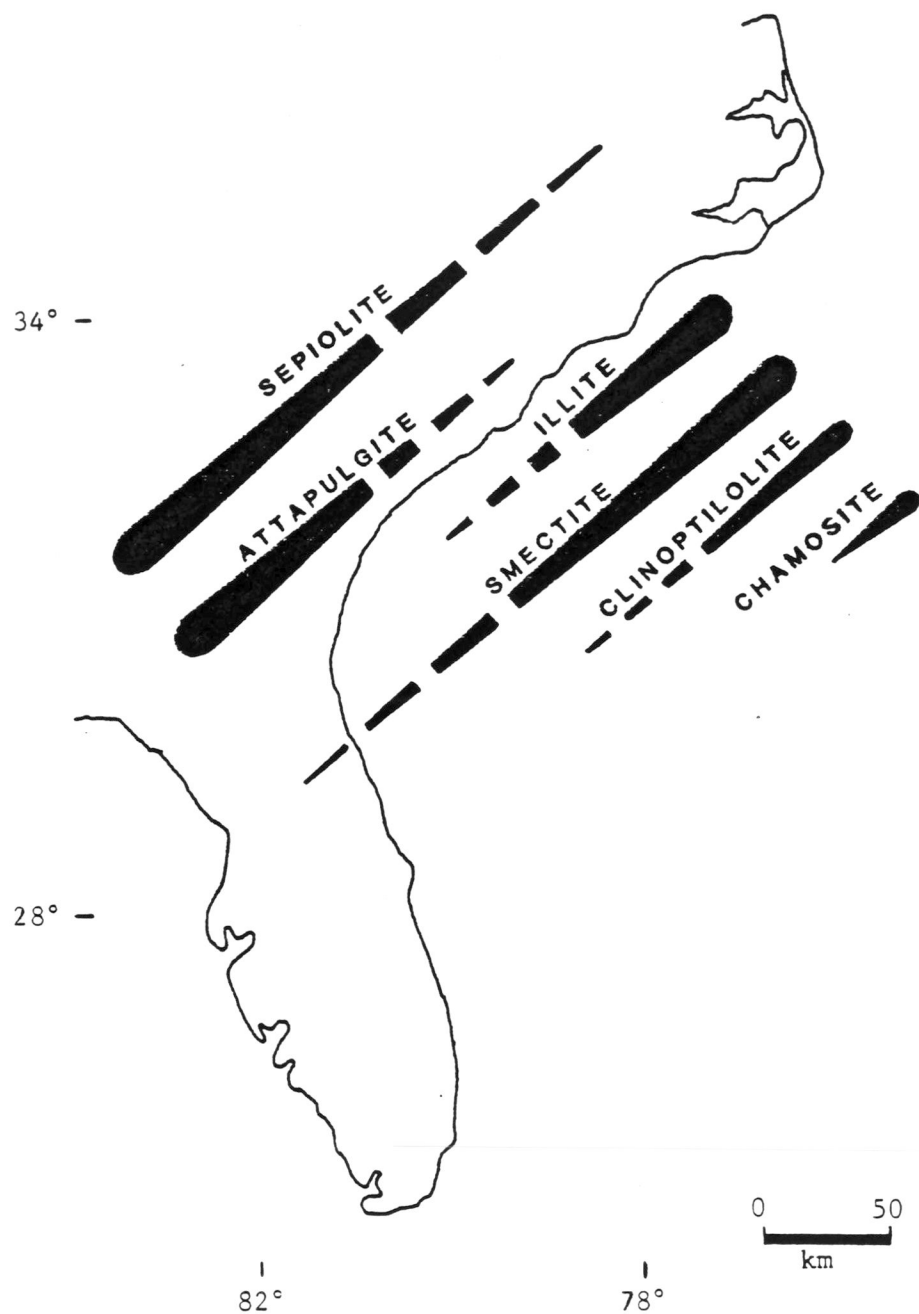


Figure 17. Generalized trends in clay mineral and zeolite distribution in Miocene sediments of the southeast United States. Bulges indicate a NE-SW direction of increasing abundance from Florida to North Carolina. (Based on Rooney, 1965; Heron and Johnson, 1966; Weaver and Beck, 1977; and on data from this project)

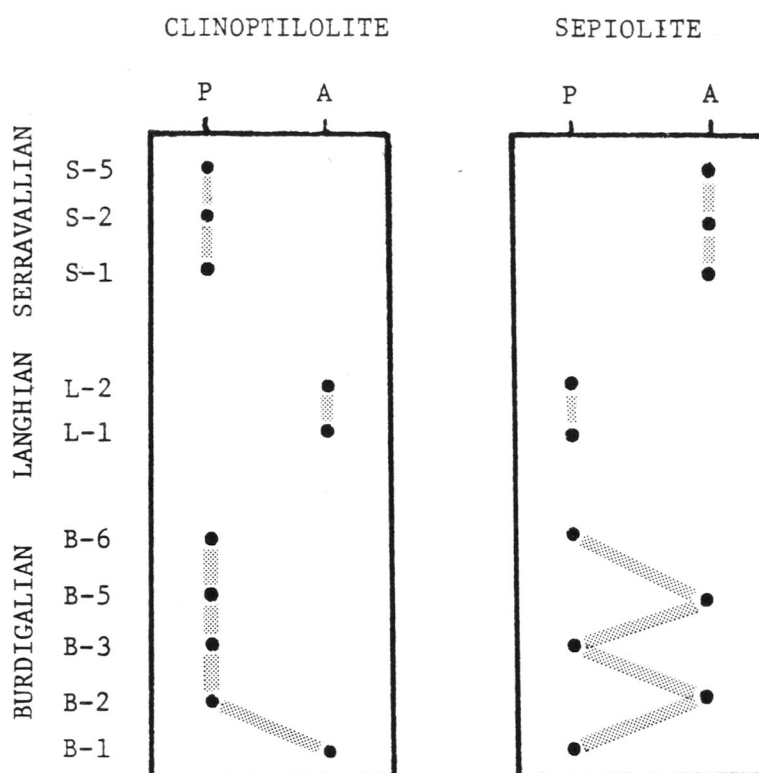


Figure 18. Plot of presence (P) and absence (A) of clinoptilolite and sepiolite in the 3 depositional sequences of the Pungo River Formation in Onslow Bay.

CONCLUSIONS

1) The clay component of the Pungo River Formation sediments in Onslow Bay consists of varying percentages of: 1) expandible, well crystallized, mica derived-montmorillonite smectite; 2) poorly crystallized illite characterized by illite polymorphs of lm, lmd, and lmd glauconite; 3) poorly crystallized sepiolite 4) poorly to moderately well-crystallized kaolinite-type chamosite; and 5) moderately well-crystallized clinoptilolite (zeolite).

2) The Burdigalian and Serravallian clay suites are predominantly smectite with subordinate illite and minor amounts of chamosite, sepiolite, and clinoptilolite. The Langhian clay suite is predominantly illite with subordinate smectite, and a minor amount of sepiolite.

3) Clay, Fe and silica, weathered from rocks in the Piedmont and Coastal Plain regions, were carried to the sea by fluvial processes, and deposited on the shelf. In addition to continental sources, dissolved silica from deep marine waters, moved onto the shelf by oceanic upwelling during intermediate sea-level stands. During transgression, upwelled silica, plus Mg, Na, and K from sea water might have produced authigenic clinoptilolite and sepiolite. The authigenic nature of clinoptilolite has been established in the Burdigalian depositional sequences, however, the zeolite

might be detrital in the Serravallian depositional sequences.

4) Degraded clay material, such as smectite and kaolinite, plus Fe and Mg, might have produced authigenic glauconite and chamosite.

5) Reducing conditions in the depositional environment are indicated by the formation of authigenic clinoptilolite, sepiolite, chamosite, and glauconite.

6) Global climatic changes appear to have had some impact on the clay mineralogy of the Pungo River Formation in Onslow Bay. Smectite and illite, the two principal clay mineral groups, are believed to be directly related to changing continental climatic weathering conditions. Illites might have formed from the alteration of micas during periods of cooler climatic conditions and lower sea-level stands. Smectites may have formed from the increased weathering of illites during periods of warmer climatic conditions and higher sea-level stands.

7) Smectite and illite are the dominant clay minerals in the northern portion in the region of the Hawthorn and Pungo River Formations, while sepiolite and attapulgite are dominant clays in the southern region. In addition,

chamosite and clinoptilolite appear to increase in concentration in a northward direction.

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APPENDIX A. Sieve and pipette data for the Onslow Bay samples.

Diameter			Sample 1-1		Sample 2-1		Sample 4-1		Sample 6-1		Sample 6-2		Sample 6-3		Sample 14-1	
			Ind. (%)	Cum. (%)	Ind. (%)	Cum. (%)	Ind. (%)	Cum. (%)	Ind. (%)	Cum. (%)	Ind. (%)	Cum. (%)	Ind. (%)	Cum. (%)	Ind. (%)	Cum. (%)
mm	phi															
SIEVE	4.0	-2.0	0	0	0	0	1.1	1.1	0	0	0	0	0	0	0	0
			0	0	.07	.07	3.0	4.1	0	0	0	0	0	0	0	0
	2.0	-1.0	.30	.30	.35	.42	4.5	8.6	1.4	1.4	0	0	0	0	3.9	3.9
			.30	.60	.55	.97	4.0	4.6	1.5	2.9	.09	.09	.05	.05	.48	4.4
	1.0	0.0	.40	1.0	.63	1.6	10.3	14.9	1.7	4.6	.07	.16	.13	.18	.16	4.5
			1.0	2.0	.79	2.4	2.3	17.2	2.9	7.5	.38	.55	.42	.60	.56	5.1
	.5000	1.0	4.0	6.0	.71	3.1	4.8	22.0	4.3	11.8	.82	1.3	.74	1.3	.76	5.9
			7.7	13.7	1.0	4.1	10.0	32.0	1.1	12.9	2.2	3.5	3.0	4.3	1.3	7.2
	.2500	2.0	12.3	26.0	1.1	5.2	8.5	51.5	7.7	30.6	5.5	9.0	2.8	7.1	3.9	11.2
			26.1	52.1	2.4	7.6	17.0	68.5	19.9	50.5	8.1	17.1	8.3	15.4	7.7	18.9
	.1250	3.0	20.7	72.8	9.0	16.6	5.9	74.4	8.0	58.5	5.6	22.7	2.8	18.2	10.6	29.5
			3.4	76.2	36.6	53.2	2.8	77.2	1.5	60.0	1.5	33.2	7.9	26.1	15.4	45.0
	.0625	4.0	1.8	78.0	15.2	78.4	4.2	81.4	2.4	62.4	20.9	54.1	17.5	43.6	13.7	58.7
PIPETTE	.0625	4.0		81.4		76.9		84.7		62.7		57.5		46.7		60.9
	.0310	5.0	6.8	88.2	3.5	80.4	3.2	87.9	7.0	69.7	18.6	76.1	9.6	56.3	15.8	76.7
	.0156	6.0	5.4	93.6	3.5	83.9	2.0	89.9	13.6	83.3	8.4	84.5	15.7	72.0	10.1	86.8
	.0078	7.0	2.3	95.9	2.6	86.5	.30	90.2	2.4	85.7	6.5	91.0	8.6	80.6	5.4	92.2
	.0039	8.0	2.0	97.9	.70	87.2	.01	90.2	1.7	88.4	3.9	94.9	7.7	88.3	3.1	95.3
	.0020	9.0	.50	98.4	.30	87.5	1.0	91.2	1.9	90.3	2.5	97.4	1.8	90.1	1.6	96.9
	.00098	10.0	.20	98.6	1.7	89.2	.10	91.3	2.0	92.3	1.7	99.1	3.4	93.5	.60	97.5
	>10.0		1.4	100	10.8	100	8.7	100	7.7	100	.90	100	6.5	100	2.5	100

Diameter mm phi			Sample 20-1		Sample 20-2		Sample 20-3		Sample 22-1		Sample 23-1		Sample 29-1		Sample 30-1	
			Ind. (%)	Cum. (%)	Ind. (%)	Cum. (%)	Ind. (%)	Cum. (%)	Ind. (%)	Cum. (%)	Ind. (%)	Cum. (%)	Ind. (%)	Cum. (%)	Ind. (%)	Cum. (%)
SIEVE	4.0	-2.0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
			0	0	0	0	0	0	0	0	0	0	0	0	0	0
	2.0	-1.0	0	0	0	0	.35	.35	1.8	1.8	0	0	0	0	0	0
			.07	.07	.06	.06	.08	.43	.05	2.3	.31	.31	0	0	0	0
	1.0	0.0	.19	.19	.09	.15	.04	.47	.80	3.1	.30	.61	0	0	0	0
			.09	.28	.28	.43	.17	.64	1.3	4.4	.35	.96	.05	.05	.09	.09
	.5000	1.0	.29	.57	.67	1.1	.46	1.1	2.9	7.3	.64	1.6	.14	.19	.01	.10
			.21	.78	2.0	3.1	1.3	2.4	9.3	16.6	1.4	3.0	1.1	1.3	.05	.15
	.2500	2.0	1.6	2.4	3.1	6.2	3.4	5.8	9.0	25.6	2.5	5.5	1.7	3.0	.04	.19
			4.8	7.6	7.0	13.2	9.7	15.5	10.6	36.2	4.7	10.2	2.5	5.5	.64	.83
PIPETTE	.1250	3.0	12.8	20.4	16.7	29.9	31.2	46.7	12.5	48.7	7.2	17.4	5.9	11.4	10.8	11.7
			5.7	26.1	10.1	40.0	15.7	62.4	10.4	59.1	9.0	26.4	29.5	40.9	27.7	39.4
	.0625	4.0	4.1	30.2	8.7	48.7	6.1	68.5	14.7	73.8	11.1	37.5	21.7	62.6	17.1	56.5
	.0625	4.0		29.7		46.3		72.1		76.5		36.2		63.7		58.5
	.0310	5.0	16.7	46.4	25.8	72.1	12.9	85.0	3.0	79.5	15.7	51.9	7.8	71.5	6.4	64.9
	.0156	6.0	19.2	65.6	14.2	86.3	7.0	92.0	5.7	85.2	20.3	72.2	11.4	82.9	9.2	74.1
	.0078	7.0	14.0	79.6	4.5	90.8	.6	92.6	8.2	93.4	6.5	78.7	2.4	85.3	4.4	78.5
	.0039	8.0	10.2	89.8	2.0	92.8	2.7	95.3	.7	94.1	8.8	87.5	4.4	89.7	7.3	85.8
PIPETTE	.0020	9.0	.5	90.3	.6	93.4	2.0	97.3	2.0	96.1	2.6	90.1	1.4	92.1	3.6	89.4
	.00098	10.0	.7	91.6	.6	94.8	1.4	98.7	.30	96.4	2.3	92.4	1.3	93.4	3.9	93.3
	>10.0		8.4	100	5.2	100	1.3	100	3.6	100	7.6	100	6.6	100	6.7	100

Diameter mm phi			Sample 30-2		Sample 30-3		Sample 30-4		Sample 34-1		Sample 35-1		Sample 42-1		Sample 44-1	
			Ind. (%)	Cum. (%)	Ind. (%)	Cum. (%)	Ind. (%)	Cum. (%)	Ind. (%)	Cum. (%)	Ind. (%)	Cum. (%)	Ind. (%)	Cum. (%)	Ind. (%)	Cum. (%)
SIEVE	4.0	-2.0	0	0	0	0	1.4	1.4	0	0	0	0	0	0	0	0
			0	0	0	0	.30	1.7	0	0	0	0	0	0	0	0
	2.0	-1.0	.14	.14	0	0	.30	2.0	0	0	.07	.07	.15	.15	2.6	2.6
			.90	.23	0	0	.30	2.3	.04	.04	.10	.17	.15	.30	1.4	4.0
	1.0	0.0	.18	.41	0	0	.40	2.7	.01	.05	.19	.36	.24	.54	1.1	5.1
			.50	.91	.01	.01	1.0	3.7	.12	.17	.25	.61	.46	1.0	3.9	9.0
	.5000	1.0	.99	1.9	.01	.02	1.8	5.5	1.0	1.2	.35	.96	1.1	2.1	6.4	15.4
			1.8	3.7	.01	.03	2.5	8.0	4.8	6.0	.54	1.5	4.4	6.5	6.7	22.1
	.2500	2.0	5.3	9.0	.11	.14	5.4	13.4	15.3	21.3	2.2	3.7	3.8	10.3	6.4	28.5
			9.6	19.4	.61	.75	9.1	22.5	15.4	36.7	6.2	9.9	6.6	16.9	6.9	35.4
PIPETTE	.1250	3.0	14.0	33.4	15.0	15.8	13.1	35.6	6.6	43.3	10.0	19.9	5.7	22.6	9.0	44.4
			8.9	52.3	17.2	43.0	19.2	56.8	2.0	45.3	5.3	25.2	6.2	28.8	3.3	47.7
	.0625	4.0	15.8	68.1	14.4	57.4	46.5	75.4	.90	46.5	6.6	31.8	15.6	44.4	1.0	48.7
	.0625	4.0		71.6		58.0		77.3		43.5		29.1		48.7		50.0
	.0310	5.0	11.0	80.6	13.8	71.8	3.5	80.8	4.9	48.4	28.7	57.8	28.8	76.5	3.9	53.9
	.0156	6.0	9.9	90.5	3.1	74.9	4.0	84.8	3.4	51.8	14.9	82.7	9.7	86.2	8.0	61.9
	.0078	7.0	4.2	94.7	4.9	79.8	3.5	88.3	11.9	63.7	7.1	89.8	6.4	92.6	4.8	76.7
	.0039	8.0	1.9	96.6	6.8	86.6	5.8	94.5	12.9	76.6	3.4	93.2	2.4	95.0	8.1	84.8
PIPETTE	.0020	9.0	.5	97.1	5.7	92.3	2.9	97.4	5.4	82.0	3.1	96.3	2.0	97.0	4.4	89.2
	.00098	10.0	.2	97.3	3.2	95.5	2.1	99.5	4.7	86.7	1.3	97.6	.6	97.6	4.8	94.0
	>10.0		2.7	100	4.5	100	.5	100	13.3	100	2.4	100	2.4	100	6.0	100

Diameter mm phi			Sample 44-2		Sample 44-3		Sample 45-1		Sample 45-2		Sample 45-3		Sample 47-1		Sample 48-1	
			Ind. (%)	Cum. (%)	Ind. (%)	Cum. (%)	Ind. (%)	Cum. (%)	Ind. (%)	Cum. (%)	Ind. (%)	Cum. (%)	Ind. (%)	Cum. (%)	Ind. (%)	Cum. (%)
SIEVE	4.0	-2.0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
			0	0	0	0	0	0	0	0	0	0	0	0	0	0
	2.0	-1.0	1.4	1.4	0	0	2.7	2.7	2.8	2.8	2.3	2.3	.06	.06	.20	.20
			2.4	2.4	0	0	3.5	6.2	2.2	5.0	3.0	5.3	.09	.15	.13	.33
	1.0	0.0	1.0	3.4	.01	.01	3.9	10.1	1.7	6.7	2.2	7.5	.09	.24	.18	.51
			1.8	5.6	.08	.09	4.4	14.5	2.6	9.3	4.0	11.5	.35	.59	.25	.76
	.5000	1.0	2.7	8.3	.15	.24	4.0	18.5	8.4	17.7	9.1	20.6	.01	.60	.34	1.1
			2.8	11.1	.16	.40	5.2	23.7	22.9	40.6	20.1	40.7	.03	.63	.70	1.8
	.2500	2.0	4.6	15.7	.80	1.2	7.2	30.9	35.7	76.3	25.7	66.4	.04	.67	1.9	3.7
			10.5	26.2	11.4	12.6	10.4	41.3	13.3	89.6	8.7	75.1	.11	.78	18.5	22.2
PIPETTE	.1250	3.0	25.6	51.8	22.5	35.1	13.0	54.3	4.3	93.9	3.0	78.1	1.2	2.0	53.0	75.2
			1.8	53.6	1.3	36.4	3.4	57.7	.80	94.7	.90	79.0	5.3	7.3	8.1	83.3
	.0625	4.0	.50	54.1	1.2	37.6	1.7	59.4	.60	95.3	.50	79.5	6.8	14.1	1.3	84.6
	.0625	4.0		68.5		35.4		63.7		96.3		78.1		15.3		84.0
	.0310	5.0	5.5	74.0	4.8	40.2	17.5	81.2	1.0	97.3	4.1	82.2	9.6	24.9	4.3	88.3
	.0156	6.0	7.5	81.5	8.1	48.3	6.7	87.9	1.3	98.6	5.9	88.1	10.8	35.7	4.1	92.4
	.0078	7.0	5.4	86.9	7.3	55.6	5.2	93.1	1.0	99.6	6.2	94.3	9.0	44.7	3.9	96.3
	.0039	8.0	6.4	93.3	13.7	69.3	2.7	95.8	.20	99.8	.30	94.6	15.7	60.4	1.8	98.1
	.0020	9.0	1.6	94.9	8.3	77.6	2.1	97.9	.001	99.8	1.0	95.6	14.5	74.9	.80	98.9
	.00098	10.0	.70	95.6	8.9	96.5	.001	97.9	.001	99.8	.001	95.6	11.3	86.2	.50	99.4
	>10.0		4.4	100	3.5	100	2.1	100	.20	100	4.4	100	13.8	100	.60	100

Diameter mm phi			Sample 51-1		Sample 52-1		Sample 53-1		Sample 53-2		Sample 53-3		Sample 57-1		Sample 60-1	
			Ind. (%)	Cum. (%)	Ind. (%)	Cum. (%)	Ind. (%)	Cum. (%)	Ind. (%)	Cum. (%)	Ind. (%)	Cum. (%)	Ind. (%)	Cum. (%)	Ind. (%)	Cum. (%)
SIEVE	4.0	-2.0	0	0	0	0	.15	.15	0	0	.95	.95	0	0	0	0
			0	0	0	0	.17	.32	.01	.01	.80	1.3	0	0	.21	.21
	2.0	-1.0	0	0	1.7	1.7	.14	.46	.14	.15	.30	1.6	0	0	.18	.39
			.02	.02	.40	2.1	.33	.79	.76	.91	.30	1.9	0	0	.38	.77
	1.0	0.0	.07	.09	.60	2.7	.91	1.7	1.5	2.4	.50	2.4	0	0	2.0	2.8
			.21	.30	.70	3.4	3.6	5.3	3.8	6.2	1.1	3.5	.002	.002	8.3	11.1
	.5000	1.0	.67	.97	1.6	5.0	11.7	17.0	6.5	12.7	1.7	5.2	.002	.004	10.1	21.2
			2.2	3.2	1.6	6.6	18.7	35.7	10.0	22.7	2.6	7.8	.08	.08	5.2	26.4
	.2500	2.0	13.1	16.3	1.8	8.4	15.1	50.8	16.6	39.3	4.4	12.2	.14	.22	3.7	30.1
			40.6	56.9	1.7	10.1	12.6	63.4	23.8	64.1	8.2	20.4	2.2	2.4	6.5	36.6
PIPETTE	.1250	3.0	19.0	75.9	2.5	12.6	7.2	70.6	13.2	77.3	17.8	38.2	15.2	17.6	3.7	40.3
			2.7	78.6	2.3	14.9	3.2	73.8	2.7	80.0	12.4	50.6	34.7	52.3	1.2	41.5
	.0625	4.0	1.1	79.7	3.1	18.0	2.6	76.4	1.8	81.8	4.4	55.0	21.7	74.0	1.2	42.7
	.0625	4.0		75.6		15.6		77.8		82.1		51.2		72.0		45.2
	.0310	5.0	4.0	79.6	15.9	31.5	1.9	79.7	1.1	83.2	7.0	58.2	3.9	76.1	.60	45.8
	.0156	6.0	5.5	85.1	3.5	35.0	3.0	82.7	1.1	84.3	4.5	62.7	5.7	81.8	3.9	49.7
	.0078	7.0	5.8	90.9	25.6	60.6	2.3	85.0	1.6	85.9	6.8	69.5	7.2	89.0	8.0	57.7
	.0039	8.0	.90	91.8	23.2	83.8	1.6	86.6	3.3	89.2	13.0	82.5	4.8	93.8	3.9	61.6
	.0020	9.0	.50	92.3	5.1	88.9	2.2	88.8	.60	89.8	1.3	83.8	1.8	95.6	9.2	70.8
	.00098	10.0	1.1	93.4	4.4	93.3	1.6	90.4	.50	90.3	3.3	87.1	1.1	96.7	17.7	87.9
	>10.0		6.6	100	6.7	100	9.6	100	9.7	100	12.9	100	3.3	100	12.1	100

Diameter mm phi			Sample 62-1		Sample 63-1		Sample 66-1		Sample 67-1	
			Ind. (%)	Cum. (%)	Ind. (%)	Cum. (%)	Ind. (%)	Cum. (%)	Ind. (%)	Cum. (%)
SIEVE	4.0	-2.0	7.3	7.3	0	0	0	0	0	0
			4.1	11.4	0	0	0	0	0	0
	2.0	-1.0	3.9	15.3	0	0	.07	.07	.04	.04
			3.3	18.6	6.5	6.5	.34	.41	.04	.08
	1.0	0.0	2.1	20.7	3.9	10.4	.79	1.2	.04	.12
			4.7	25.4	4.1	14.5	.40	1.6	.16	.28
	.5000	1.0	3.6	29.0	3.4	17.9	3.1	4.7	.52	.80
			1.2	31.8	4.6	22.5	5.2	9.9	1.5	2.3
	.2500	2.0	4.9	36.7	5.4	27.9	5.9	15.8	4.6	6.9
			17.5	54.2	6.6	34.5	10.0	25.8	7.3	14.2
	.1250	3.0	26.2	80.4	8.0	42.5	14.8	40.6	14.2	28.4
			9.4	89.5	6.3	48.8	10.2	50.8	39.0	67.4
	.0625	4.0	4.1	93.6	5.5	54.3	5.4	56.2	10.6	78.0
PIPETTE	.0625	4.0		95.7		53.4		58.7		80.5
	.0310	5.0	1.6	97.3	7.3	66.7	4.6	63.3	1.6	82.1
	.0156	6.0	1.1	98.4	11.5	78.2	5.6	68.9	1.7	83.8
	.0078	7.0	.20	98.6	10.5	88.7	4.1	73.0	1.6	85.4
	.0039	8.0	.30	98.9	3.4	92.1	2.5	75.5	1.9	87.3
	.0020	9.0	.10	99.0	1.4	93.5	11.0	86.5	1.8	89.1
	.00098	10.0	.40	99.4	1.8	95.3	1.9	88.4	1.2	90.3
		10.0	.60	100	4.7	100	11.6	100	9.7	100

APPENDIX B. Staining technique for thin section study.

1. Etch the polished surface for 10 to 15 seconds in concentrated (52%) hydrofluoric acid.
2. Dip the thin section in water.
3. Immerse the thin section in a saturated solution of sodium cobaltinitrite for 1 minute.
4. Wash the thin section in tap water to remove excess cobaltinitrite.
5. Allow thin section to air dry.
6. Immerse the thin section for 15 seconds in 5% barium chloride solution.
7. Dip the thin section once quickly in water and allow to air dry.
8. Immerse the thin section for 16 seconds in Amaranth red solution (1 ounce of 92% pure coal-tar dye in 2 liters of water).
9. Dip the thin section once quickly in water.
10. Remove excess dye from the surface of the thin section by shaking vigorously.

Table B: - Staining technique for thin section study (from Carver, 1971).

APPENDIX C. Cumulative probability curves for the Onslow Bay samples.

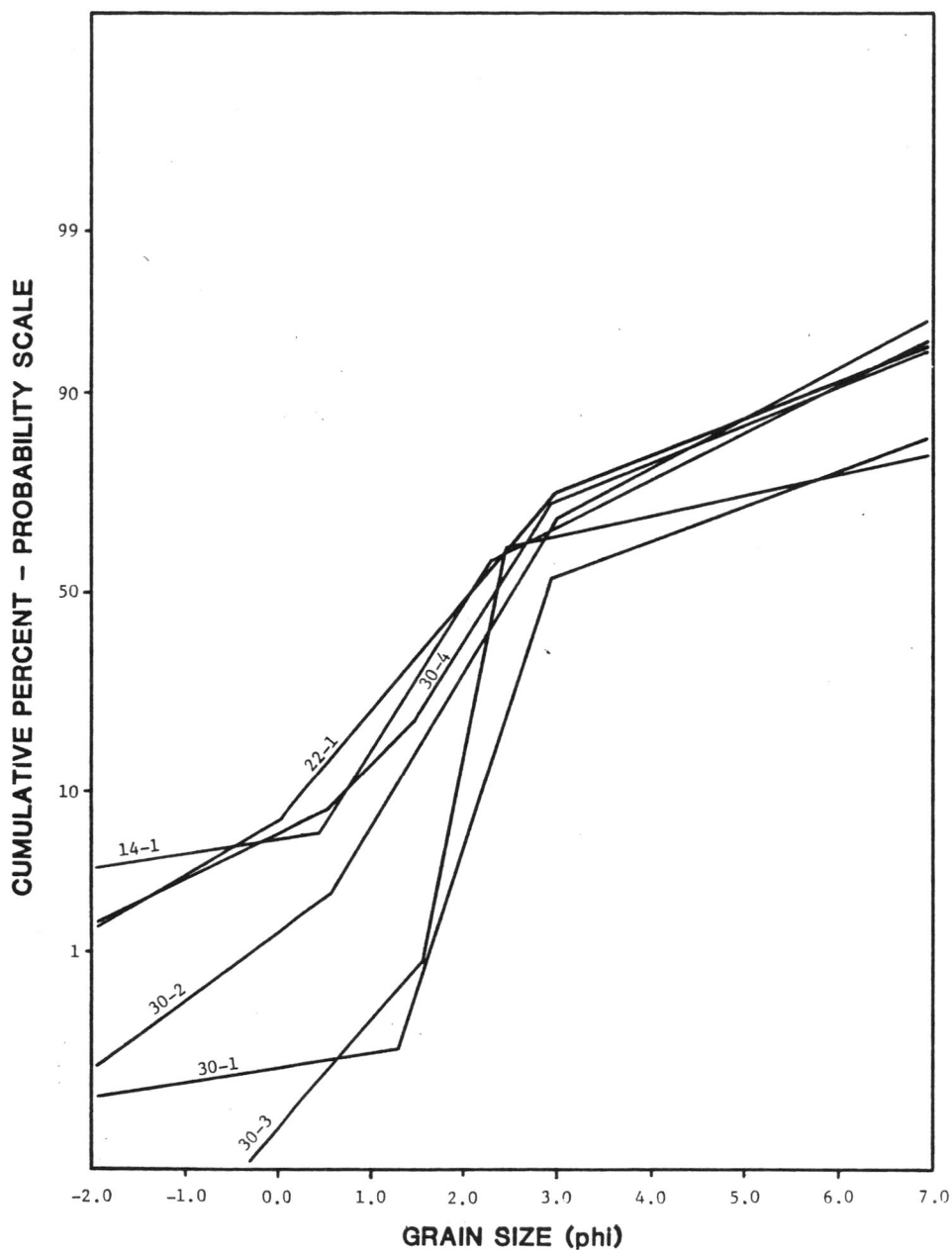


Figure C-1: Cumulative probability curves for the lower portion of the Burdigalian depositional sequence. Percentiles were taken from the curves for the statistical parameter formulas.

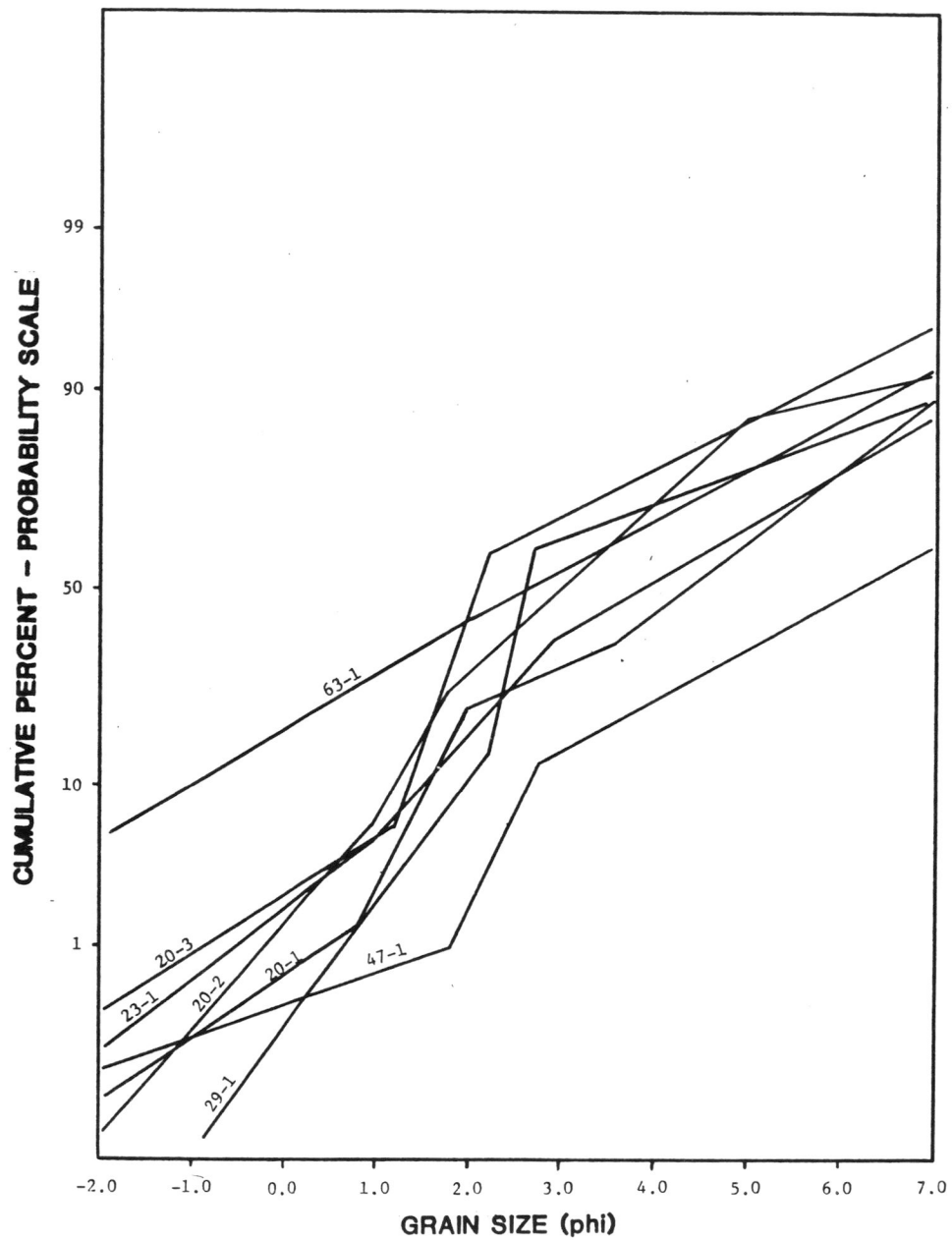


Figure C-2: Cumulative probability curves for lower portion of the Burdigalian depositional sequence. Percentiles were taken from the curves for statistical parameter formulas.

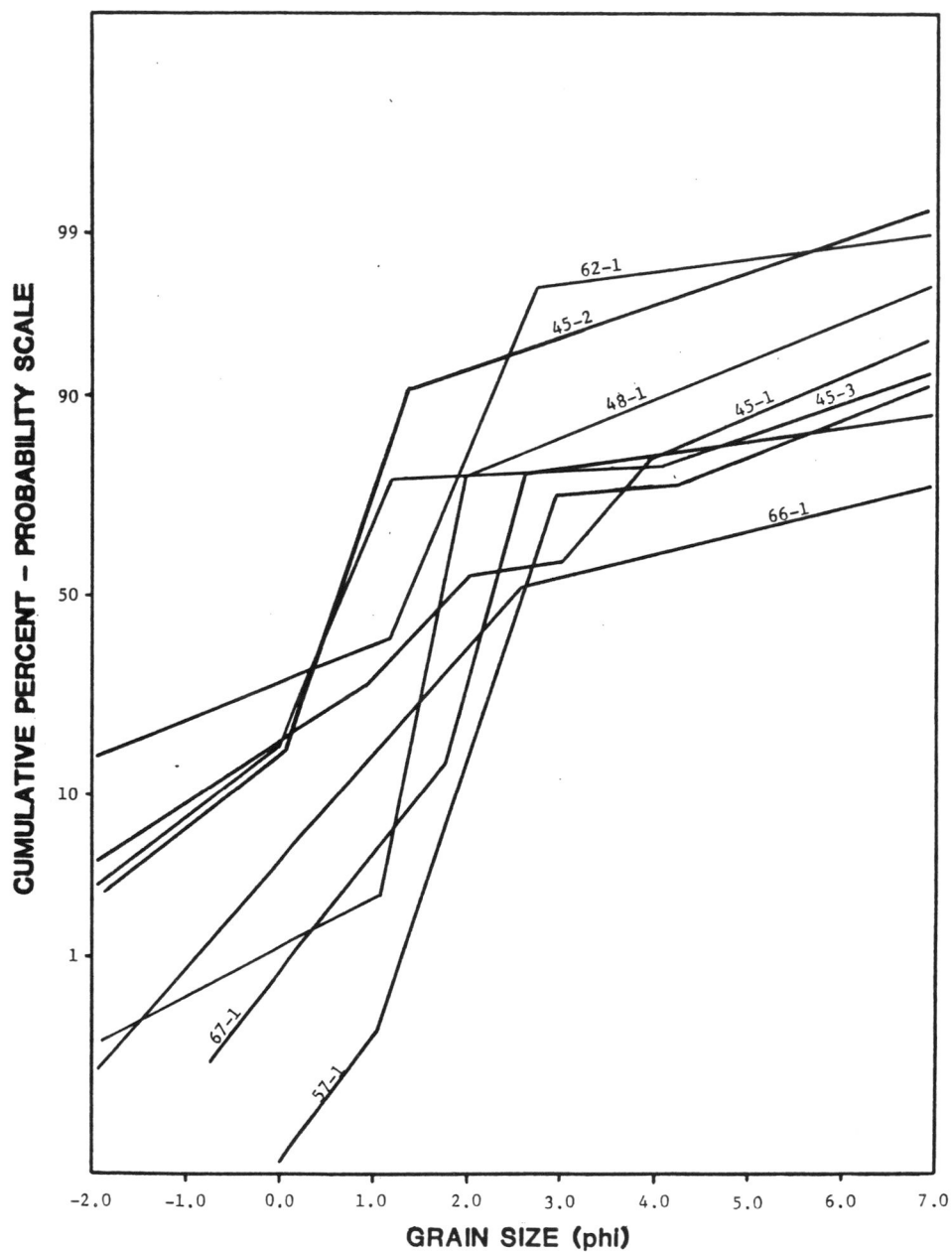


Figure C-3: Cumulative probability curves for the upper portion of the Burdigalian depositional sequence. Percentiles were taken from the curves for the statistical parameter formulas.

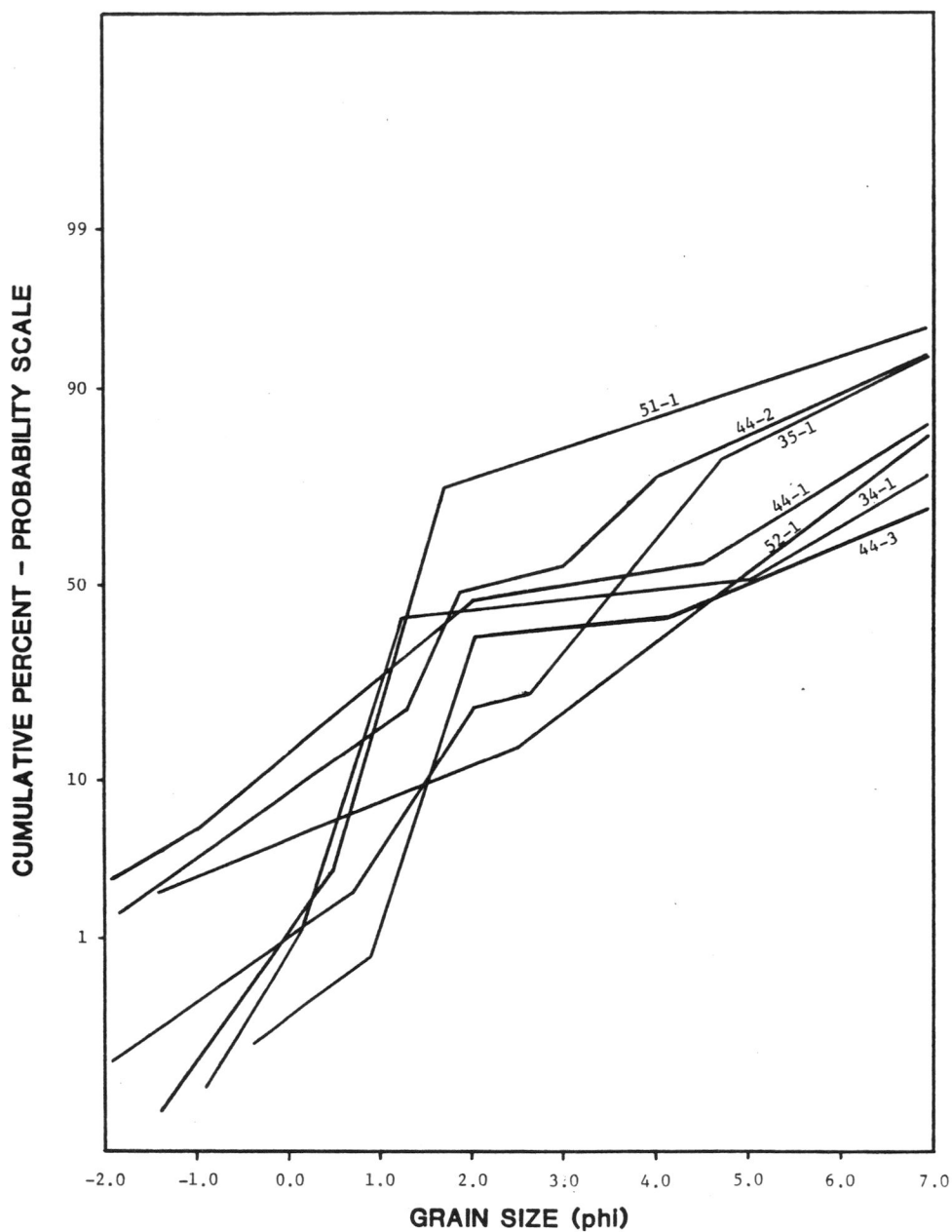


Figure C-4: Cumulative probability curves for the Langhian depositional sequence. Percentiles were taken from the curves for the statistical parameter formulas.

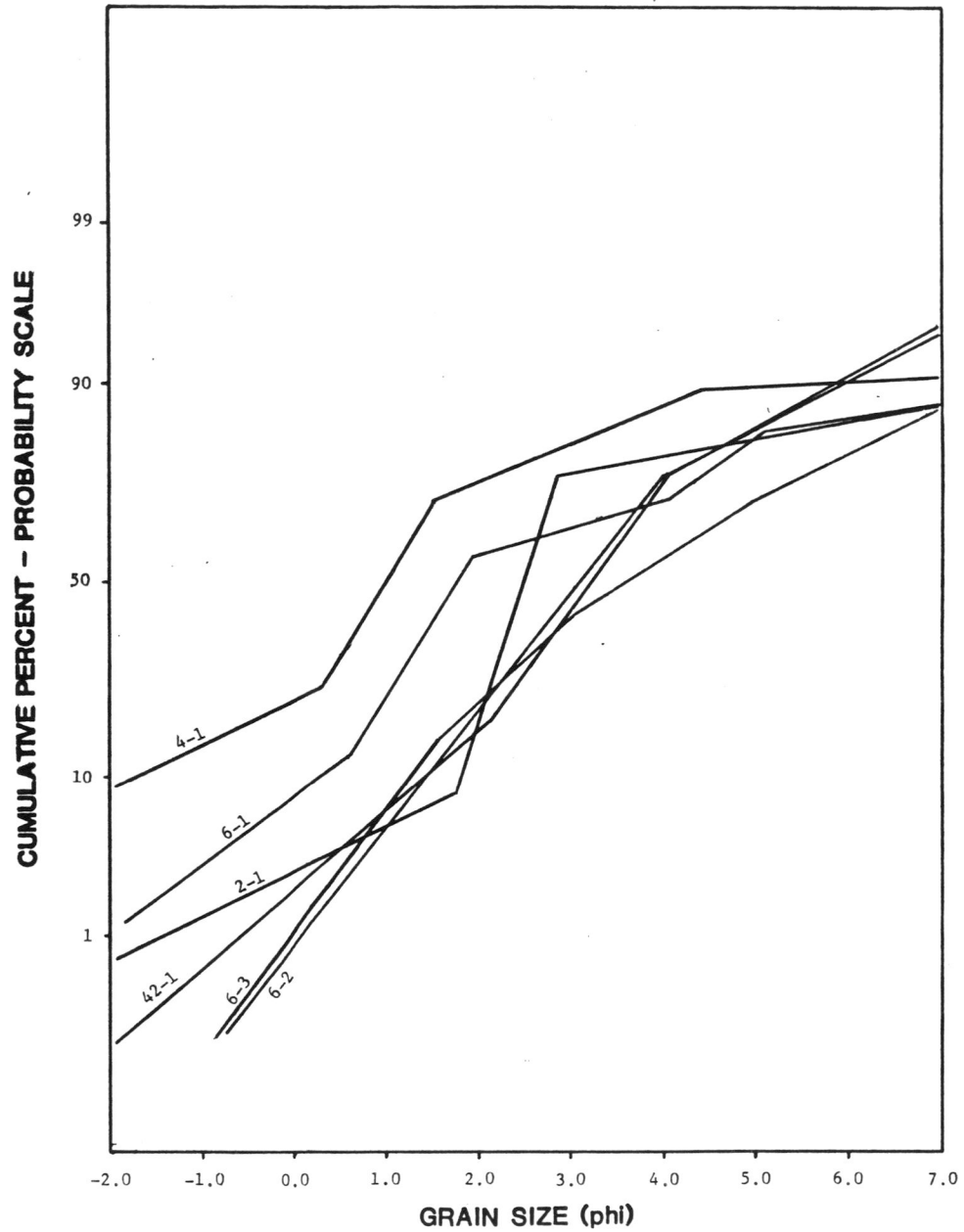


Figure C-5: Cumulative probability curves for the lower portion of the Serravallian sequence. Percentiles were taken from the curves for the statistical parameter formulas.

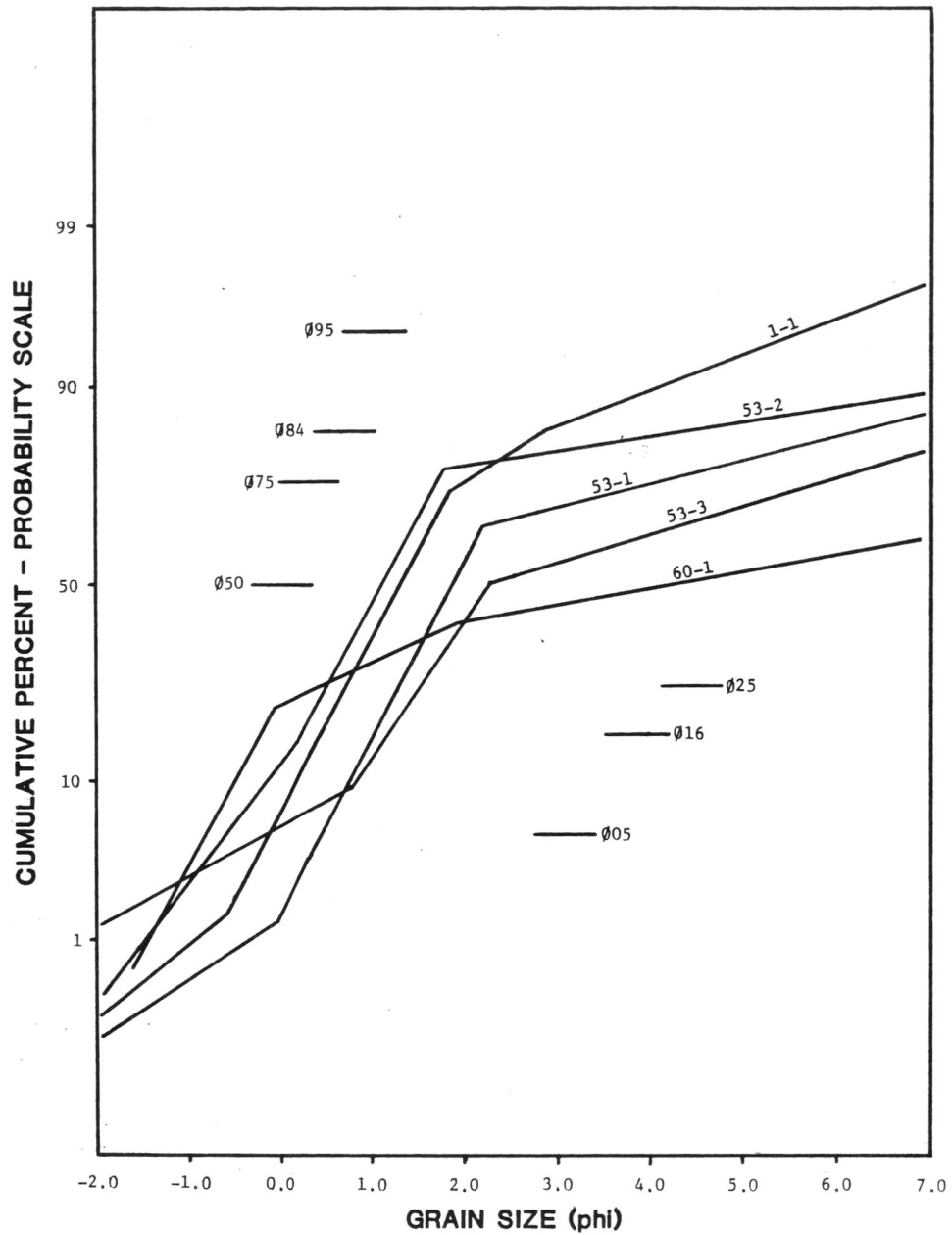


Figure C-6: Cumulative probability curves for the lower portion of the Serravallian sequence. Percentiles were taken from the curves for the statistical parameter formulas.

APPENDIX D. Formulas used for computing the statistical parameters.

Graphic Mean (M_z):

$$M_z = (\phi 16 + \phi 50 + \phi 84) / 3$$

Inclusive Graphic Standard Deviation (σ_1):

$$\sigma_1 = \frac{\phi 84 - \phi 16}{4} + \frac{\phi 95 - \phi 5}{6.6}$$

Inclusive Graphic Skewness (Sk_1):

$$Sk_1 = \frac{\phi 16 + \phi 84 - 2(\phi 50)}{2(\phi 84 - \phi 16)} + \frac{\phi 5 + \phi 95 - 2(\phi 50)}{2(\phi 95 - \phi 5)}$$

Kurtosis (K_g):

$$K_g = \frac{\phi 95 - \phi 5}{2.44 (\phi 75 - \phi 25)}$$

Mode (Mo):

"Using the graph of the sample plotted on probability paper, one selects a point where the mode ought to be, and measures the percentage of the sample that occurs within the diameter range from 1/4 ϕ coarser than that point to 1/4 ϕ finer than that point (i.e. within 1/2 ϕ interval centered on the presumed modal point). Then he moves over a small distance (say 0.1 or 0.2 ϕ) to a new presumed mode and measures the percentage occurring in the 1/2 ϕ interval centered on that new point. This is done repeatedly until the highest value is obtained which then corresponds to the modal diameter." (Folk, 1980)

Table D. Statistical parameters used for the textural analysis (from Folk, 1980).

APPENDIX E. Maturity diagram for textural analysis.

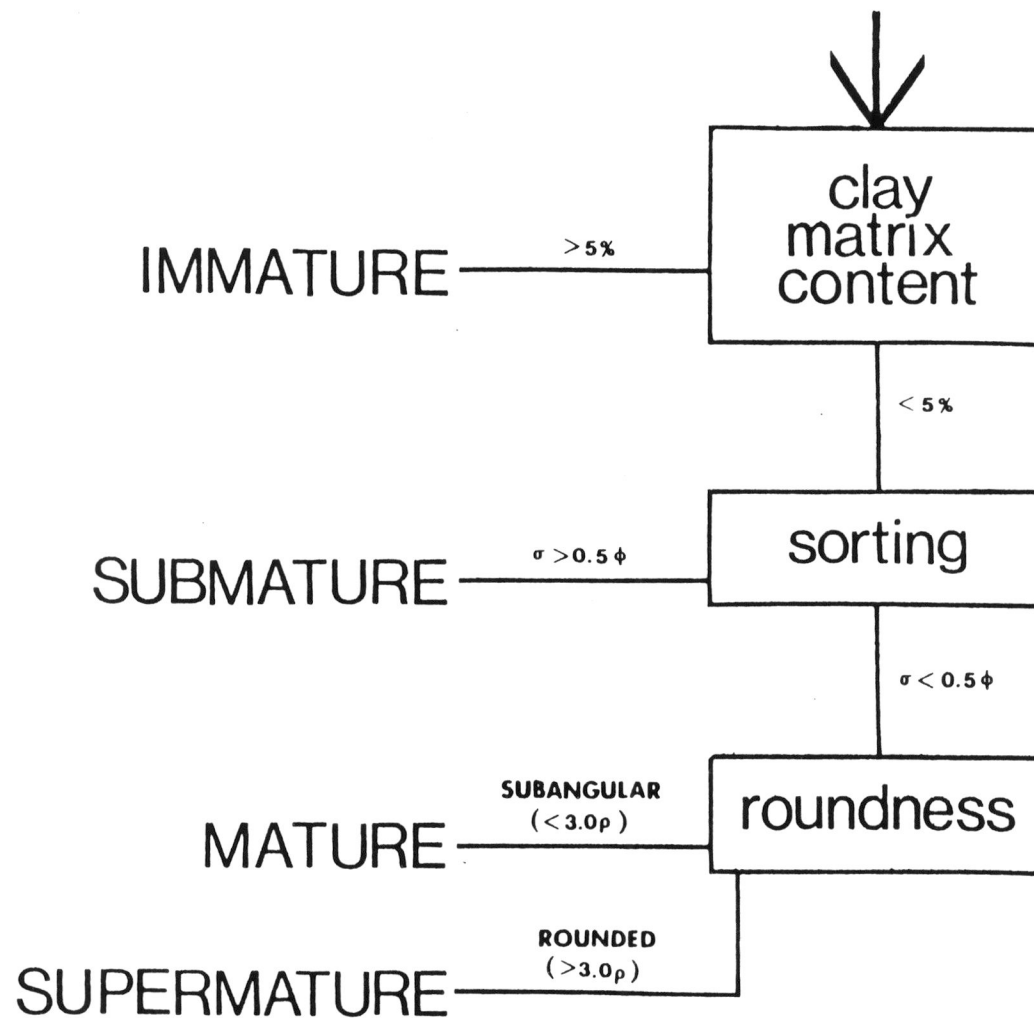


Figure E. Maturity classification scheme used for the textural samples.
 σ = sorting; ρ = roundness (from Scholle, 1979).

APPENDIX F. Textural data for samples selected from the Serravallian, Langhian, and Burdigalian depositional sequences.

UNIT	CORE	SAMPLE	DEPTH (m)	TERRIGENOUS (%)	SAND (%)	SILT (%)	CLAY (%)	COLOR
B-1	20	1	1.00-1.25	14	30	59	11	Olive Gray - 5Y 3/2
B-1	20	2	3.50-3.75	28	49	44	7	Olive Gray - 5Y 3/2
B-1	20	3	5.50-5.75	67	68	26	6	Olive Black - 5Y 2/2
B-1	23	1	2.00-2.25	23	37	50	13	Olive Black - 5Y 2/1
B-1	29	1	2.75-3.00	42	62	27	11	Olive Gray - 5G 3/2
B-1	14	1	4.75-5.00	23	60	35	5	Olive Gray - 5Y 4/1
B-1	22	1	4.75-5.00	29	74	20	6	Olive Black - 5Y 2/2
B-1	30	1	1.00-1.25	39	56	29	15	Olive Black - 5Y 2/2
B-1	30	2	1.75-2.00	46	68	28	4	Olive Black - 5Y 2/2
B-1	30	3	2.50-2.75	64	75	19	6	Olive Black - 5Y 2/2
B-1	30	4	5.00-5.25	43	57	29	14	Light Olive Gray - 5Y 5/2
avg.	14*	21*		43	62	27	11	

Table F-1: Textural data for the lower portion of the Burdigalian depositional sequence. Sample depths are measured down from the top of each core. Terrigenous percentages are from thin section point counts. Sand, silt, and clay percentages are from sieve and pipette data. Color is based on Goddard and others (1975). *= denotes total number of cores and samples studied in the Burdigalian sequence.

UNIT	CORE	SAMPLE	MEAN PHI	SORTING	SKEWNESS	KURTOSIS	MATURITY	MODES (ϕ)
B-1	20	1	5.1 m silt	4.7 x poor	.21 fine	1.1 mesokurtic	immature	3;6;8
B-1	20	2	4.1 c silt	3.8 v poor	.25 fine	1.4 leptokurtic	immature	3;5
B-1	20	3	3.5 vf sand	3.3 v poor	.55 s fine	1.5 leptokurtic	immature	3;5
B-1	23	1	5.1 m silt	4.7 x poor	.30 fine	1.5 leptokurtic	immature	6
B-1	29	1	4.4 c silt	4.5 x poor	.70 s fine	1.8 v leptokurtic	immature	3.5
B-1	14	1	3.9 vf sand	3.3 v poor	.18 fine	1.4 leptokurtic	immature	3.5;5
B-1	22	1	3.5 vf sand	3.2 v poor	.32 s fine	1.4 leptokurtic	immature	1.5;3;4
B-1	30	1	4.9 c silt	4.8 x poor	.74 s fine	1.1 mesokurtic	immature	3.5;6
B-1	30	2	3.7 vf sand	3.3 v poor	.32 s fine	1.2 leptokurtic	submature	3.5;6
B-1	30	3	3.8 vf sand	2.0 poor	.37 s fine	2.1 v leptokurtic	immature	3.5;7
B-1	30	4	4.8 c silt	4.6 x poor	.73 s fine	.92 mesokurtic	immature	3.5;5
avg.	14*	21*	3.9 vf sand	3.5 v poor	.41 s fine	1.7 v leptokurtic		

Table F-1(cont.): Textural data for the lower portion of the Burdigalian depositional sequence. f= fine; vf= very fine; m= medium; c= coarse; v= very; x= extremely; s= strongly. *= denotes the total number of cores and samples studied in the Burdigalian.

UNIT	CORE SAMPLE		DEPTH (m)	TERRIGENOUS (%)	SAND (%)	SILT (%)	CLAY (%)	COLOR
B-6	45	1	1.75-2.00	15	59	36	5	Olive Gray - 5Y 4/1
B-6	45	2	3.50-3.75	40	95	4	1	Olive Gray - 5Y 4/1
B-6	45	3	5.00-5.25	80	79	15	6	Olive Gray - 5Y 4/1
B-6	62	2	4.25-4.50	50	93	6	1	Olive Gray - 5Y 4/1
B-6	66	1	3.00-3.25	83	56	19	25	Olive Gray - 5Y 3/2
B-6	67	1	3.50-3.75	35	78	9	13	Light Olive Gray - 5Y 3/2
B-5	57	1	4.75-5.00	78	74	19	7	Olive Black - 5Y 2/2
B-3	48	1	4.00-4.25	69	85	13	2	Olive Gray - 5Y 3/2
B-2	47	1	5.00-5.25	23	12	47	41	Grayish Olive - 10Y 4/2
B-2	63	1	2.25-2.50	22	54	37	9	Greenish Black - 5G 2/1

Table F-2: Textural data for the upper portion of the Burdigalian depositional sequence. Sample depths are measured down from the top of the core. Terrigenous percentages are from thin section point counts. Sand, silt, and clay percentages are from sieve and pipette data. Color codes are from Goddard and others (1975).

UNIT	CORE	SAMPLE	MEAN PHI	SORTING	SKEWNESS	KURTOSIS	MATURITY	MODES (ϕ)
B-6	45	1	3.0 f sand	2.8 v poor	.25 s fine	1.0 mesokurtic	immature	3;5
B-6	45	2	1.6 m sand	1.4 poor	.16 fine	2.1 v leptokurtic	submature	2
B-6	45	3	2.8 f sand	3.1 v poor	.68 s fine	2.9 v leptokurtic	immature	2
B-6	62	2	2.1 f sand	1.7 poor	-.11 coarse	.64 v platykurtic	submature	3
B-6	66	1	4.7 c silt	3.1 v poor	.57 s fine	.81 mesokurtic	immature	3
B-6	67	2	4.6 c silt	2.5 v poor	1.0 s fine	4.6 x leptokurtic	immature	3.5
B-5	57	1	4.2 c silt	4.1 x poor	.70 s fine	2.9 v leptokurtic	immature	3.5;7
B-3	48	1	3.0 f sand	2.9 v poor	.68 s fine	3.7 x leptokurtic	submature	3
B-2	47	1	7.0 f silt	5.7 x poor	-.06 sym	.85 platykurtic	immature	5;8
B-2	63	1	3.6 vf sand	3.4 v poor	.17 fine	.94 mesokurtic	immature	3

Table F-2 (cont.): Textural data for the upper portion of the Burdigalian depositional sequence. f= fine; vf= very fine; m= medium; c= coarse; v= very; x= extremely; s= strongly; sym= symmetric.

UNIT	CORE SAMPLE		DEPTH (m)	TERRIGENOUS (%)	SAND (%)	SILT (%)	CLAY (%)	COLOR
L-2	34	1	2.00-2.25	27	47	30	23	Olive Gray - 5Y 3/2
L-2	52	1	3.50-3.75	61	18	66	16	Grayish Olive - 10 4/2
L-1	35	1	3.75-4.00	12	32	61	7	Medium Olive - 5Y 5/1 Gray
L-1	44	1	1.75-2.00	30	49	35	16	Olive Gray - 5Y 4/1
L-1	44	2	3.00-3.25	43	54	39	7	Medium Olive - 5Y 4/2 Gray
L-1	44	3	5.50-5.75	57	37	31	32	Olive Gray - 5Y 3/2
L-1	51	1	4.00-4.25	75	80	12	8	Olive Gray - 5Y 3/2
avg.	5*	7*		43	45	39	16	

Table F-3: Textural data for the Langhian depositional sequence. Sample depths are measured down from the top of each core. Terrigenous percentages are from thin section point counts. Sand, silt, and clay percentages are from sieve and pipette data. Color is based on Goddard and others (1975). *= denotes total number of cores and samples studied for the Langhian sequence.

UNIT	CORE	SAMPLE	MEAN PHI	SORTING	SKEWNESS	KURTOSIS	MATURITY	MODES (Ø)
L-2	34	1	5.7 m silt	4.9 x poor	.12 fine	.74 platykurtic	immature	2.2;5
L-2	52	1	6.0 m silt	4.7 x poor	.07 sym	1.5 leptokurtic	immature	5;7
L-1	35	1	4.6 c silt	3.9 v poor	.04 sym	1.3 leptokurtic	immature	3;5
L-1	44	1	4.5 c silt	3.7 v poor	.05 sym	.78 platykurtic	immature	3;7
L-1	44	2	3.8 vf sand	3.7 v poor	.56 s fine	1.5 leptokurtic	immature	3;6
L-1	44	3	5.8 m silt	4.6 x poor	-.17 coarse	.55 v platykurtic	immature	3;6
L-1	51	1	3.2 vf sand	3.7 v poor	.75 s fine	4.2 x leptokurtic	immature	2;5
avg.	5*	7*	4.8 c silt	4.2 x poor	.20 fine	1.5 leptokurtic		

Table F-3 (cont.): Textural data for the Langhian depositional sequence. f= fine; vf= very fine; m= medium; c= coarse; v= very; sym= symmetric; x= extremely; s= strongly. *= denotes total number of cores and samples studied in the Langhian sequence.

UNIT	CORE	SAMPLE	DEPTH (m)	TERRIGENOUS (%)	SAND (%)	SILT (%)	CLAY (%)	COLOR
S-5	1	1	5.00-5.25	53	76	10	14	Grayish olive - 10Y 4/2
S-2	53	1	1.25-1.50	61	78	20	2	Greenish Black - 5GY 2/1
S-2	53	2	3.75-4.00	57	82	7	11	Greenish Black - 5GY 2/1
S-2	53	3	5.25-5.50	48	55	28	17	Greenish Black - 5GY 2/1
S-2	60	1	5.50-6.00	42	42	20	40	Olive Gray - 5Y 4/1
S-1	2	1	4.50-4.75	82	78	8	14	Olive Gray - 5Y 3/2
S-1	4	1	5.50-5.75	76	81	9	10	Olive Gray - 5Y 3/2
S-1	6	1	0.50-0.75	74	62	26	12	Olive Black - 5Y 2/1
S-1	6	2	3.00-3.25	79	54	41	5	Olive Black - 5Y 2/1
S-1	6	3	7.25-7.50	64	44	45	11	Olive Black - 5Y 2/1
S-1	42	1	2.50-2.75	43	44	51	5	Olive Gray - 5Y 3/2
avg.	7*	11*		58	64	24	12	

Table F-4: Textural data for the Serravallian depositional sequence. Sample depths are measured down from the top of each core. Terrigenous percentages are from thin section point counts. Sand, silt, and clay percentages are from sieve and pipette data. Color codes are from Goddard and others (1975). *= denotes total number of cores and samples studied in the Serravallian sequence.

UNIT	CORE	SAMPLE	MEAN PHI	SORTING	SKEWNESS	KURTOSIS	MATURITY	MODES (Ø)
S-5	1	1	2.8 f sand	4.1 x poor	2.8 s fine	2.9 leptokurtic	submature	2.5;5
S-2	53	1	3.8 vf sand	4.2 x poor	.67 s fine	1.6 v leptokurtic	immature	1.5
S-2	53	2	3.2 vf sand	3.7 v poor	.63 s fine	3.4 x leptokurtic	immature	2.5
S-2	53	3	6.5 m silt	6.0 x poor	2.8 s fine	.90 platykurtic	immature	3
S-2	60	1	5.4 m silt	4.4 x poor	-.10 coarse	.65 v platykurtic	immature	1;2.5
S-1	2	1	4.1 c silt	4.3 v poor	.67 s fine	5.1 x leptokurtic	immature	3.5
S-1	4	1	2.2 f sand	3.0 v poor	.43 s fine	2.5 v leptokurtic	immature	-1;2
S-1	6	1	3.7 vf sand	3.4 v poor	.54 s fine	.90 platykurtic	immature	1;2.5;6
S-1	6	2	4.1 c silt	3.7 v poor	.27 s fine	1.5 leptokurtic	immature	2.5;4;5
S-1	6	3	4.8 c silt	4.4 x poor	.33 s fine	1.3 leptokurtic	immature	2.5;4;6
S-1	42	1	4.1 c silt	3.4 v poor	.03 sym	1.6 v leptokurtic	immature	2.5;7
avg.	7*	11*	3.5 vf sand	4.1 x poor	1.4 s fine	2.2 v leptokurtic		

Table F-4 (cont.): Textural data for the Serravallian depositional sequence. f= fine; v= very; vf= very fine; m= medium; c= coarse; x= extremely; s= strongly; sym= symmetric; *= denotes the total number of cores and samples studied in the Serravallian sequence.

APPENDIX G. Ternary diagrams of sand-silt-clay percentages for the samples selected for textural study.

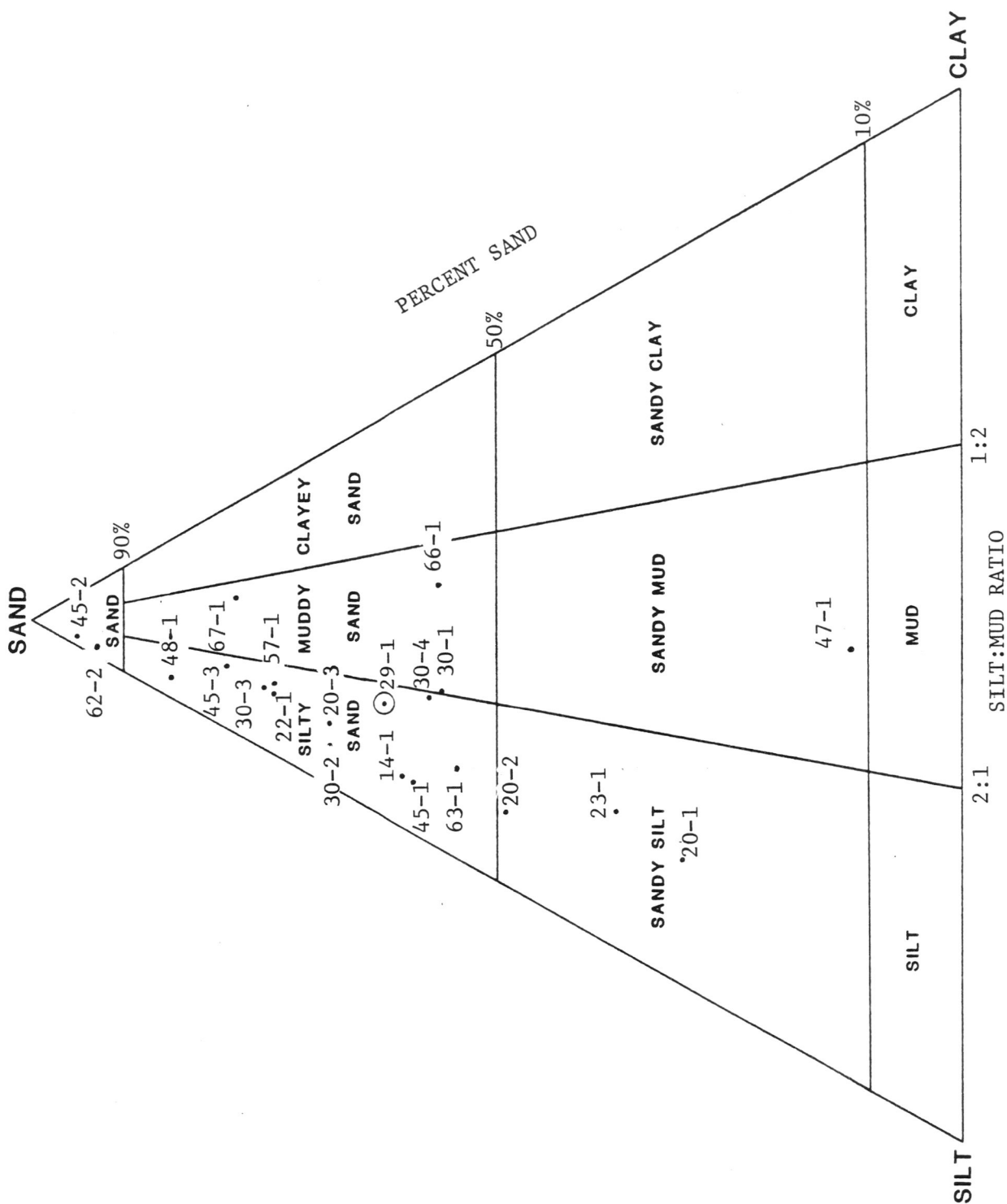


Figure G-1: Ternary diagram of sand, silt, and clay percentages for the Burdigalian depositional sequence. Circled dot is the average sand-silt-clay value for the sequence which also corresponds to the value for sample 29-1.

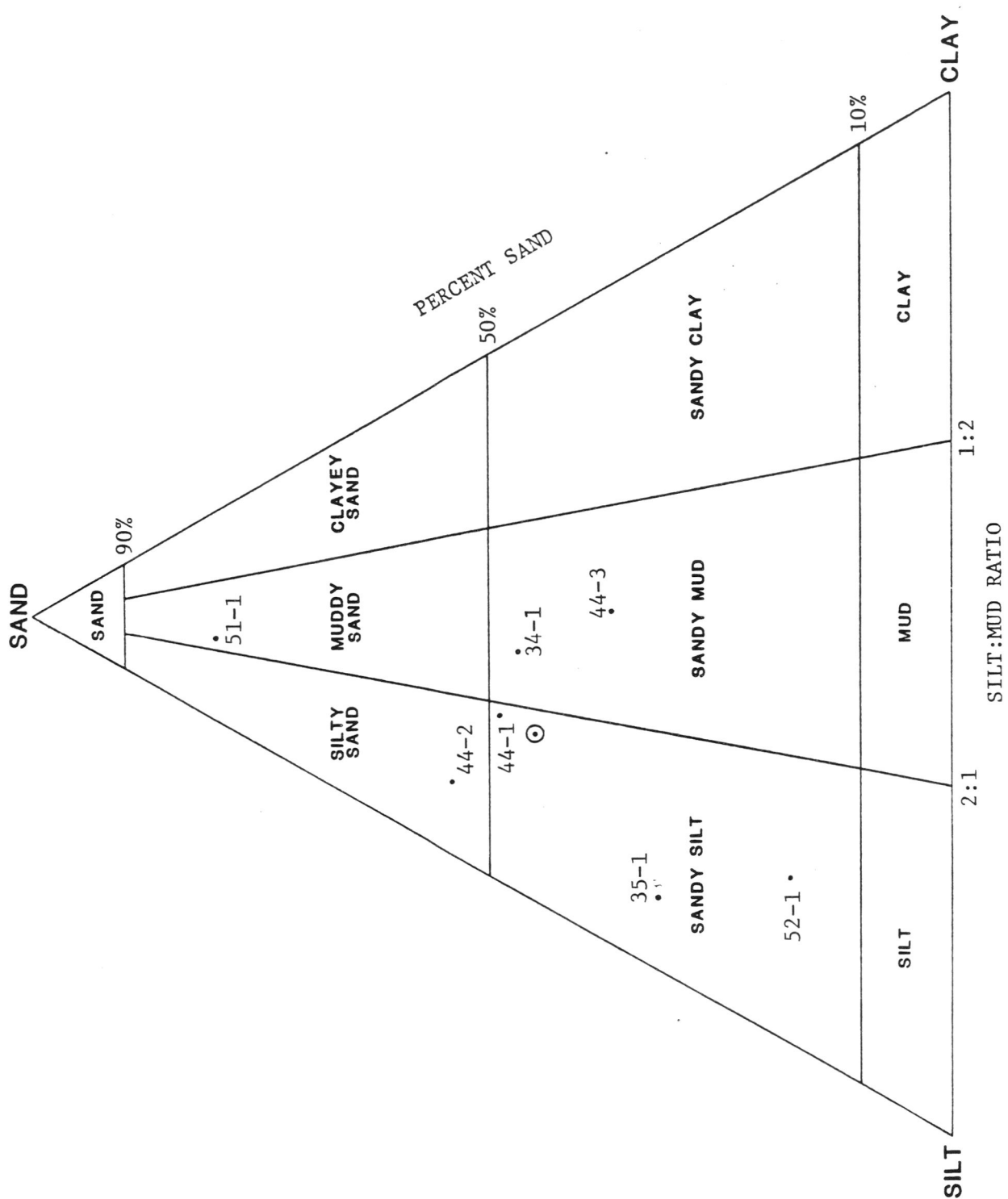


Figure G-2: Ternary diagram of sand, silt, and clay percentages for the Langhian depositional sequence. Circled dot is the average sand-silt-clay value for the sequence. Classification is from Folk (1980).

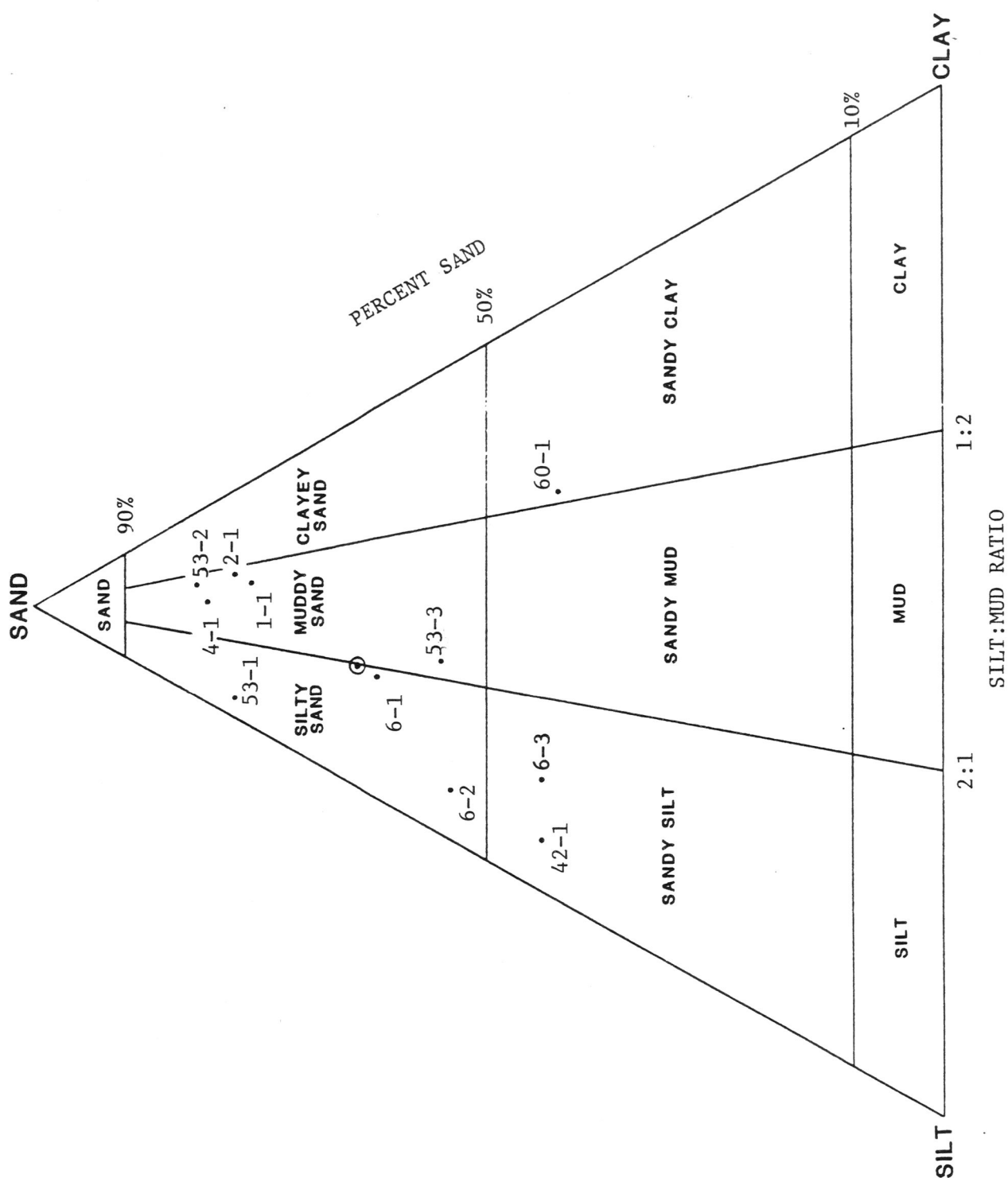


Figure G-3: Ternary diagram of sand, silt, and clay percentages for the Serravallian depositional sequence. Circled dot is the average sand-silt-clay value for the sequence. Classification is from Folk (1980).

APPENDIX H. Point count data from samples selected from the Burdigalian, Langhian, and Serravallian depositional sequences.

UNIT	CORE	SAMPLE	Qu	Ks	Un	Tw	Mi	Zr	Ca	Rh	Sh	Sf	Ph	Cr	Cs	Op	Gl	Ch	Ma
B-1	20	1	11	2	-	2	1	-	-	-	12	11	3	-	-	-	1	-	57
B-1	20	2	25	1	-	-	2	-	2	-	7	4	9	-	-	-	1	-	49
B-1	20	3	66	-	-	1	-	-	-	-	-	6	4	-	-	-	-	-	23
B-1	23	1	29	1	-	-	T	-	-	-	13	13	34	-	-	T	T	-	8
B-1	29	1	41	2	1	2	T	-	-	-	8	6	3	1	-	4	T	-	31
B-1	14	1	21	2	T	T	T	-	-	T	-	-	T	-	-	-	T	-	74
B-1	22	1	24	1	1	1	1	T	-	T	8	2	33	-	-	-	T	T	27
B-1	30	1	34	1	2	T	T	-	-	2	-	T	26	-	-	T	T	-	32
B-1	30	2	40	2	2	1	1	T	-	T	-	-	25	-	-	-	T	-	27
B-1	30	3	59	1	2	2	T	-	T	-	T	-	15	-	-	T	1	-	18
B-1	30	4	37	5	1	-	T	-	4	4	-	-	T	-	-	1	T	-	46

Table H-1: Point count data in percent for samples from the lower portion of the Burdigalian sequence. Qu= quartz; Ks= potassium feldspar; Un= untwinned feldspar; Tw= twinned feldspar; Mi= muscovite mica; Zr= zircon; Ca= calcite; Rh= dolomite rhombs; Sh= shells; Sf= shell fragments; Ph= phosphate; Cr= clay rims; Cs= clay clasts; Op= opaques; Gl= glauconite; Ch= chert; Ma= matrix; T= trace or <1%.

UNIT	CORE	SAMPLE	Qu	Ks	Un	Tw	Mi	Zr	Ca	Rh	Sh	Sf	Ph	Cr	Cs	Op	Gl	Ch	Ma
B-6	45	1	15	T	-	-	-	-	6	T	4	9	-	-	-	1	-	-	63
B-6	45	2	35	5	T	T	-	-	-	1	-	-	1	-	-	1	-	-	56
B-6	45	3	76	3	1	T	-	-	-	T	-	1	1	T	-	1	-	-	16
B-6	62	2	51	1	1	-	T	-	T	1	2	3	-	-	-	2	-	-	38
B-6	66	1	79	3	T	T	-	-	-	-	-	-	3	-	-	T	-	T	13
B-6	67	1	32	3	-	-	-	-	4	-	39	12	T	-	-	T	-	1	8
B-5	57	1	67	6	2	2	T	-	-	-	-	-	T	-	-	-	-	-	22
B-3	48	1	71	-	T	-	-	-	-	-	-	-	-	2	-	-	1	-	25
B-2	47	1	21	-	-	2	-	-	T	T	-	-	-	-	-	T	T	-	74
B-2	63	1	16	3	1	3	-	-	-	1	21	10	5	-	-	T	-	-	40
avg.	14*	21*	40	2	T	T	T	T	T	T	5	4	8	T	T	T	T	T	36

Table H-1 (cont.): Point count data in percent for samples from the upper portion of the Burdigalian depositional sequence. *= denotes total number of cores and samples studied in the Burdigalian sequence. Qu= quartz; Ks= potassium feldspar; Un= untwinned feldspar; Tw= twinned feldspar; Mi= muscovite mica; Zr= zircon; Ca= calcite; Rh= dolomite rhombs; Sh= shells; Sf= shell fragments; Ph= phosphate; Cr= clay rims; Cs= clay clasts; Op= opaques; Gl= glauconite; Ch= chert; Ma= matrix; T= trace or <1%.

UNIT	CORE	SAMPLE	Qu	Ks	Un	Tw	Mi	Zr	Ca	Rh	Sh	Sf	Ph	Cr	Cs	Op	Gl	Ch	Ma
L-2	34	1	22	2	T	T	T	-	-	T	-	T	T	-	-	T	T	-	72
L-2	52	1	58	2	-	2	T	-	2	1	-	8	-	-	-	-	-	-	27
L-1	35	1	10	-	-	-	-	-	-	1	1	-	T	-	-	-	-	T	87
L-1	44	1	14	-	-	2	T	-	-	T	-	-	-	-	-	-	-	T	82
L-1	44	2	37	4	1	-	T	-	2	-	-	-	2	T	-	T	-	T	52
L-1	44	3	50	4	2	T	T	-	-	5	-	-	4	-	T	1	-	T	31
L-1	51	1	69	2	1	-	T	-	-	1	-	-	1	-	-	-	-	-	25
avg.	5*	7*	37	2	T	T	T	-	T	1	T	1	1	T	T	T	T	T	53

Table H-2: Point count data in percent for samples from the Langhian depositional sequence. *= denotes total number of cores and samples studied in the Langhian sequence. Qu= quartz; Ks= potassium feldspar; Un= untwinned feldspar; Tw= twinned feldspar; Mi= muscovite mica; Zr= zircon; Ca= calcite; Rh= dolomite rhombs; Sh= shells; Sf= shell fragments; Ph= phosphate; Cr= clay rims; Cs= clay clasts; Op= opaques; Gl= glauconite; Ch= chert; Ma= matrix; T= trace or <1%.

UNIT	CORE	SAMPLE	Qu	Ks	Un	Tw	Mi	Zr	Ca	Rh	Sh	Sf	Ph	Cr	Cs	Op	Gl	Ch	Ma
S-5	1	1	52	1	-	-	-	-	-	8	-	-	8	-	-	1	1	-	29
S-2	53	1	59	1	-	-	-	-	-	-	-	1	2	-	-	-	-	1	36
S-2	53	2	55	1	T	T	-	-	-	T	T	T	21	-	-	-	-	T	19
S-2	53	3	46	T	-	-	T	-	3	-	3	11	24	-	-	-	T	-	12
S-2	60	1	40	T	1	-	-	-	-	-	-	T	1	-	-	-	-	-	57
S-1	2	1	76	3	-	-	1	T	-	-	-	-	T	5	-	T	2	2	8
S-1	4	1	74	1	T	-	-	-	-	-	-	1	3	3	-	T	T	-	16
S-1	6	1	60	2	T	T	1	-	5	1	-	2	9	5	-	T	T	T	12
S-1	6	2	63	3	3	2	2	T	2	T	-	-	5	3	-	T	T	T	15
S-1	6	3	56	2	1	2	2	-	T	-	-	-	7	T	6	T	T	T	22
S-1	42	1	40	1	T	T	T	-	-	T	-	-	4	T	T	T	1	-	50
avg.	7*	11*	56	2	T	T	T	T	1	1	T	1	8	1	T	T	T	T	25

Table H-3: Point count data in percent for samples from the Serravallian depositional sequence. *= denotes total number of cores and samples studied in the Serravallian sequence. Qu= quartz; Ks= potassium feldspar; Un= untwinned feldspar; Tw= twinned feldspar; Mi= muscovite mica; Zr= zircon; Ca= calcite; Rh= dolomite rhombs; Sh= shells; Sf= shell fragments; Ph= phosphate; Cr= clay rim; Cs= clay clasts; Op= opaques; Gl= glauconite; Ch= chert; Ma= matrix; T= trace or <1%.