1987

Clay Mineral Distribution and Source Discrimination of Holocene Sediments in Lower Chesapeake Bay, Virginia

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Recommended Citation

Skrabal, Stephen A., "Clay Mineral Distribution and Source Discrimination of Holocene Sediments in Lower Chesapeake Bay, Virginia" (1987). *Dissertations, Theses, and Masters Projects.* Paper 1539617578.
https://dx.doi.org/doi:10.25773/v5-x236-rq60

CLAY MINERAL DISTRIBUTION AND SOURCE DISCRIMINATION OF HOLOCENE SEDIMENTS IN LOWER CHESAPEAKE BAY, VIRGINIA

A Thesis
Presented to
The Faculty of the School of Marine Science
The College of William and Mary in Virginia

In Partial Fulfillment
of the Requirements for the Degree of
Master of Arts

by
Stephen Andrew Skrabal
1987

APPROVAL SHEET

This thesis is submitted in partial fulfillment of
the requirements of the degree of

Master of Arts

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ACKNOWLEDGMENTS

I am grateful to my committee members for their cooperation and constructive criticisms offered during the course of this research. John Boon served as chairman of my committee, and provided valuable guidance on matters statistical. His insightful comments greatly improved the final draft, and forced me to think more clearly about the research problem. Carl "Woody" Hobbs provided several valuable references concerning this research, including a preprint of one of his papers. I also thank Woody and Rick Berquist for providing me with a research assistantship. Maynard Nichols offered wisdom concerning various aspects of sedimentation in the James River estuary. Bill MacIntyre led me to some of the seminal texts on clay mineral chemistry. Howard Kator provided helpful criticisms which especially improved the methods section.

I am greatly indebted to Pat Barthle, who kindly sacrificed her time to help me get a crucial computer program running. Mal Green graciously contributed his time to help with the formatting of this thesis. Faculty, staff, and students of the Chemical Oceanography and Microbiology departments helped me to obtain various pieces of laboratory equipment. Stephen Clement at the William and Mary Department of Geology provided valuable guidance on operation of the x-ray diffractometer; I thank the department for allowing me extensive use of their facilities over the course of my stay at VIMS.

I thank all my friends at VIMS, especially in the Department of Geological and Benthic Oceanography, who, at one time or another, offered their help and encouragement. In particular, Sandy Booth provided hospitality and friendship, especially during a hectic time.

I am grateful to my family and friends for their constant support and good humor.

To my wife Tracy Lee, I owe inexpressible gratitude, not only for her considerable help in assembling this thesis, but for all her support and encouragement, and for helping me to keep it all in perspective.

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ABSTRACT

Although surfical distributions and sources of clay minerals have been studied in the lower Chesapeake Bay, subsurface patterns have not been investigated. In this study, two size subfractions (2-0.2 um and <0.2 um) of thirty samples from five cores of Holocene sediment in the lower bay were analyzed by semi-quantitative x-ray diffraction methods in order to determine the relative significance of marine and fluvial sources of clay minerals in the lower bay, and identify possible pathways of Holocene sedimentation, with special reference to Thimble Shoal Channel.

Overall clay mineral compositions were in good agreement with previous investigations, showing, in decreasing abundance, illite, mixed-layer clays, vermiculite, dioctahedral vermiculite, kaolinite, montmorillonite, and chlorite. Although clay mineral distributions showed no outstanding variations with depth, significant compositional differences existed between cores. A series of discriminant function analyses were employed to determine the significance of mineral variations between two groups of cores. One group was assumed to reflect a marine source, based on proximity to Thimble Shoal Channel, a major axial channel of the bay; the other was assumed to reflect a dominantly continental source. These assumptions were based on previous determinations of source "end-members" in surficial sediments.

Results from the discriminant analyses indicated that samples from cores near Thimble Shoal Channel are effectively discriminated from the other samples on the basis of clay mineral composition. The species contributing most to the separation was illite, which was enriched in samples near the Channel. The previously established association of illite with a marine origin, in conjunction with distributions of other clay minerals consistent with this origin, suggested that Thimble Shoal Channel is dominated by, and acts as a conduit for, inputs from the continental shelf. This pattern is consistent with results of previous studies showing that the shelf is a dominant source of sandy sediment in the lower bay. This interpretation is at odds with Ludwick's (1981) assertion that sedimentation in the landward portion of the Channel is dominated by deposition from the ebb plume of the James River.

The two size subfractions of the total clay fraction showed marked differences in mineralogy, consistent with the probable modal size distributions of the various species. Lack of consistent correlations between grain size and mineralogy suggested that mineralogy is essentially independent of texture in these sediments.

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I. INTRODUCTION

Background

The determination of sources and transport pathways of sediments in lower Chesapeake Bay has been the subject of many studies using various methods of analysis. Calculation of a sediment budget for the region (Byrne et al., 1982) and analyses of cores and seismic-reflection data (Meisburger, 1972; Colman and Hobbs, 1987; Hobbs et al., 1986) have strongly suggested that the ocean is a quantitatively significant source of sediment for the lower bay. As shall be discussed, several studies have approached the problem by examining mineralogic gradients in these sediments; this work has shown that river-borne material can generally be distinguished from marine material on the basis of mineralogic composition.

Sand is a major component of the sediment fill in the lower Bay, and consequently has been the subject of the majority of mineralogic studies in the area. The distribution of sand-sized heavy minerals has been analyzed in several studies in both two-dimensions (e.g., Ryan, 1953; Goodwin and Thomas, 1973; Firek et al., 1977) and three dimensions (Berquist, 1986). In the latter study, Berquist examined heavy mineral distributions in cores throughout the lower bay, and was able to distinguish land-derived sands overlying compositionally distinct material derived from the continental shelf. These findings supported the evidence of Meisburger (1972), Byrne et al. (1982), Boon et al. (1983), and Hobbs et al. (1986), which indicated that the shelf is an important source of sediment for the lower bay.

Few studies have been devoted to fine-grained sediments which are important constituents of the lower Bay, particularly in deposits of the lower James River estuary (Nichols, 1972), in turbid plumes from that river (Ludwick, 1981) and in the Bay entrance (Ludwick and Melchor, 1972), and in low-energy channels and embayments. The analysis of clay minerals has been shown to be an effective method for identifying sources and pathways of fine-grained sediments, primarily because of their sensitivity to transport.

Hathaway (1972) has shown that the composition of clay mineral suites in estuaries of the east coast of the United States, including the Chesapeake Bay estuarine system, is strongly influenced by continentally-derived, river-borne material, and by sediment transported from the shelf. In one of the few studies of clay mineral distributions of sediments of the lower bay, Feuillet and Fleischer (1980) have identified mineralogic gradients in surficial sediments along the James River estuary. They attributed these gradients to the mixing of river-derived and shelf-derived clay mineral suites by classical, two-layered estuarine circulation. The dilution of the continental suite by the marine suite was taken as evidence by them of Meade's (1969) observation of the transport of bottom sediments by landward currents in estuaries of the Atlantic Coastal Plain.

Presently there are no means of determining whether multiple sources exist among subsurface, fine-grained sediments in Chesapeake Bay and, if so, what means may best be used to discriminate one source from another. Because we lack knowledge of the three-dimensional distribution of clay minerals in the lower bay, research is needed to determine these distributions in order to pose the question of their utility as source discriminators of fine-grained sediments.

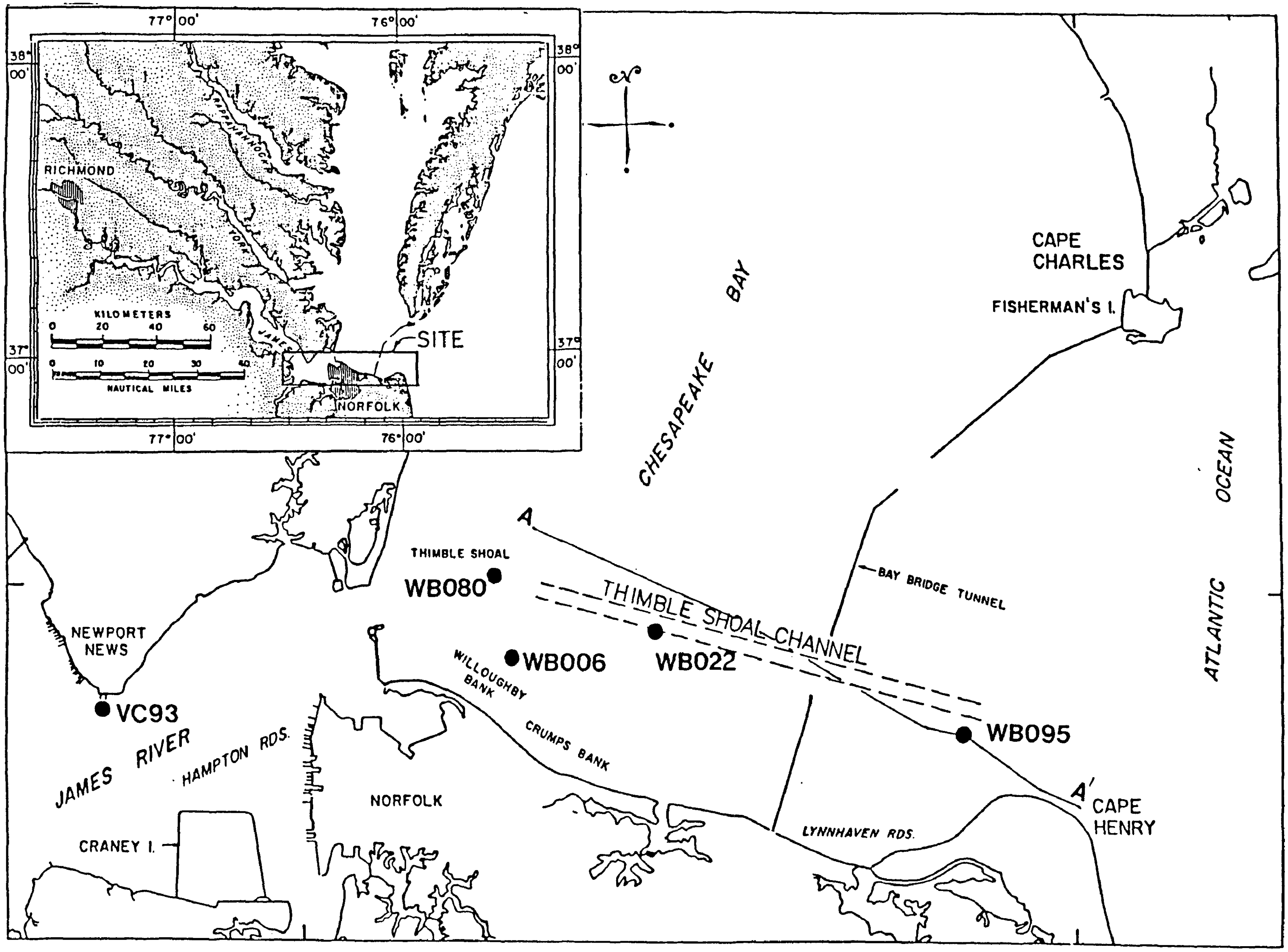
Study objectives

The purposes of this study were to determine possible variations in the clay mineralogy of two size subfractions in five cores of Holocene sediment in the lower Chesapeake Bay, to determine the relative significance of marine and fluvial sources of clay minerals to the bay, and to identify possible pathways and processes of Holocene sedimentation in the lower bay. The dominant source of clay minerals in Thimble Shoal Channel was determined in order to evaluate its role as a conduit for sediment in the lower Bay.

Study area

The study area, depicted in Figure 1, spans a portion of the mixing zone between the James River estuary and the mouth of the Chesapeake Bay. This area has been the focus of relatively dense sampling by vibracoring (Hobbs et al., 1984; Swean, 1986); this large inventory of cores was made available to the author by these investigators.

Figure 1. Map of study area with core locations and major geomorphic and geographic features. Transect A-A′ is depicted in Figure 2.


77° 00'
76° 00'
38° 00'
37° 00'
RICHMOND
RAPPAHANNOCK
YORK
JAMES
KILOMETERS
0 20 40 60
0 10 20 30 40
NAUTICAL MILES
SITE
NORFOLK
N
CAPE CHARLES
FISHERMAN'S I.
CHESAPEAKE BAY
ATLANTIC OCEAN
BAY BRIDGE TUNNEL
A
A'
THIMBLE SHOAL
WB080
THIMBLE SHOAL CHANNEL
WB006
WB022
WB095
WILLOUGHBY BANK
CRUMPS BANK
NEWPORT NEWS
VC93
JAMES RIVER
HAMPTON RDS.
NORFOLK
CRANEY I.
LYNNHAVEN RDS.
CAPE HENRY

Four cores (WB006, WB022, WB080, and WB095) were chosen from a set of cores previously collected by Hobbs et al. (1984) for an inventory of sand resources in the southern Chesapeake Bay. An additional core (VC93) was obtained from the United States Army Corps of Engineers from a set of vibracores collected for the Norfolk Harbor and Channels Deepening Project (Swean, 1986). The locations of the five cores are given in Figure 1. Core logs and location coordinates appear in the Appendix. Selection of the cores was based on 1) relatively high silt and clay content thoughout the length of the core, and 2) relatively large thickness of the Holocene section as identified by stratigraphic and lithologic criteria (Berquist, 1986).

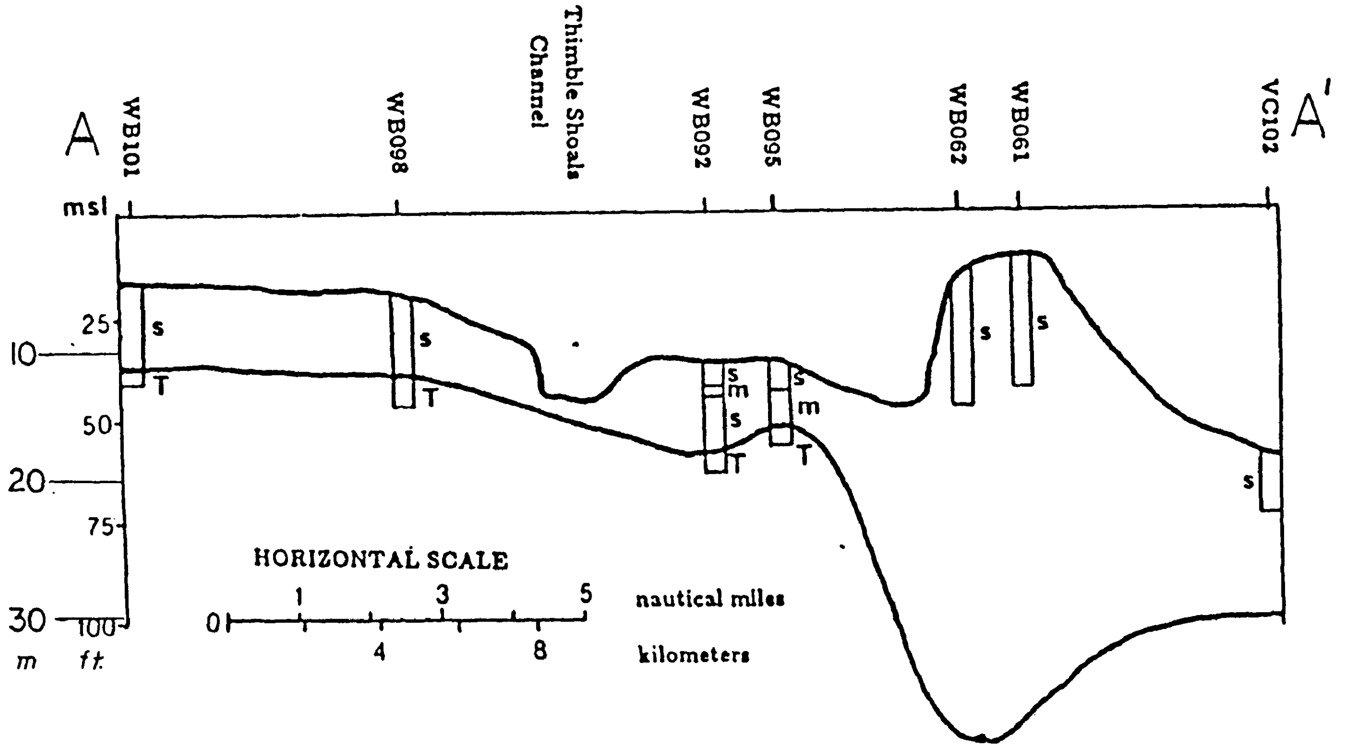
Stratigraphic framework and geologic history

Chesapeake Bay is one of the world's largest estuarine systems, encompassing about 8000 km^2 of the Atlantic Coast of the United States. A relatively young geologic feature, the bay was formed during the Holocene transgression beginning approximately 18,000 years ago when the rising seas inundated the valleys of the Susquehanna and James rivers and their tributaries. A brief discussion of the stratigraphy and geologic history of the region since the Late Tertiary is presented to provide a framework for understanding sedimentation in the lower bay during the Holocene.

The basement and borderlands of the bay are underlain by the Miocene and Pliocene formations of the Chesapeake Group, representing deposits of the shallow seas which alternately invaded and retreated between 25,000,000 and 1,800,000 years ago. These semi-lithified to unconsolidated deposits consist of generally fossiliferous marine sands, silts, clays, and shell beds, interspersed with fluvial and lagoonal fine sands and muds (Johnson and Peebles, 1984). During the late Tertiary, the discontinuous lowering of sea level, possibly caused by regional uplift, led to emergence of the land and to the development of an extensive paleodrainage system, comprising the main channels and tributaries of the Delaware, Potomac, and Susquehanna Rivers (Byrne et al., 1982). High stands of sea level during the late Tertiary resulted in the deposition of nearshore-marine, estuarine, and fluvial sands and muds and of sandy beach and barrier ridge sediments. Low stands during this time resulted in emergence and fluvial dissection of the Coastal Plain deposits.

The Pleistocene epoch was dominated by numerous, glacially-mediated fluctuations in sea level. With the exception of a few high stands, sea level during this time generally remained below that of the present during this epoch (Zellmer, 1979). The most recent glaciation, the Wisconsinan, ended about 18,000 years ago, at which time sea level stood approximately 100 m below that of the present. During this emergence, the Susquehanna and James Rivers and their tributaries flowed across what is now the continental shelf, producing another extensive erosional surface. Geological cross-sections compiled by Meisburger (1972), and modified by Berquist (1986) and Colman and Hobbs (1987) show these paleochannels, modified during the Pleistocene, cutting into older Tertiary sediments [Figure 2].

Figure 2. Geologic cross section across A-A′ showing generalized stratigraphy, structure, and depth of Holocene deposits. Core WB095, which was used in this study, lies in the central part of the section. Symbols depict sand (s), mud (m), and Tertiary basement (T). Transect A-A′ is labeled in Figure 1. See text for further explanation.

A
A'
WB101
WB098
Thimble Shoals
Channel
WB092
WB095
WB062
WB061
VC102
msl
25
10
50
20
75
30
100
m
ft.
s
T
s
T
s
m
s
T
s
m
T
s
s
s
HORIZONTAL SCALE
0
1
3
5
nautical miles
4
8
kilometers

The Tertiary substrate, which is a prominent seismic reflector in the lower bay (Harrison et al., 1965; Meisburger, 1972; Colman and Hobbs, 1987), consists largely of the Pliocene Yorktown Formation. The extensive fluvial and subaerial erosion of the Pleistocene left few late Pleistocene remnants, most of which are coarse lag deposits located at the base of paleochannels.

It should be noted that the transect shown in Figure 2 was based on cores used by Berquist (1986), only one of which (WB095) was used in this study. However, his interpretation of stratigraphic relationships in the lower bay is considered to be generally representative of the subsurface geology of my study area. In particular, it depicts the stratigraphy near Thimble Shoal Channel, proximal to three cores used in this study.

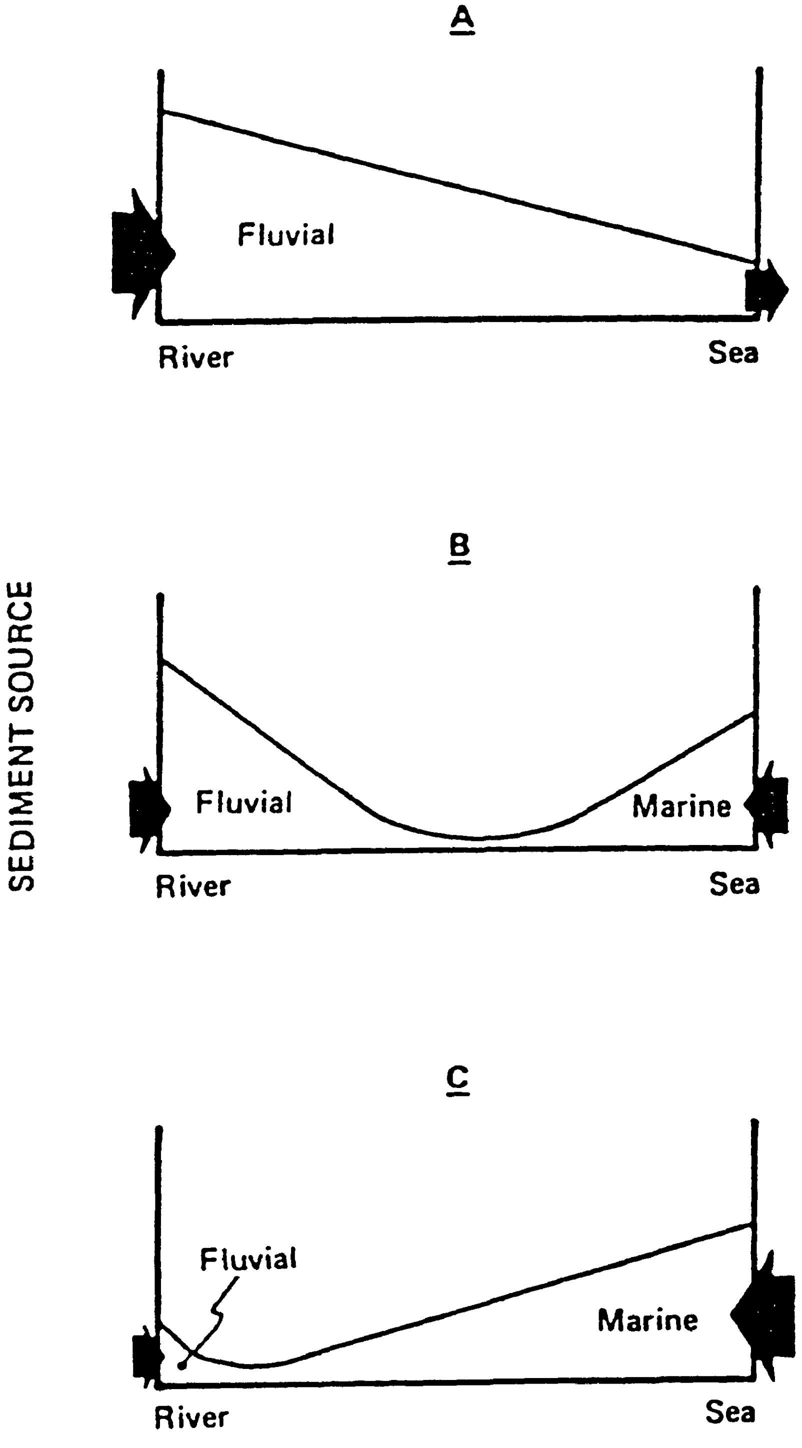
The post-Wisconsinan transgression, beginning about 18,000 years ago, has resulted in a sea level rise of approximately 100 m which flooded the Late Pleistocene river valleys. Progradation of the southern Delmarva peninsula during this time progressively embayed the estuarine reaches of the drowned Susquehanna River valley (Mixon, 1985), eventually to form the pre-Wisconsinan Chesapeake Bay. The paleovalleys were rapidly infilled with nearshore-marine and estuarine sediments during the early Holocene (Byrne et al., 1982). At present, there are relatively high but variable rates of sedimentation in most portions of the bay (Officer et al., 1984).

Regional sedimentary distribution and dynamics

Sedimentation in the lower bay, as in estuaries in general, is controlled chiefly by the dynamic processes of river discharge, tides, and meteorologic forcings (Meade, 1972). Chesapeake Bay, a partially-mixed estuary (Pritchard, 1955), exhibits net two-layered flow, with seaward-flowing, less dense river water overlying denser, landward-flowing sea water. This circulation pattern tends to trap both river-borne and shelf-borne material within the bay, as depicted in the conceptual model of Biggs and Howell (1984) [Figure 3].

This landward flow of sea water was identified by Meade (1969) as the means by which shelf sediments are brought into Coastal Plain estuaries of the eastern United States. Shelf-derived sands and silts have been identified near the mouth of the bay by Meisburger (1972), Shideler (1975), Byrne et al. (1982), and Hobbs et al. (1986), thereby supporting this observation. Studies of fine-grained suspended sediment in the bay mouth led Schubel and Carter (1976, 1984) to conclude that the bay is a net importer of fine-grained sediment from the shelf. Considering that estuaries in the northern Atlantic Coastal Plain of the United States carry low average suspended loads and continue to accumulate relatively large volumes of fine-grained sediment, and are not essentially filled to capacity as are estuaries of the southern Coastal Plain (Meade, 1969), it is probably reasonable to assume that net importation of sediments from the continental shelf into the bay has been taking place throughout the Holocene transgression. This is in fact supported by the analysis of subsurface sands (Berquist, 1986). Whether net importation is true for fine-grained sediments is a question

Figure 3. Conceptual model of Biggs and Howell (1984) depicting sources and intensities of deposition in some coastal sedimentary systems. A represents a system dominated by river flow, such as the Mississippi River. Most river sediment in such systems escapes to the sea, while negligible marine sediment enters the river mouth. B depicts an estuarine system such as the Chesapeake Bay, within which both fluvial and marine sediments are deposited. C represents a system such as a coastal lagoon, where river input is small relative to marine input. These views represent axial sections. Catastrophic events may cause significant short-term changes in any of these systems. After Biggs and Howell (1984).


A
Fluvial
River
Sea
SEDIMENT SOURCE
B
Fluvial
Marine
River
Sea
C
Fluvial
Marine
River
Sea

for the present study to resolve.

Late Quaternary sedimentation in the region of the bay is also a function of the paleotopography of underlying Plio-Pleistocene erosional features (Shideler et al., 1972, 1984; Swift et al., 1977; Carron, 1979; Colman and Hobbs, 1987). The paleovalley of the ancestral James River, located by Carron (1979) at a sediment depth of about 43 m (141 ft), extends across the inner shelf of southern Virginia and was a locus of deposition for sediments in the James River estuary and lower bay.

Fine sediments in the bay were observed by Meisburger (1972), Shideler (1975), and Byrne et al. (1982) to be concentrated in channels and protected embayments. Nichols (1972) found that fine-grained sediments (generally silty clays) are deposited within the channels of the James River, and decrease in abundance downriver. In the lower estuary off Newport News, sand grades perpendicularly offshore into sandy clay; slightly upstream, clayey sand grades into sandy silty clay. Concentration of sand generally remains below 50% in the lower estuary, except on the shores along the estuary mouth, particularly on the northern side. A series of cores taken in the 16.8 m (55 ft) anchorage area by the Corps of Engineers for the Norfolk Harbor and Channels Deepening Project (Swean, 1986) indicated that fine-grained sediment is present to a depth of at least 6.1 m (20 ft) in certain areas. Nichols' (1972) observation of rapidly decreasing mud content in the downriver direction supports that of Shideler (1975), who suggested that the relatively sheltered location of the river mouth allows most of the river-borne mud to settle out before reaching the bay.

In the landward portion of Thimble Shoal Channel (see Figure 1), Ludwick (1981) calculated relatively high depositional rates which he attributed to the settling of fines from the ebb plume of the James River. This suggests that significant mud bypasses the James River "settling basin." He interpreted sedimentation in the more seaward reaches of the Channel as being largely influenced by the movement of both suspended fine matter and relict sand ridges from outside the bay. Unfortunately there are few detailed studies describing fine sediment transport into the bay. The studies of many investigators, e.g., Officer and Nichols (1980), Byrne et al. (1982), and Schubel and Carter (1984), suggest that Chesapeake Bay is an efficient sediment trap, a premise which guides the present study.

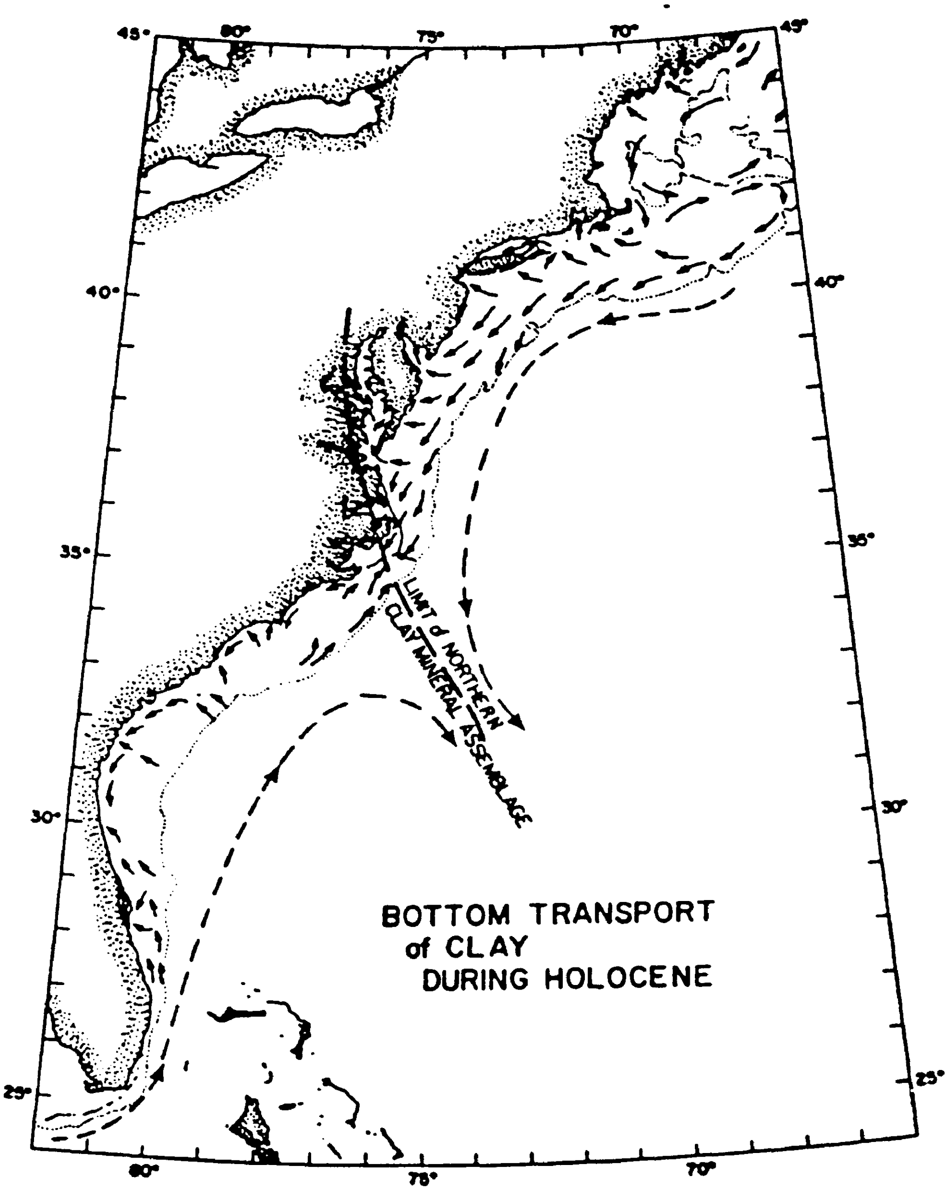
II. CLAY MINERAL DISTRIBUTIONS

Regional sources of clay minerals

Hathaway (1972) described the Chesapeake Bay as a transitional region within which the clay mineral distribution reflects mixing between a predominantly glacially-derived, northern suite rich in illite and chlorite, and a southern, predominantly chemically-weathered suite rich in kaolinite and montmorillonite. Illite and chlorite of the northern suite were considered by Hathaway to be weathered primarily from Pleistocene glacial deposits derived from Paleozoic rocks of the northern Appalachian ranges. Hathaway determined that bottom currents on the shelf move clays southerly and into the entrances of estuaries such as the Chesapeake Bay [Figure 4].

Neiheisal and Weaver (1967) and Pevear (1972) found kaolinite and montmorillonite, common weathering products of feldspars and volcanic material respectively, to be characteristic of sediments in rivers draining the Piedmont south of North Carolina. Hathaway (1972) found dioctahedral vermiculite to be a common but minor constituent in rivers of his northern suite; Rich and Obenshain (1955) showed that this species is a weathering product of muscovite schists in the Virginia Piedmont. Vermiculite has been found in rivers both south and north of the Chesapeake Bay, but appears to increase in abundance toward the north (Pevear, 1972).

Figure 4. Map showing inferred transport patterns of clay minerals during the Holocene. The delimiting line represents the southern extent of Hathaway's (1972) northern clay mineral suite, dominated by illite and chlorite. Kaolinite and montmorillonite are the dominant clay minerals to the south of this limit. Arrows represent directions of bottom currents suggested by the data of Bumpus, 1965; Lee et al. (1965); Lauzier, 1967; Muench (1965, unpub. data); and Norcross and Stanley (1967). After Hathaway (1972).


45°
80°
75°
70°
45°
40°
40°
35°
35°
30°
30°
25°
25°
80°
75°
70°
LIMIT of NORTHERN
CLAY MINERAL ASSEMBLAGE
BOTTOM TRANSPORT
of CLAY
DURING HOLOCENE

Biscaye (1965) found that kaolinite in deep-sea sediments can be attributed to erosion of adjacent tropical continental regions and that chlorite is found offshore of generally temperate regions of higher latitude. The relationship between latitude and clay mineralogy can probably be attributed to the degree of chemical versus mechanical weathering occurring on the eroding continents. Kaolinite and montmorillonite, which generally reflect a high degree of chemical weathering, are characteristic of non-glaciated, temperate to tropical climates. In contrast, chlorite and illite originating from glacially-mediated, mechanical erosion of rock, are more characteristic of regions of higher latitude.

Regional clay mineral studies

The first attempt to quantitatively describe the clay minerals of the Chesapeake Bay region and to propose a mechanism for their observed distribution was Powers (1954, 1957). He found kaolinite, illite, chlorite, and sporadic mixed-layer chlorite-illite in the surficial sediments of the Patuxent and York River estuaries. Bottom sediments of the James River estuary contained these same minerals, with the addition of small amount of mixed-layer chlorite-vermiculite. A general down-estuary increase in chlorite and decrease in illite was observed; kaolinite remained relatively constant. Powers (1954, 1957) proposed a mechanism for the diagenesis of chlorite from weathered (degraded) illite whereby the latter forms through the precipitation of magnesium upon the basal surfaces of the clay in response to increasing salinity downstream.

Nelson (1960) qualitatively studied the clay minerals in bottom sediments of the Rappahannock River and estuary. Sediments of the upper river were found to contain only kaolinite, illite, and dioctahedral vermiculite. Progressively downstream, there appeared what Nelson described as montmorillonites with 12.4 Å and 14.2 Å basal spacings. The 12.4 Å species probably represents a mixed-layer species; the 14.2 Å clay may be the "true" montmorillonite. In estuarine reaches, illite crystallinity improved, the amounts of weathered illite, kaolinite, and 12.4 Å montmorillonite decreased, and chlorite and feldspar first appeared.

Nelson (1958) found that the bottom sediments of the Rappahannock estuary were mineralogically related to changes in bedrock except in the most saline portions of the estuary. The compositions of the suspended and bottom loads were similar except in the lower estuary, suggesting that differential transport (Nelson, 1958) or differential flocculation (Nelson, 1963) were not important distributive mechanisms. Nelson (1960) noted that the material identified as chlorite by Powers (1954) and Griffin and Ingram (1955) had the same properties as that mineral which he identified as dioctahedral vermiculite. The presence of the "true" (thermally stable) chlorite was attributed by Nelson (1963) to diagenesis in saline reaches, probably from the alteration of vermiculite.

Within the bay between the Potomac and Rappahannock Rivers, Harrison et al. (1964) have identified illite, chlorite, and mixed-layer clay (illite-montmorillonite or chlorite-montmorillonite) with traces of kaolinite. In bottom sediments of the James River estuary, Nichols

(1972) reported illite and chlorite to be the dominant clay species present, with lesser amounts of montmorillonite and kaolinite.

As described in the previous section, Hathaway (1972) concluded that the Chesapeake Bay is a transitional zone between a northern, glacially-influenced illite-chlorite clay suite and a southern kaolinite-montmorillonite suite. In estuaries of the lower bay, Hathaway found that typical values for kaolinite ranged from 40 to 50% of the <2 um fraction; for illite and dioctahedral vermiculite, 10-20%; and for chlorite and montmorillonite, trace amounts to 10%. Hathaway (1972) found no evidence for Powers' (1957) theory of diagenesis of chlorite from dioctahedral vermiculite since many estuaries which receive fluvial inputs of the latter contain no chlorite. It was concluded that the observed distributions of clay minerals were mainly attributable to processes of erosion, redeposition, and circulation.

Analyses of a few samples in the lower bay by Byrne et al. (1982) show results similar to that of Hathaway (1972). Chlorite, illite, kaolinite, montmorillonite, and sporadic vermiculite were reported. They noted that the contribution of kaolinite by the weathering of southern formations, in concert with the net up-estuary circulation in the bay, produces a mid-bay kaolinite maximum.

Feuillet and Fleischer (1980) identified and proposed a mechanism of distribution for the clay minerals in the James River estuary. Analyses of 151 samples of bottom sediment taken along the river from Jordan Point in the fresh-water reach to Cape Henry at the bay mouth have revealed significant along-river trends in clay mineralogy. Two distinct clay mineral suites were identified: a James River suite dominated by kaolinite, illite, and dioctahedral vermiculite, and a bay entrance suite enriched in illite, chlorite, and montmorillonite. The clay gradients observed were attributed to the mixing effects of two-layered estuarine circulation. The effects of diagenesis, differential settling, and flocculation were shown to be minor.

Implications of size-fractionation

Towe (1974) stressed that the quantitative distribution of clay minerals in fine-grained sediments cannot be assumed to be independent of the size-fractionation procedure used. He suggested, therefore, that quantitative analyses of clay minerals would be more accurate if several size fractions were individually analyzed instead of analyzing in bulk the "traditional" <2 μm fraction. For example, as Towe pointed out, any <2 μm (equivalent spherical diameter) particles of heavy minerals will be excluded from the analysis by use of Stokes Law for the separation of clay minerals. Therefore, it can not be assumed that all minerals are represented in the <2 μm fraction.

Appreciable differences in the average compositions of the various clay subfractions has been noted in previous studies (Gibbs, 1977; Carson and Arcaro, 1983; Kelley, 1983), suggesting that the distribution of clay minerals in fine-grained sediments is at least partially size-dependent. For example, Gibbs (1977) showed clay minerals of the continental shelf off of the Amazon River to have distinctive, although relatively wide, ranges in size. Montmorillonite ranged from about 0.1 to 0.9 μm, kaolinite averaged 1-2 μm and illite (10 Å mica) ranged from sand-sized to 0.4 μm, with an average size between 2-4 μm. Carson and

Arcaro (1983) reported general decreases in illite and chlorite, and an increase in montmorillonite with decreasing size.

Carson and Arcaro (1983) split the <2 µm fractions of their samples of abyssal plain sediment into three subfractions (2.0-0.98 µm, 0.98-0.49 µm, <0.49 µm), as did Kelley for his samples of New Jersey coastal muds, although he used different size intervals (2.0-0.49 µm, 0.49-0.25 µm, and <0.25 µm). In both studies, two silt-sized fractions were examined (7.8-3.9 µm and 3.9-2.0 µm by Carson and Arcaro; 31-7.8 µm and 7.8-2.0 µm by Kelley) and varying amounts of clay minerals were found. Within these silt fractions, Carson and Arcaro found ~10-20% montmorillonite and ~35-50% illite and chlorite; Kelley found 6-24% illite, 3-12% chlorite, 0-3% kaolinite, as well as quartz and feldspar. These results demonstrated that clay minerals are not confined solely to the <2 µm fraction. Fortunately, most clay mineral studies have been able to show that most of the mineralogic variations can be discerned in this "traditional" fraction.

In this work, a decision had to be made as to how many subfractions from each bulk sample could be analyzed completely yet in a timely fashion. It was judged appropriate to fractionate each bulk sample into 2-0.2 µm and <0.2 µm subfractions for semi-quantitative analyses; in addition, a 20-2 µm fine silt subfraction was extracted and random samples qualitatively analyzed for clay minerals. This scheme allowed for relatively consistent comparisons between the same size fractions and for sufficiently accurate assessment of the importance of size-fractionation effects on the clay mineral distribution.

III. A BRIEF REVIEW OF CLAY MINERALOGY

The following review of the structure and chemistry of clay minerals is derived in general from the works of Grim (1968), van Olphen (1977), Weaver and Pollard (1973) and Hurlbut and Klein (1977). The interested reader is referred to these sources for detailed information.

The term clay has two sedimentologic meanings. In the one sense it refers to those sediment particles which have a nominal diameter of less than two micrometers. In the second sense it describes those phyllosilicate minerals which typically possess a layer-lattice structure, a flaky, fibrous, or platy habit, and the ability of some species to incorporate and expel water according to ambient moisture and temperature conditions. Most of these minerals inhabit the size class termed clay.

As van Olphen (1977, p. 59) stated, "the principal building elements of the clay minerals are two-dimensional arrays of silicon-oxygen tetrahedra and two-dimensional arrays of aluminum- or magnesium-oxygen-hydroxyl octahedra." Within the tetrahedral arrays, each silicon atom is coordinated with four oxygen atoms, each of which is located at the corners of a regular tetrahedron, equidistant from the central silicon atom. Three of the oxygen atoms in the tetrahedron are shared by neighboring tetrahedra in the sheet; the silicon:oxygen ratio in the sheets is therefore 2:5. The fourth, unshared oxygen atom is oriented downward out of the plane formed by the sheet. Rings of six oxygen atoms result from this orientation, imparting a hexagonal symmetry to the tetrahedral sheet.

In the octahedral sheets, iron, aluminum, or magnesium atoms are coordinated with six oxygen atoms or hydroxyl radicals, forming a regular octahedron. The oxygen atoms and hydroxyl radicals lie in two parallel planes with aluminum, magnesium, or iron atoms at their centers. Sharing of oxygens and hydroxyls by neighboring octahedra results in a sheet structure exhibiting hexagonal close packing. When the central cations in the octahedral sheet are divalent, such as Mg^{2+} or Fe^{2+}, each cation site will be occupied, and the geometry and composition of the sheet will resemble those of brucite, $Mg(OH)_2$. In the brucite structure, each oxygen or hydroxyl is surrounded by three cations, and is said to be in trioctahedral coordination. When the central cation is trivalent, such as Al^{3+}, charge balance requires that only two cations surround each oxygen or hydroxyl. In such a case, the cation coordination is described as dioctahedral, and the sheet structure and composition represent those of gibbsite, $Al(OH)_3$.

The different groups of clay minerals are generally distinguished by a characteristic arrangement of tetrahedral and octahedral sheets, a single series of which composes a unit layer of the mineral structure. The distance between a specific plane in the unit layer and the same plane in the adjoining unit layer is called the basal, or c-spacing. Individual species of certain groups vary in type by the degree of isomorphous substitution by ions of similar size and charge in the crystal lattices, as of aluminum, silicon, iron, magnesium, calcium, or lithium.

The two-layer clay minerals, of which kaolinite is a well-known example, consist of a tetrahedral silica sheet bound with an octahedral sheet. In kaolinite ($Al_2Si_2O_5 \cdot 4OH$), the octahedral sheet is of gibbsite composition. In three-layer clays, such as illite or montmorillonite, each unit layer consists of a octahedral sheet sandwiched by two tetrahedral sheets. Certain three-layer clays, including montmorillonite and vermiculite, possess the ability to admit exchangeable cations and water between adjoining unit layers. In the presence of water or other polar molecules spaces between unit layers may be penetrated and consequently swell to a size commensurate to the amount and type of molecule or exchangeable cation present. These so-called expandable clays may be identified by various treatments including saturations with various cations and treatments with polar liquids. The organic liquid glycerol, for example, increase the normal ~14 Å basal spacing of montmorillonite to ~18 Å. It is suspected that in three-layer non-expandable clays, such as illite, cations strongly bind adjoining unit layers so that expansion is not possible.

The methods and criteria for identifying the clay minerals in this study are described in Chapter V.

IV. METHODOLOGY

Sampling

Each of the five cores used in the study had been stored wrapped but unrefrigerated, and in some cases were somewhat dessicated. Feuillet and Fleischer (1980), who used both stored and fresh samples, concluded that dessication does not detectably affect semi-quantitative clay mineral analyses. W.G. MacIntyre (1986, pers. comm.) suggested that clay minerals do not effectively dehydrate in the humidities and temperatures typically encountered in storage. Hence, storage effects are deemed to have negligible impact on analyses performed in the present study.

Samples of approximately 90 cm^3 size were taken at intervals stated in the core logs (see Appendix), and included material 2 cm above and below the stated depth. Relatively dry samples were homogenized by gentle crushing and mixing. Moist samples, particularly those from core VC93, were homogenized by mixing with a flexible spatula, with the addition of a small amount of deionized water. All samples were split into sub-samples for size analysis and clay mineral analysis.

The clay splits were chemically treated to remove carbonates, organic matter, and iron oxides, all of which are cementing materials and interfere with semi-quantitative x-ray diffraction analysis by decreasing reproducibility. The procedures to remove carbonates and iron oxides followed those of Jackson (1973). Organic matter was oxidized using the method of Anderson (1963). These workers noted no discernible alteration of clay minerals resulting from the chemical treatments.

Removal of carbonates

Carbonates were dissolved using a 0.6 N (for samples of cores WB080 and WB095) or 1.0 N (for remaining samples) solution of sodium acetate buffered to pH 5 with glacial acetic acid. Each sample was divided if necessary into two 50 ml centrifuge tubes. Twenty to 30 ml of acetate solution was added and the suspension heated for thirty minutes in a near-boiling water bath. After treatment, the suspensions were centrifuged for 5 to 10 minutes at 900g, and the supernatant decanted and discarded. This procedure was repeated for a total of three treatments for each sample.

Removal of organic matter

Organic matter was oxidized using a 5.25% solution of sodium hypochlorite (Chlorox bleach) brought to pH 9.5 with hydrochloric acid. The portions of clay in each tube were suspended in approximately 20 ml of solution and heated to 95-100° C in a water bath for 15 minutes. After centrifuging at 500g-900g for 5-10 minutes, the supernatant was decanted and discarded. This procedure was repeated twice more for a total of three treatments per sample. The portions were then sequentially rinsed and centrifuged with 30 ml of 1 N sodium acetate solution of pH 5, 15 ml of 95% methanol or ethanol and 1 N neutral sodium acetate solution. Divided samples were combined into 400 or 600 ml beakers by rinsing with additional neutral sodium acetate solution, and allowed to settle overnight or longer. The supernatant was decanted and discarded.

Removal of iron oxides

The neutralized samples were treated to remove iron oxides using the sodium citrate-bicarbonate-dithionite technique. Sodium dithionite (hydrosulfite) reduces the iron in the sediment, sodium citrate chelates the ferrous iron, and sodium bicarbonate buffers the solution. Using the modification of Feuillet (1976), 200 ml of 0.3 M sodium citrate solution and 25 ml of 1 M sodium bicarbonate solution were added to the sample. The suspension was heated to 75-80° C in a water bath, and approximately 5 g of sodium dithionite was added. The mixture was constantly stirred for five minutes to prevent the formation of iron sulfide, then removed and allowed to cool. Fifty ml each of saturated sodium chloride solution and acetone were added to promote flocculation. The samples were transferred to 50 ml centrifuge tubes, using two tubes per sample when necessary, and centrifuged at 900g for 5-10 minutes. The supernatant was decanted and discarded. The rinsed samples remaining in the tubes were then ready for size-fractionation.

Size-fractionation

Centrifugation times for the removal of the 2-0.2 µm and <0.2 µm sub-fractions were calculated using equation 3-7 of Jackson (1973):

$$t_{min} = [(63.0 \times 10^8) \; n \log (R/S)] \;/\; [N_m^2 \; D_u{}^2 \; (s_p - s_1)]$$

where t_{min} = centrifugation time in minutes;

n = water viscosity in poises;

R = radius of rotation in cm of top of sediment in tube;

S = radius of rotation in cm of surface of suspension in tube;

N_m = revolutions per second;

D_u = particle diameter in micrometers;

s_p = specific gravity of solvated particle (assumed to be 2.65 for 2-0.2 µm particles and 2.5 for <0.2 µm particles);

s_1 = specific gravity of suspension liquid (assumed to be 1 for deionized water).

The appropriate parameters were measured for the separation of the 2-0.2 µm fraction with the IEC model HC II centrifuge equipped with IEC model 958 rotor and for the <0.2 µm fraction with the IEC model HT centrifuge fitted with an IEC model 856 fixed-angle head. All samples were suspended in deionized water for fractionation. Effective separation was achieved after six to eight centrifugations and decantations for each subsample.

The 20-2 µm sub-fraction was separated from the remaining >20 µm material by repeated settling and decantation in deionized water following the method of Jackson (1973). Five samples of this subfraction were chosen for qualitative x-ray diffraction analysis to determine if clay minerals were present. The remaining coarse silt (20-63 µm) and sand (>63 µm) were not analyzed.

Saturation with Mg^{2+} and K^+

The procedure employed by Feuillet (1976) to identify and quantify the clay minerals in a mixture requires x-ray patterns of both Mg^{++} - and K^+-saturated splits. Hence, splits from each size fraction of each sample were saturated in Mg^{++} and K^+ solutions using slightly modified procedures of Feuillet (1976).

One half of the 2-0.2 µm and <0.2 µm sub-fractions were each placed in 50 ml centrifuge tubes with approximately 25 ml of 1 N magnesium chloride. Following centrifugation at 225g for 5 min, the supernatant was decanted and discarded. This procedure was repeated two more times for each split. Two rinses with 25 ml of 1 N magnesium acetate followed to remove exchangeable H^+, with subsequent centrifugation and decantation. Excess salts were removed with by washing and centrifuging once with 80% acetone and twice with 95% acetone. The remaining halves of the sub-fractions were saturated with K^+, using the above procedure, substituting 1 N potassium chloride and 1 N potassium acetate in place of the magnesium chloride and acetate. The cation-saturated sub-fractions were then ready to be mounted for XRD analysis.

Sample mounting

Each sub-fraction was mounted for XRD analysis using porous, unglazed ceramic tile. This technique is one recommended by Gibbs (1965, 1968) to reduce errors in semi-quantitative analysis caused by the possible segregation of clay species caused by differential settling of grains with different equivalent spherical diameters (e.g., montmorillonite versus illite). A suspension of material placed upon the dry tile is drawn down by capillary action, thereby encouraging the rapid deposition of the grains in a basal orientation. The tiles also have the ability to withstand the high temperatures necessary for the analysis.

Approximately 2 ml of the clay suspension was pipetted onto an unglazed porous ceramic tile set upon a level surface. When the water disappeared from the surface of the slide, approximately 1 ml of 10% glycerol solution was applied, and the slides were allowed to air-dry.

X-ray diffraction analysis

All x-ray diffraction (XRD) runs were performed on a General Electric XRD-5 diffractometer using Ni-filtered Cu K-alpha radiation, voltage of 30 kV, current of 30 mA, 1° divergence slit, 0.2° receiving slit, time constant of 2 s, and a scanning rate of 2° 2θ per minute. Although no external standards were employed to monitor variations in x-ray intensity, such machine error is believed to be small in comparison to the other potential sources of error in this procedure.

The rationale and calculations concerning the quantification method are detailed in the following chapter; the procedures followed in the instrumental analysis are described here.

In general, two or more slides of both the Mg^{++}- and K^{+}-saturated sub-fractions of 2-0.2 µm size were made and x-rayed at least twice each. The Mg^{++}-saturated slides were then heated at 600° C for approximately 90 minutes and re-run at least twice each. The heights of the 001 (basal) peaks at the 2θ positions noted for each species in Table 1 were measured with a millimeter scale from a smoothed baseline fitted to the background of each diffraction pattern with a flexible curve. The measurements for each type of slide were subsequently averaged for use in the quantification procedure. Clay films of most slides of the <0.2 µm fractions separated from the ceramic tiles after drying, so a slightly different procedure was used for those sub-fractions. Two slides each of the Mg^{++}- and K^{+}-saturated sub-fractions were made. One of the Mg^{++}-saturated slides and both K^{+}-saturated slides were cemented back to the ceramic tiles using Duco cement thinned with acetone. Duco cement is an x-ray amorphous cement which did not detectably affect the x-ray diffraction patterns of these clays. The Mg^{++}-slide was then x-rayed at least twice, and the peak values averaged in the final analysis. The K^{+}-slides were generally run once each, and their peak values averaged. The remaining Mg^{++}-slide was heated to 600° C, then the clay film was cemented to the tile. These slides were run at least twice and the peak values averaged. In a few cases, for both the 2-0.2 µm and <0.2 µm sub-fractions, it was necessary to make additional slides to obtain adequate patterns for the quantification procedure. Inadequate patterns could be discerned by their obviously low, diffuse peaks or anomalously high background. These patterns were rejected for use in the quantification procedure.

The five samples of 20-2 µm material were kept in a sodium-saturated state until mounting by the regular procedure. After treatment with glycerol, the slides were x-rayed, and x-rayed again after heating to 600° C. The peak heights and positions were noted, but semi-quantitative analysis was not performed.

Size analyses

Analyses were performed to determine the proportions of the >63 um (sand), 63-20 µm (coarse-medium silt), 20-2 µm (fine silt), 2-0.2 µm (coarse clay), and <0.2 µm (fine clay) fractions in the total size distribution of each sample. Splits retained for size analysis were soaked in 50 ml of 10% Calgon solution, disaggregated ultrasonically, and wet-sieved through a <63 µm screen. The sand fraction remaining on the screen was dried and weighed. The mud fraction passing through the sieve was loaded into 1000 ml sedimentation cylinders with deionized water for standard pipette analysis; withdrawal times for the 63-20 µm, 20-2 µm, 2-0.2 µm, and <0.2 µm sub-fractions were calculated using the modified Stokes equation (Folk, 1980). The withdrawn aliquots were placed into pre-weighed aluminum pans, oven-dried, and weighed after equilibration at constant humidity. All but a few samples were analyzed in duplicate and the values averaged.

Splits for size analysis from core WB095 were treated with 30% hydrogen peroxide to remove organic matter. This treatment was discontinued in subsequent analyses due to difficulties encountered in removing the soluble organic residue without significant loss of the very fine material. I was also advised that comparisons of pipette analyses of treated and untreated samples from another study showed minor differences (C. Fischler, 1986, pers. comm.). The degree of accuracy desired in these analyses was judged to be obtainable without removal of organics, carbonates, or iron oxides.

V. CLAY MINERAL ANALYSIS

Identification criteria for the XRD analysis of clay minerals

Feuillet (1976) has identified the major species of clay minerals in surficial sediments of the James River estuary and lower bay. From the summary appearing in Table 1, it is apparent these identifications can be achieved by a series of procedures involving Mg^{++}- and K^{+}-saturations, glycerol treatment, and heating to 600° C. The effects of these treatments on the various clay minerals are generally described in Grim (1968). In the following sections, brief descriptions and identification criteria are given for the species found in study area. The three digit notations which appear refer to the Miller indices corresponding to the stated lattice spacings.

Illite

Illite is a general term for mica-like clay minerals, including biotite and muscovite, which are composed of two tetrahedral silica sheets sandwiching an dioctahedral or trioctahedral sheet. These closely related species, which are not individually distinguished in the study, give strong basal reflections at about 10 Å; this peak is therefore used to quantify the abundance of this group. The linking

Table 1. X-ray diffraction characteristics of clay minerals in the study area (Adapted from Feuillet, 1976)

Clay Mineral	Mg^{2+}-saturated lattice spacing (1)	K^{+}-saturated lattice spacing	Lattice spacing after 600 °C	Mg^{2+}-glycerol treated lattice spacing
Kaolinite	7.18 Å 001	7.18 Å 001	Amorphous	7.18 Å 001
	3.58 Å 002	3.53 Å 002		3.58 Å 001
Montmorillonite	14.4 Å 001	12.3 Å 001	10.0 Å 001	18.0 Å 001
Chlorite	14.1 Å 001	14.1 Å 001	13.8 Å 001	14.1 Å 001
	7.05 Å 002	7.05 Å 002		7.05 Å 002
	3.52 Å 004	3.52 Å 004		3.52 Å 004
Vermiculite	14.3 Å 001	10.4 Å 001	10.0 Å 001	14.3 Å 001
Dioctahedral vermiculite	14.2 Å 001	14.2 Å 001	10.0 Å 001	14.2 Å 001
Illite	10.0 Å 001	10.0 Å 001	10.0 Å 001	10.0 Å 001
	5.0 Å 002	5.0 Å 002	5.0 Å 002	5.0 Å 001
	3.3 Å 003	3.3 Å 003	3.3 Å 003	3.3 Å 003
Mixed-layer clay	Integral series of basal spacings	Variable; dependent on species present	Variable; dependent on species present	Variable; dependent on species present

(1) Miller indices are given with the corresponding lattice spacing.

effect of K^+ ions prevents expansion of unit layers under hydration and glycerol treatment, and the structure is not affected by heating to 600° C. Slight intensification of the 10 Å peak may occur after saturation with K^+, possibly due to adsorption by K^+-deficient species (Feuillet, 1976).

Kaolinite

Unit layers of kaolinite consist of one tetrahedral silica sheet linked with one dioctahedral sheet of gibbsite composition. Cation saturation and glycerol do not affect basal spacings. Heating above 600° C destroys the crystalline structure of kaolinite, making it amorphous to x-rays. The 7.2 Å 001 peak of kaolinite is used in its quantification.

Chlorite

The chlorites are a large group of hydrous aluminosilicates within which amounts of iron, aluminum, and magnesium vary widely. The unit layer of a typical chlorite consists of a unit of tetrahedral silica sheets sandwiching an trioctahedral sheet alternating in some way with a dioctahedral brucite-like sheet. Chlorite spacings are not affected by cation exchange procedures or by glycerol.

The identification and quantification of chlorite pose a problem in that the 18 Å 001 peak of glycerol-treated montmorillonite and the 7.18 Å 001 peak of kaolinite respectively interfere with the 14 Å 001 and 7.05 Å 002 peaks of chlorite. After heating to 600° C, however, chlorite recrystallizes, intensifying its 001 peak at 13.8 Å. This heat treatment also collapses the 18 Å montmorillonite peak to 10 Å and causes kaolinite to become amorphous, thereby eliminating its 7.18 Å peak. Thus chlorite can be quantified by measuring its 001 peak height after heat treatment.

Montmorillonite

A unit layer of minerals of the montmorillonite (smectite) group generally consists of a dioctahedral sheet of gibbsite structure sandwiched between tetrahedral silica sheets. Montmorillonites exhibit the ability to admit and expel water and other polar molecules between these layers, resulting in interlayer expansion. Accordingly, the 14 Å 001 peak is increased to 18 Å after glycerol treatment, thus affording a means to differentiate it from the 001 chlorite peak. Heating to 600° C collapses the Mg^{++}-saturated 001 spacings to 10 Å, while the 001 chlorite peak remains.

Vermiculite

The vermiculite structure consists of alternating layers of trioctahedral mica and water molecules; these layers are subject to reversible dehydration at temperatures up to 500° C. The 14.3 Å 001 peak of vermiculite interferes with the 001 peak of chlorite; however, upon heating to 600° C, the former peak collapses to 10 Å, while the latter peak remains. When saturated with K^+, the montmorillonite and vermiculite 001 peaks collapse to 12.3 Å and 10.4 Å, respectively, thereby allowing a means for differentiating between the phases. Positive identification is possible because glycerol expands Mg^{++}-saturated 001 peak of montmorillonite to 18 Å, but does not affect the Mg^{++}-saturated vermiculite peak (Walker, 1961).

Dioctahedral vermiculite

In this species, the layer between the silica sheets is of dioctahedral coordination. The 14.2 Å 001 peak is not affected by K^+-saturation or glycerol, but does collapse to 10 Å after heating to 600^oC. This phase may therefore be differentiated from vermiculite, montmorillonite, and chlorite.

Mixed-layer clays

According to Weaver and Pollard (1973, p. 107), "the most common type of mixed-layer clay is composed of expanded, water-bearing layers and contracted, non-water-bearing layers (i.e., illite-montmorillonite, chlorite-vermiculite, chlorite-montmorillonite)". Analysis by XRD may allow estimation of the percentage of each type of clay mineral in a mixed-layer clay (e.g., Reynolds, 1980, 1983). However, quantitative variability of these species often makes them of limited usefulness in sedimentologic analysis. Feuillet and Fleischer (1980) stated that mixed-layer clays in surficial sediments of the James River estuary are composed chiefly of interstratified montmorillonite and illite.

Semi-quantitative analysis

The determination of clay mineral abundances in sediments by x-ray diffraction analysis is considered semi-quantitative because of the high degree of uncertainty resulting from variations in clay composition, equipment response, degree of basal orientation, background scatter, sample thickness, assumptions of the mass adsorption characteristics of the clays, and error in measurements of the peak heights. Furthermore, the concentrations of clays in a mixture are determined in a relative sense only, and are not to be considered as absolute values.

The approach used in this study follows that taken by Feuillet and Fleischer (1980) in their study of clay minerals in the lower Bay. As many workers have pointed out, quantifications of clay mixtures by XRD analysis are sensitive to sample preparation techniques as well as to those variables listed above. Hence, comparisons of clay mineral data generally are valid only if similar methods are used. Methodologies followed in clay mineral studies should therefore be described in detail. The similarity of methods between the present study and that of Feuillet and Fleischer (1980) should allow for valid comparison.

The quantification method follows the multiple ratio methods (Johns et al., 1954) as used in a series of equations originally developed by Schultz (1964) and modified by Feuillet and Fleischer (1980). In general, the height of the most intense peak of a given mineral is multiplied by a "mineral intensity factor" which is dependent upon intrinsic characteristics of the clay and the particular peak used in the analysis, as well as upon certain aspects of the diffractometer and sample. In this method, illite is given an intensity factor of one;

intensities for peaks of all other species are then normalized to that of illite. Intensity factors must be determined empirically or approximated by using values obtained from analyses of pure clay standards.

The height of the 10 Å peak after heating to 600° C contains contributions from illite, montmorillonite, vermiculite, dioctahedral vermiculite, and mixed-layer clays, all of which give approximately the same intensity for equal quantities of clay (Schultz, 1964). This peak is assigned an intensity of one. Intensity factors for kaolinite reported by various workers (Johns et al., 1954; Biscaye, 1965; Pierce and Siegal, 1969) fall between 1.5 and 2.0; Feuillet and Fleischer (1980) used an averaged value of 1.8. The intensity of kaolinite is therefore divided by 1.8 to normalize it with respect to illite. After heating to 600° C, chlorite is the only mineral remaining with a 14 Å peak. The height of this peak was divided by an intensity factor of three (Schultz, 1964; Biscaye, 1965). The relative peak intensity of montmorillonite has been found to be about four times stronger than that of illite (Johns et al., 1954; Schultz, 1964), therefore, the 18 Å peak heights for the mineral are divided by four.

The 7 Å peak height on a Mg^{++}-saturated, glycerol-treated mount was used to quantify kaolinite. An intensity factor for this mineral is required to account for the presence of the 002 peak of chlorite at this angle. Feuillet and Fleischer (1980) employed a dimethylsulfoxide (DMSO) treatment, which shifts the 001 kaolinite peak from 7.18 to 11.2 Å but does not affect the 14 Å 001 and 7 Å 002 peaks of chlorite, to positively identify kaolinite and to determine the intensity ratio between the 14 Å 001 and 7 Å 002 chlorite peaks. They obtained an average value of about 0.78 for this ratio. A ratio of 0.8 was assumed in this study.

Using this method, the percentage Q of any species in the clay mixture may be generalized by the equation:

$$Q = 100\ M\ N\ /\ [(TK\ /\ 1.8) + (H10AH) + (H14AH\ /\ 3)],$$

where M = the mineral intensity factor;

N = the measured peak height of the species;

D = {(TK / 1.8) + (H10AH) + (H14AH / 3)}, which takes into account all the clay minerals in the mixture;

H10AH = The height of the 10 Å 001 peak of Mg^{++}-saturated, glycerol-treated chlorite after heating to 600° C;

H14AH = the height of the Mg^{++}-saturated, glycolated 14 Å peak after heating to 600° C;

TK = H7A - (H14A / 0.8), representing the height of the 7 Å peak after the contribution of the 002 chlorite peak is removed, where

H7A = the height of the Mg^{++}-saturated, glycolated peak; and

H14A = the height of the Mg^{++}-saturated, glycolated peak.

The effect of kaolinite ("true kaolinite") on the 7 Å peak height after the contribution from chlorite has been removed is given by:

$$TK = H7A - (H14A\ /\ 0.8).$$

Normalizing the kaolinite intensity by dividing by 1.8 allows computation of the percentage of kaolinite in the sample:

$$KAO = 100\ [(TK\ /\ 1.8)\ /\ D].$$

Chlorite is the only remaining 14 Å peak after heating to 600° C, hence the percentage in the sample is given by:

$$\text{CHL} = 100\ [(\text{H14AH} / 3.0) / \text{D}],$$

where H14AH = the height of the Mg^{++}-saturated, glycolated peak after heating to 600° C.

The percentage of montmorillonite is simply expressed as:

$$\text{MON} = 100\ [(\text{H18A} / 4.0) / \text{D}],$$

where H18A is the height of the Mg^{++}-saturated, glycolated 18 Å peak. The percentage of illite is expressed as:

$$\text{ILL} = 100\ [\text{H10A} / \text{D}],$$

where H10A is the height of the Mg^{++}-saturated, glycolated 10 Å peak.

The percentage of vermiculite may be estimated by measuring the differences in heights of the 14 Å peaks of K^{+}- and Mg^{++}-saturated mounts. Feuillet (1976) showed that the empirical intensity factor 0.77 normalized the K^{+} intensity with that of the Mg^{++}-saturated peak. Furthermore, the 14 Å intensity was assumed to be three times stronger than that of illite (Fleischer, 1970), so the 14 Å adjusted vermiculite height is divided by this factor. The percentage of vermiculite may then be expressed by:

$$\text{VER} = 100\ [(\text{H14A} - ((0.77)(\text{H14AK})) / 3.0) / \text{D}],$$

where H14AK = the height of the K^{+}-saturated, glycolated 14 Å peak. In K^{+}-saturated samples, only the dioctahedral vermiculite and chlorite peaks remain at 14 Å, while that of vermiculite shifts to 10 Å. Only the chlorite 14 Å peak remains after heating to 600° C (Carroll, 1970). The peak intensity of dioctahedral vermiculite is normalized to that of illite by dividing by three (Fleischer, 1970). The computation for this species becomes:

$$\text{DIV} = 100\ [((\text{H14AK})(0.77) - (\text{H14AH} / 3.0)) / \text{D}].$$

The percentage of mixed-layer clays is computed by summing the percentages of these six species and subtracting the value from 100%:

$$MLC = 100 - (ILL + KAO + MON + CHL + VER + DIV)$$

The above procedure was utilized as shown for calculating abundances in the 2-0.2 μm subfractions. In the calculations of abundances in the <0.2 μm subfractions, it was decided to attribute the entire 7 Å peak to kaolinite, rather than to consider the contribution of the chlorite 002 peak, since chlorite was in such low abundance. All other calculations remained the same.

VI. RESULTS

Size analyses

The results of size analyses performed on thirty samples appear in Table 2. Core VC93 in the lower James estuary was described by Swean (1986) as consisting primarily of highly plastic silty clay to clayey silt. Results from this study similarly depict a relatively homogeneous core composed of sandy silty clay to silty clay. Total clay (<2 µm fraction) averages about 65% throughout the core, divided nearly equally between the coarse (2-0.2 µm) and fine (<0.2 µm) clay subfractions.

Cores WB006 and WB022 contain similar amounts of clay, with both averaging about 42%. However, the cores differ markedly in sand and silt content, with the former core averaging 40% silt and 19% sand and the latter averaging 28% silt and 30% sand. Core WB022 is significantly richer in coarse clay over fine clay, while core WB006 contains nearly equal amounts of both fine and coarse clay.

Sand is the dominant constituent of core WB080, with the exception of one sample at -600 cm, which is a sandy clayey silt. Sand, silt, and clay average 49%, 26%, and 25%, respectively, throughout the core. Core WB095 is dominantly silty throughout its length. Sand, silt, and clay contents average 11%, 60%, and 29%, respectively.

Table 2. Size distributions.

Core number	Depth of sample (cm)	Weight percent in size class				
		>63 µm	63-20 µm	20-2 µm	2-0.2 µm	<0.2 µm
VC93	- 60	10	12	14	36	28
	-140	6	16	15	35	27
	-220	7	12	20	21	41
	-300	11	13	17	30	30
	-380	10	13	8	42	28
	-460	2	8	24	32	34
	-540	1	4	27	33	35
WB006	- 40	22	11	21	20	26
	-120	7	18	28	21	26
	-200	11	27	22	19	21
	-280	11	22	26	18	23
	-360	19	22	16	20	23
	-420	42	12	12	17	18
WB022	- 60	27	19	9	31	13
	-140	38	13	8	29	12
	-220	41	13	12	22	12
	-300	27	19	13	24	17
	-380	24	16	13	29	18
	-460	22	23	13	19	22
WB080	- 60	44	10	19	8	19
	-150	50	12	14	9	15
	-240	57	9	13	7	15
	-330	55	13	9	10	13
	-420	54	11	11	9	15
	-510	62	8	6	11	13
	-600	18	30	18	16	18
WB095	- 60	30	30	24	9	7
	- 90	7	34	36	10	14
	-150	3	24	43	13	17
	-270	4	12	37	25	22

Sand content was found to be appreciably higher in cores WB006, WB022, WB080, and WB095 than that estimated by Hobbs et al. (1984) in their original descriptions. Most of this discrepancy is probably due to the different analytical methods used and to the fact that the sand is extremely fine-grained.

Clay minerals

The clay mineral compositions of the coarse and fine clay fractions are shown in Tables 3 and 4, respectively. The composition of the total clay (<2 μm) fraction was estimated using the size distribution data; these calculations appear in Table 5. The total clay fractions analyzed in twenty-nine samples average 33% illite, 26% mixed-layer clays, 11% kaolinite, 10% each of vermiculite and dioctahedral vermiculite, and 5% each of chlorite and montmorillonite. These values are in good agreement with the data of Hathaway (1972), Feuillet and Fleischer (1980), and Byrne et al. (1982).

The coarse and fine clay subfractions show distinctive differences in mineralogy. The 2-0.2 μm subfractions of the samples are dominated by illite (48%), mixed-layer species (14%), kaolinite (12%), and dioctahedral vermiculite (10%), with lesser amounts of chlorite and vermiculite (7% each) and montmorillonite (2%). In contrast, mixed-layer clays (39%) are the most abundant constituent of the <0.2 μm subfractions, with significant amounts of illite (18%), vermiculite (14%), and kaolinite and dioctahedral vermiculite (10% each), and minor amounts of montmorillinite (7%) and chlorite (3%).

Table 3. Clay minerology of the 2-0.2 μm subfractions.

Core number	Depth of sample (cm)	Percentage of 2-0.2 µm size fraction (1)						
		ILL	KAO	CHL	DIV	VER	MON	MLC
VC93	- 60	46	10	7	15	7	2	13
	-140	45	12	7	12	6	3	15
	-220	44	12	6	15	4	2	17
	-300	45	6	7	13	10	1	17
	-380	42	11	6	12	8	2	20
	-460	39	13	5	8	7	2	25
	-540	43	12	5	12	7	2	18
WB006	- 40	42	13	8	8	4	2	23
	-120	47	7	7	7	10	1	21
	-200	42	10	6	11	5	2	24
	-280	48	14	6	12	5	1	13
	-360	42	12	6	11	4	2	23
	-420	47	12	6	11	6	2	17
WB022	- 60	54	16	8	11	5	2	4
	-140	50	14	8	7	7	2	12
	-220	50	12	7	12	6	2	10
	-300	46	11	7	5	6	2	22
	-380	48	14	8	9	6	2	13
	-460	51	10	8	10	7	2	11
WB080	- 60	48	18	8	8	3	2	12
	-150	57	11	8	8	8	3	5
	-240	54	11	8	8	10	2	7
	-330	53	13	8	9	6	2	9
	-420	53	10	8	6	8	2	13
	-510	54	11	8	11	7	2	7
	-600	55	14	8	12	5	2	4
WB095	- 60	51	10	8	8	8	2	13
	- 90	47	7	8	10	9	2	16
	-150	54	9	8	10	9	2	8
	-270	55	14	5	7	3	2	15

(1) Abbreviations:

ILL = illite
KAO = kaolinite
CHL = chlorite
DIV = dioctahedral vermiculite
VER = vermiculite
MON = montmorillonite
MLC = mixed-layer clay

Table 4. Clay minerology of the <0.2 µm subfractions.

Core	Depth of	---Percentage of <0.2 µm size fraction (1)---						
number	sample (cm)	ILL	KAO	CHL	DIV	VER	MON	MLC
VC93	- 60	15	11	2	9	15	6	42
	-140	16	12	3	11	21	9	28
	-220	16	10	2	12	13	7	39
	-300	12	12	2	10	13	7	43
	-380	14	14	2	11	15	9	35
	-460	15	13	3	12	13	7	37
	-540	16	15	2	9	16	7	34
WB006	- 40	16	8	3	11	13	5	44
	-120	16	9	2	6	23	10	33
	-200	16	9	3	8	17	10	38
	-280	14	9	4	20	14	9	30
	-360	13	10	2	12	17	8	37
	-420	19	10	3	7	20	9	31
WB022	- 60	25	11	3	6	12	6	37
	-140	15	6	2	13	13	6	46
	-220	17	10	3	11	17	9	34
	-300	17	8	3	10	12	7	44
	-380	14	7	3	7	13	7	49
	-460	17	9	3	8	16	5	42
WB080	- 60	27	13	3	10	11	2	34
	-150	15	7	1	7	9	4	57
	-240	19	9	0	9	15	10	37
	-330	16	8	3	12	4	5	53
	-420	19	9	4	9	17	6	37
	-510	23	12	2	14	15	7	27
	-600	15	10	2	16	11	5	41
WB095	- 60	NA	NA	NA	NA	NA	NA	NA
	- 90	26	12	3	9	18	8	24
	-150	22	10	4	7	9	7	42
	-270	28	8	3	11	5	4	42

(1) Abbreviations:

ILL = illite
KAO = kaolinite
CHL = chlorite
DIV = dioctahedral vermiculite
VER = vermiculite
MON = montmorillonite
MLC = mixed-layer clay
NA = not analyzed

Table 5. Clay minerology of the <2 μm fractions.

Core number	Depth of sample (cm)	Weight % clay	-Percentage of <2 µm size fraction (1)						
			ILL	KAO	CHL	DIV	VER	MON	MLC
VC93	- 60	64	33	11	5	12	11	4	25
	-140	62	32	12	5	12	12	6	20
	-220	62	26	11	3	13	10	6	32
	-300	60	29	9	5	12	12	5	31
	-380	70	31	13	5	11	11	5	26
	-460	66	27	13	4	10	10	5	31
	-540	68	29	14	3	11	11	5	27
WB006	- 40	46	27	11	5	9	9	4	35
	-120	47	30	8	4	6	17	6	27
	-200	40	28	10	5	9	11	6	31
	-280	41	29	11	5	16	10	5	23
	-360	43	27	11	4	11	11	5	31
	-420	35	33	11	5	9	13	6	24
WB022	- 60	44	45	14	7	10	8	3	14
	-140	41	39	12	7	9	9	3	21
	-220	34	38	12	6	12	10	4	18
	-300	41	34	9	5	7	9	4	31
	-380	47	35	12	6	9	9	4	27
	-460	41	33	10	6	9	12	4	28
WB080	- 60	27	33	14	4	9	9	2	28
	-150	24	30	8	4	7	9	4	38
	-240	22	30	10	3	9	13	8	27
	-330	23	32	11	5	11	5	4	34
	-420	24	32	10	6	8	14	5	28
	-510	24	37	12	5	13	11	5	18
	-600	34	34	12	5	14	8	4	24
WB095	- 60	NA	NA	NA	NA	NA	NA	NA	NA
	- 90	24	35	10	5	9	15	6	21
	-150	30	35	10	5	8	9	5	27
	-270	47	42	11	4	9	4	3	28

(1) Abbreviations:

ILL = illite
KAO = kaolinite
CHL = chlorite
DIV = dioctahedral vermiculite
VER = vermiculite
MON = montmorillonite
MLC = mixed-layer clay
NA = not analyzed

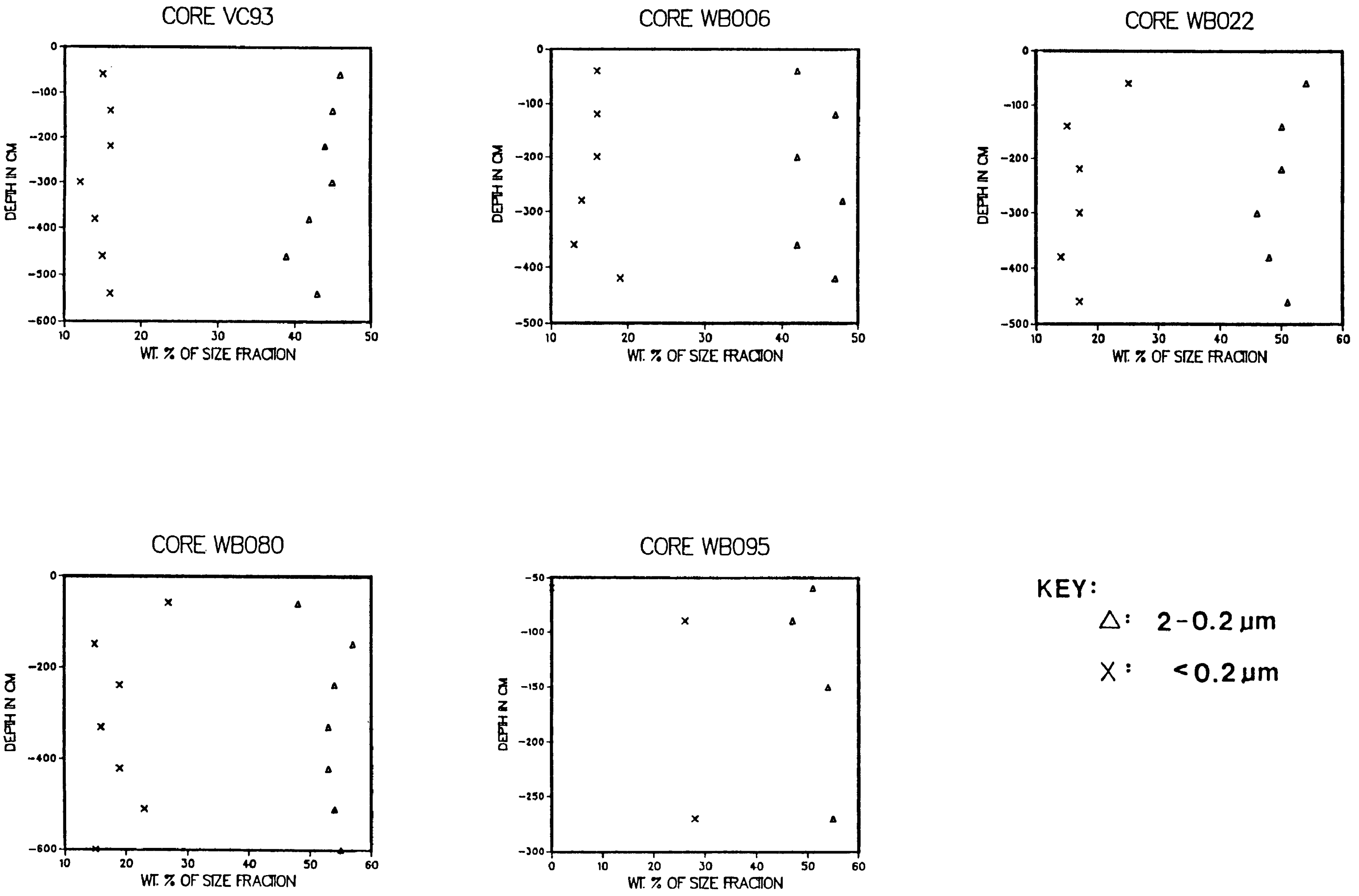
Plots of percentages of the clay mineral species versus depth of sample for each of the two clay subfractions reveal no consistent or otherwise remarkable vertical trends in mineralogy, suggesting compositional homogeneity within cores (Figures 5a to 5g). A comparison of the average values of illite, and, to a lesser degree, dioctahedral vermiculite, suggests that compositional variations do exist between cores. The most obvious differences appear in the coarse clay subfractions. Values of 2-0.2 µm illite in cores VC93 and WB006 average 43% and 45%, respectively, while in cores WB022, WB080, and WB095, values of 50%, 53%, and 52% are found. Values of <0.2 µm illite average 15% and 16% in cores VC93 and WB006, respectively, and in cores WB022, WB080, and WB095 average 18%, 19%, and 25%, respectively. The difference in 2-0.2 µm dioctahedral vermiculite, however, is more subtle, with cores VC93 and WB006 averaging 12% and 10%, respectively, and cores WB022, WB080, and WB095 averaging 9% each.

The reproducibility of the semi-quantitative analyses was estimated by averaging the standard deviations of clay percentages calculated from sets of measurements, including duplicates and multiple runs, of five samples for each subfraction. The approximate values calculated for the 2-0.2 µm subfractions are: kaolinite, 2.1; chlorite, 0.6; montmorillonite, 0.5; illite, 3.3; vermiculite, 2.1; dioctahedral vermiculite, 1.9; and mixed-layer clays, 5.3. For the <0.2 µm subfractions, the values are: kaolinite, chlorite, montmorillonite, vermiculite, and dioctahedral vermiculite, 1; illite and mixed-layer clays, 2.

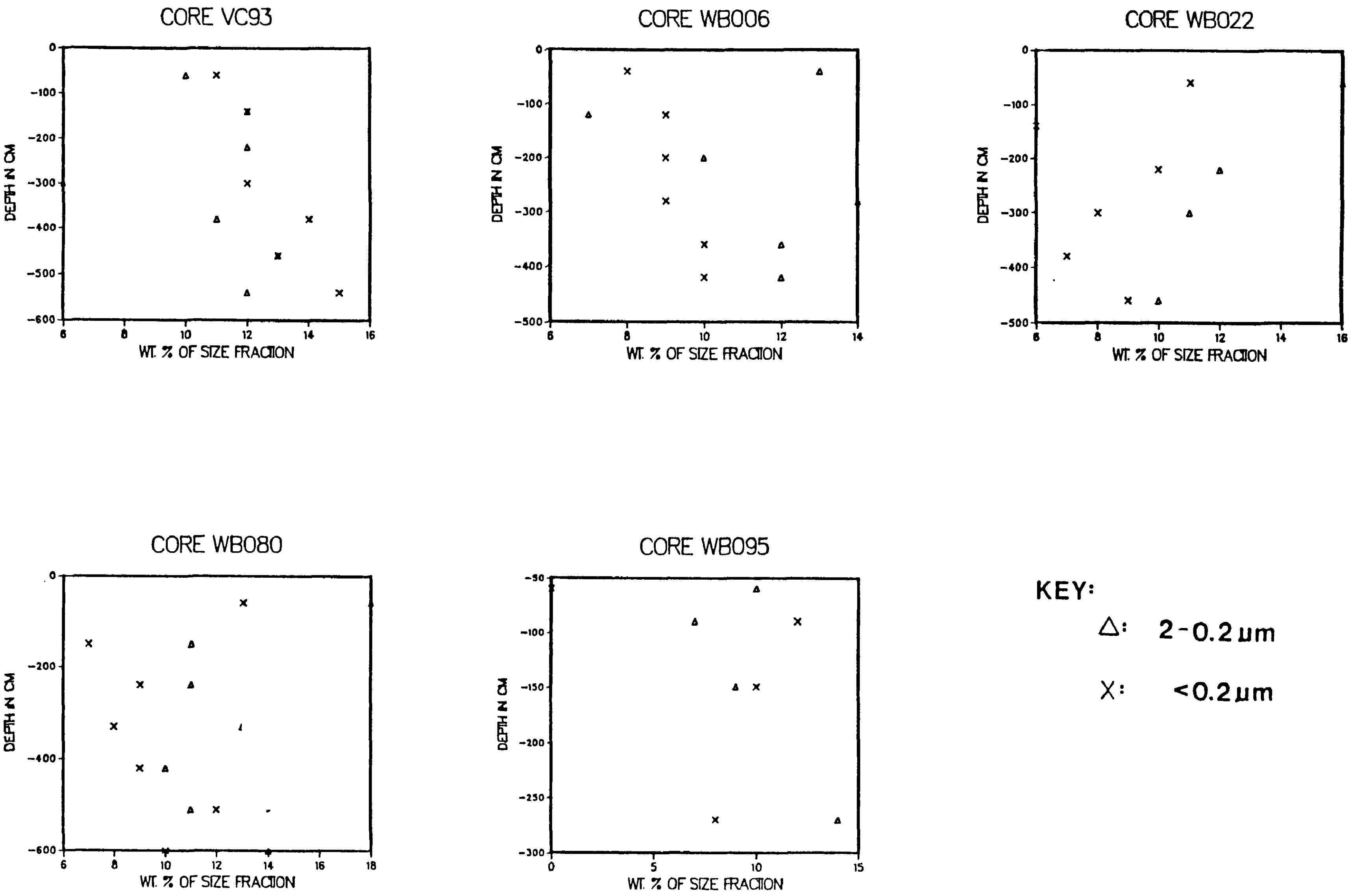
The five samples of 20-2 µm material, including one sample from each core, all show appreciable amounts of quartz, illite, (or mica),

Figure 5. Profiles of clay mineral percentages versus depth for two clay subfractions: a) illite; b) kaolinite; c) chlorite; d) dioctahedral vermiculite; e) vermiculite; f) montmorillonite; g) mixed-layer clays.

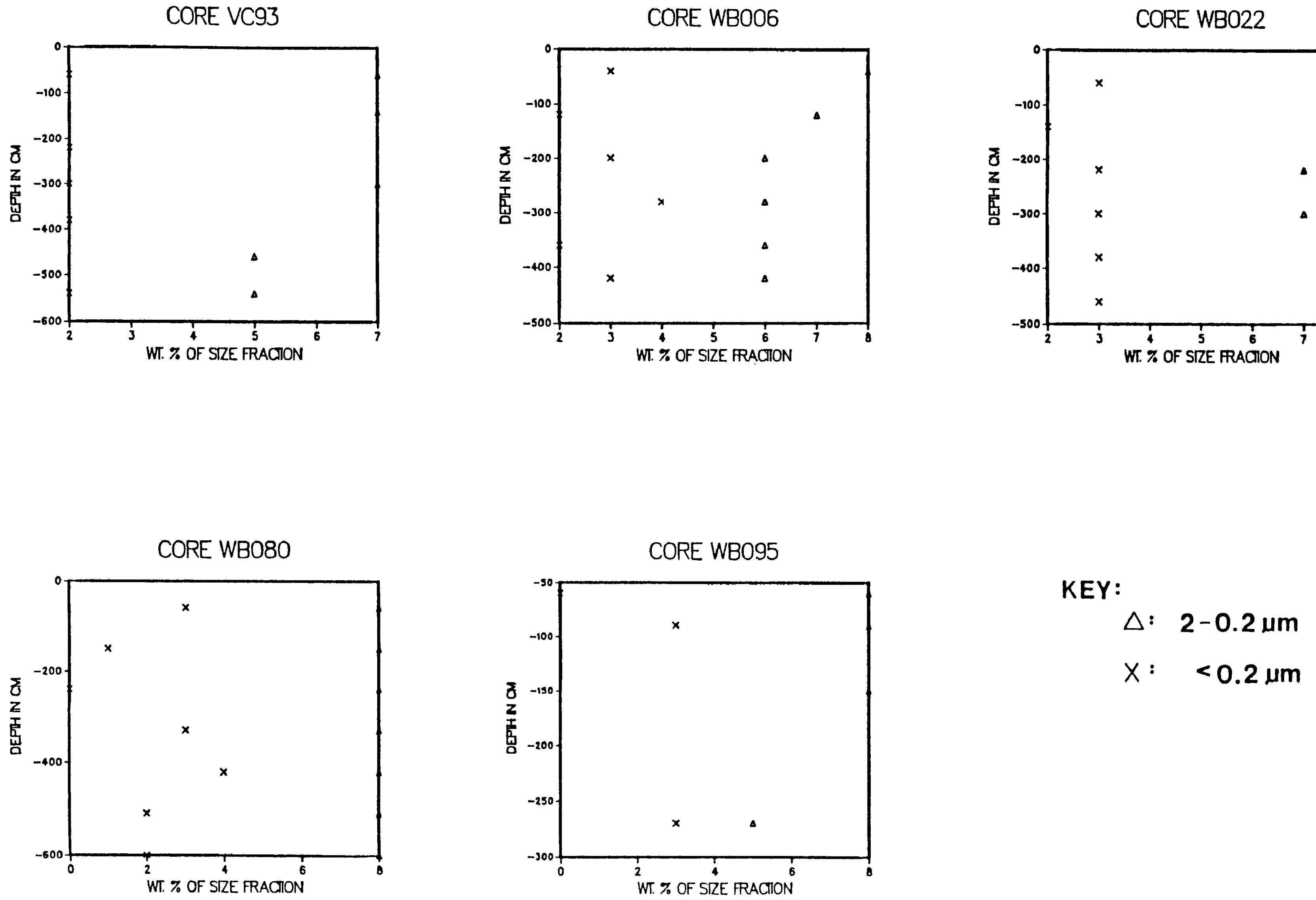
PERCENT ILLITE V. DEPTH



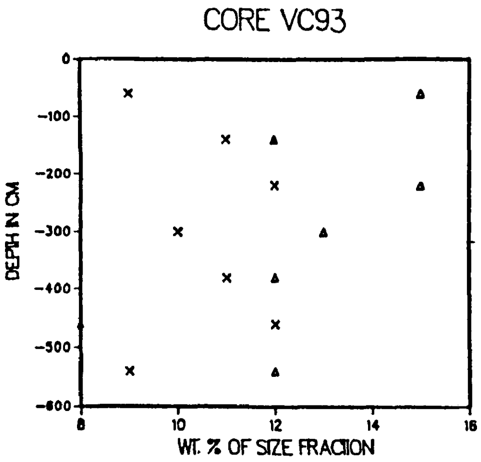
PERCENT KAOLINITE V. DEPTH

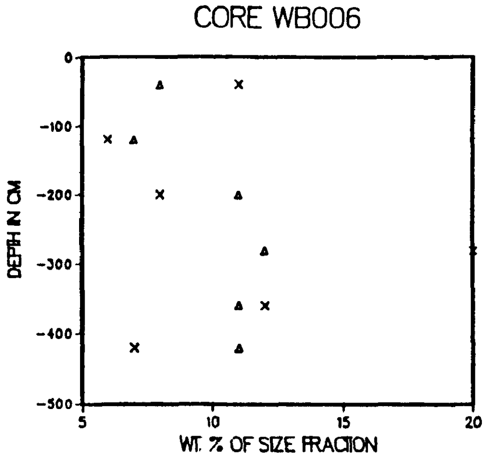


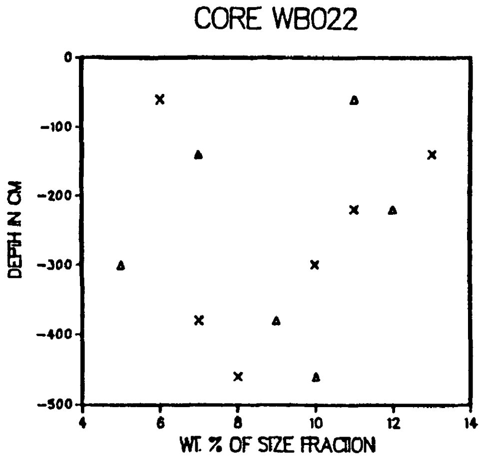
PERCENT CHLORITE V. DEPTH

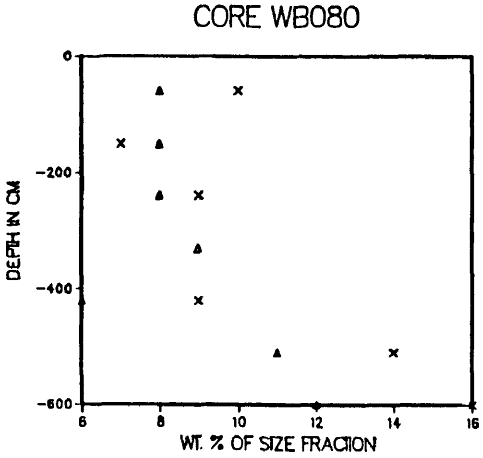


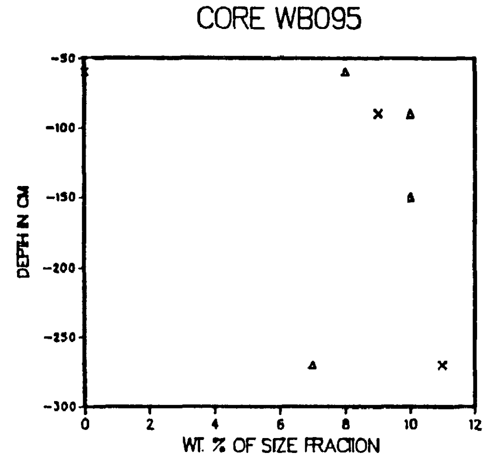
PERCENT DIOCT. VERMICULITE V. DEPTH


CORE VC93


CORE WB006


CORE WB022


CORE WB080

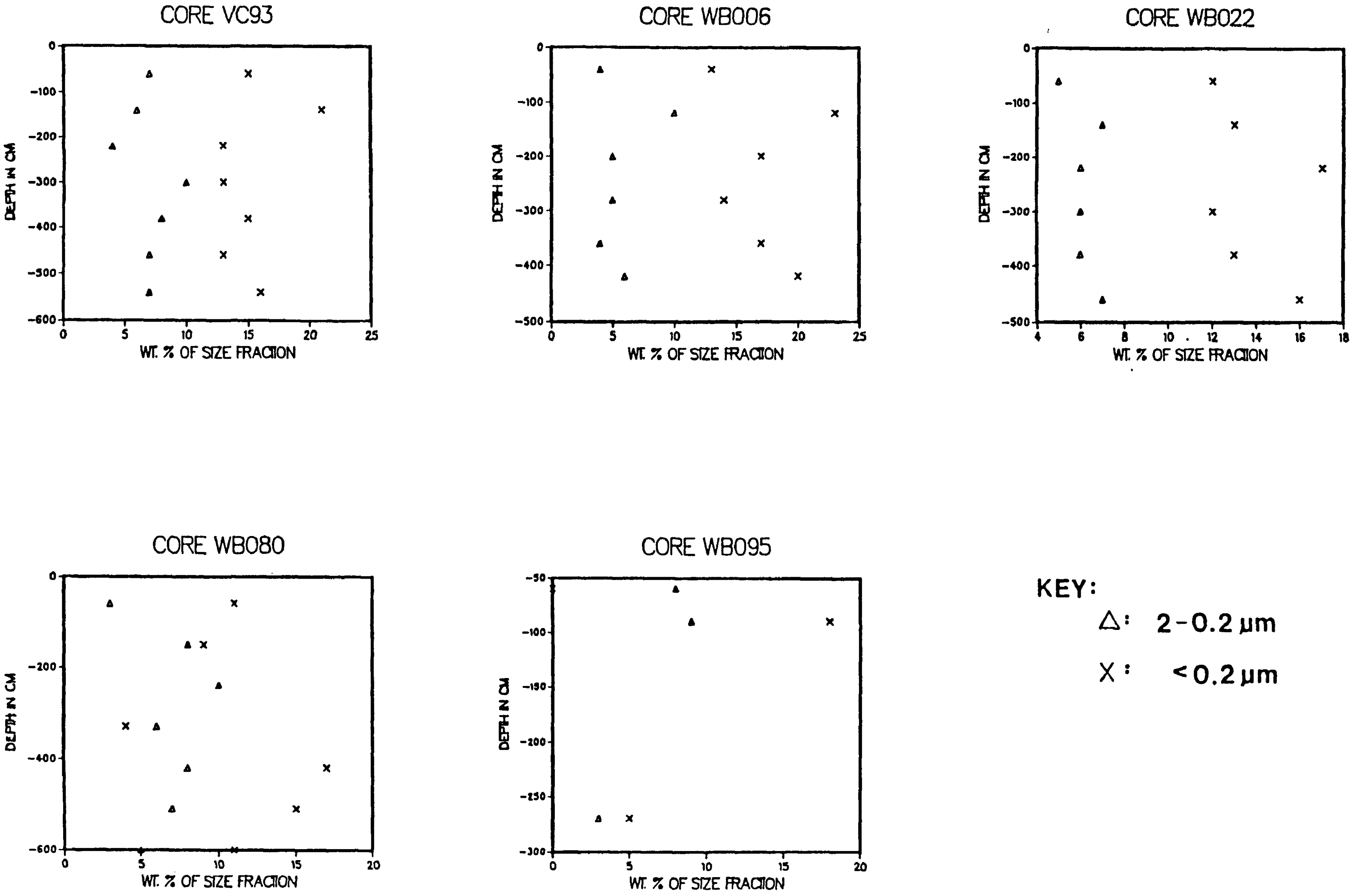

CORE WB095

KEY:

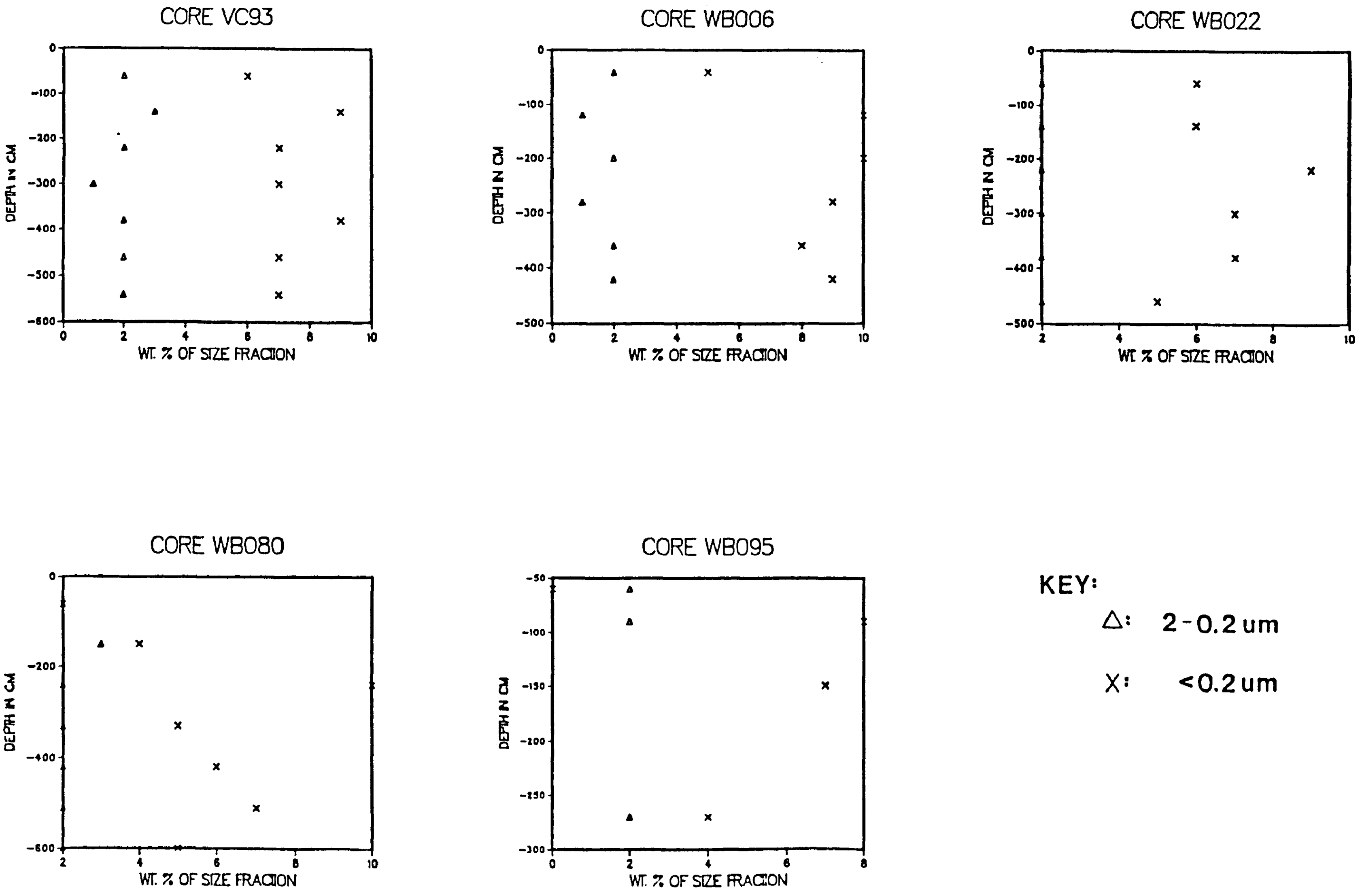
Δ: 2-0.2μm

X: <0.2μm

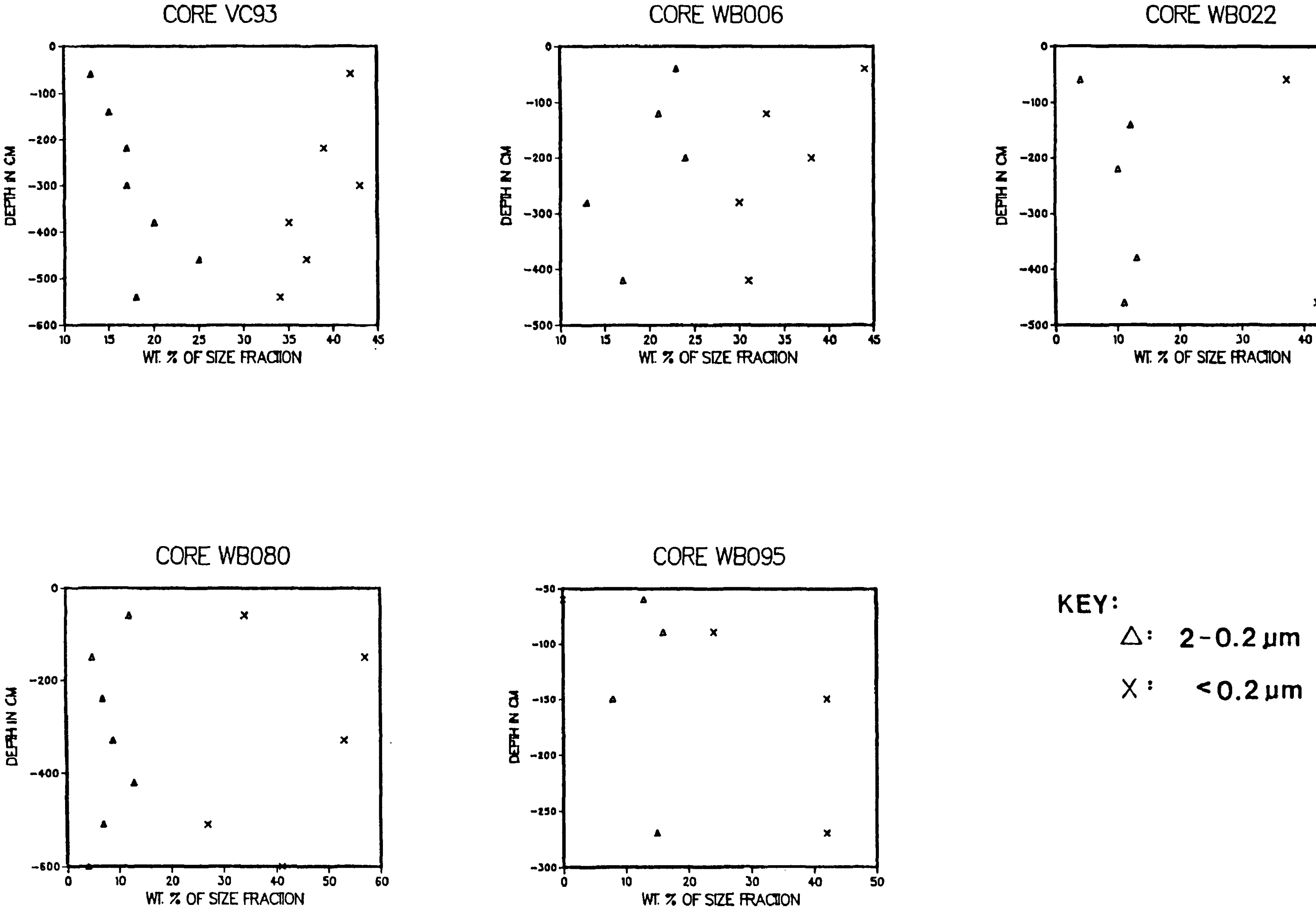
PERCENT VERMICULITE V. DEPTH



PERCENT MONTMORILLONITE V. DEPTH



PERCENT MIXED-LAYER CLAYS V. DEPTH



kaolinite, and chlorite. Undifferentiated vermiculite or dioctahedral vermiculite was thought to be present in considerable amounts in the one sample taken from core VC93. These results agree qualitatively with the findings by Carson and Arcaro (1983) and Kelley (1983) of considerable amounts of clay minerals in silt-sized material. This underscores the importance of Towe's (1974) assertion that clay minerals are not confined solely to the "traditional" <2 µm fraction.

Values for mixed-layer clays are much higher in the fine clay subfractions than in the coarse. Part of this difference is considered to be the cumulative errors inherent in the measurement of diffraction peaks of the fine clay, which were broadened and less discrete than those of the coarse subfractions. The value obtained by the semi-quantitative method used in this study contains the sums of the errors of all the other clay minerals (Feuillet and Fleischer, 1980), hence the true value of the content of mixed-layer species is indeterminant. However, the remainder of the difference is probably real, reflecting possibly complex interlayering of two or more clay mineral species. The high background between the glycerol-montmorillonite and vermiculite peaks, particularly in the <0.2 µm subfractions, suggests a mixed-layer species dominated by these two minerals. Broadening of the 10 Å illite peak toward the low-angle side, found in diffractograms of both subfractions, suggests the presence of interstratified illite-montmorillonite. The complex nature and inherent variability of mixed-layer species limit their usefulness in this study.

VII. STATISTICAL ANALYSES

Discriminant function analyses

Rationale

A common characteristic of cores WB022, WB080, and WB095 is their proximity to Thimble Shoal Channel, a prominent geomorphic feature in the lower bay. Colman and Hobbs (1987) described the Channel as a tributary to Chesapeake Channel, the main axial channel of the bay. They have shown that relatively thick upper Holocene deposits surround Thimble Shoal Channel, representing part of the fill which enters the bay from the shelf via tidal processes. Ludwick (1981) described the Channel as a product of two mutually evasive tidal channels which support relatively high sedimentation rates. Inasmuch as the primary objective of the study is to determine the relative influence of fluvial versus shelf-derived clay mineral suites, samples from the three cores in the vicinity of Thimble Shoal Channel were grouped together and assumed to reflect the mineralogic composition typical of shelf sediments; i.e., dominated by illite, chlorite, and montmorillonite. The remaining samples from cores VC93 and WB006, based on their relative proximity to the debouching waters of the James River, were assumed to have compositions representative of fluvial origin; i.e., rich in kaolinite, illite, and dioctahedral vermiculite.

A series of discriminant function analyses were performed to determine whether samples from these groups could be considered to be statistically distinct based upon their clay mineral compositions. This multivariate technique has been successfully utilized in previous studies of clay mineral distributions (e.g., Knebel et al., 1968; Carson and Arcaro, 1983). A description of the procedure is provided in the following section.

Overview

The purpose of discriminant function analysis is to assign a sample, on the basis of its various measured characteristics, to one of two or more groups which have been distinguished by *a priori* criteria. The two groups considered in this study were samples in cores assumed to show the dominant influence of 1) a continental source (based on proximity to the James River); and 2) a marine source (based on proximity to Thimble Shoal Channel). The clay mineral suites in these two sources have been previously identified for surficial sediments in the study area by Hathaway (1972) and Feuillet and Fleischer (1980).

In essence, the discriminant function converts a set of variables measured for each sample into a single discriminant score, which may then be plotted on the line defined by the function (Davis, 1973). Miller and Kahn (1962) described the technique in terms of Hoel's (1947) geometric analogy, an explanation of which follows.

Consider two variables, each of which is measured in samples from groups A and B. If the values of the variables for each sample are plotted on a two-dimensional scatter plot, with variable 1 forming one axis and variable 2 the other, then two clusters of related values will emerge, possibly with considerable overlap between the clusters. If a third dimension is introduced, and the plotted values are projected onto a new plane R, a clearer separation may emerge. The problem then becomes one of maximizing separation between the clusters while minimizing spread within them (Davis, 1973). The discriminant function represents the equation of the plane, i.e.,

$$R = \lambda_1 x_1 + \lambda_2 x_2,$$

where x_1 and x_2 are the measured variables and $_1$ and $_2$ are the coefficients of discrimination, whose values produce the optimum separation.

The following explanation is derived from Davis (1973). As the computational procedures for this technique are performed using matrices, the matrix of λ values can be found by solving the matrix equation

$$[s_p^2]\ [\lambda] = [D],$$

where $[s_p^2]$ is the matrix of pooled variances and covariances and [D] is the matrix of multivariate mean differences between groups for each variable. The point along the discriminant function line which is exactly halfway between the centers of groups A and B is the discriminant index, R_0. This is calculated by inserting the values of $x_j = (\bar{A}_j + \bar{B}_j) / 2$ into the discriminant function equation. This represents the midpoint between group means in A and B for the jth variable under consideration. The points R_A and R_B, representing the respective centers of groups A and B on the discriminant function line, are obtained by setting $x_j = \bar{A}_j$ and $x_j = \bar{B}_j$, where $\bar{A}_j$ and $\bar{B}_j$ are the multivariate means of the jth variable for each of the two groups.

A measure of the separation or "distance" between the groups may be calculated simply by subtracting R_A from R_B, or equivalently, by substituting the vector matrix of mean differences between groups into the discriminant function equation. This distance is designated as the standardized squared distance, D^2, or Mahalanobis' distance, and expresses the amount of separation between groups in units of the pooled variance. The statistical significance of this separation can be tested by use of a one-tailed F-test of the form

$$F = [(n_a + n_b - m - 1) / (n_a + n_b - 2) m] [n_a n_b / n_a + n_b] D^2,$$

where n_a and n_b are the number of samples in groups A and B, respectively, and m is the number of variables. The degrees of freedom associated with this test are m and $(n_a + n_b - m - 1)$. The null hypothesis being tested is that the distance between multivariate means is zero, or equivalently, that the difference $R_A - R_B$ is equal to zero.

In multivariate discrimination it is often desirable to identify those variables which are most effective is distinguishing one group from the others. A simple measure of this effectiveness is the value

$$E_j = \lambda_j D_j / D^2,$$

where D_j is the between-group difference of the mean of the jth variable. Values of E_j can be expressed as percentages by multiplying by one hundred. These values, however, consider only the direct contribution of the jth variable to the discrimination, and not of possible interactions between variables.

The two-variable discriminant function can be generalized to more than two variables and groups by multidimensional analogy. The extended function for m variables takes the form

$$R = \lambda_1 x_1 + \lambda_2 x_2 + \ldots + \lambda_m x_m.$$

Discriminant function tests were performed using the Fortran IV mainline program DISCRM and required subroutines found in Davis (1973). The programs were slightly modified and compiled in Fortran 77 on the VIMS PRIME 9955 computer system. Samples from cores VC93 and WB006 will herein be referred to as group 1 (continental) and samples of cores WB022, WB080, and WB095 will constitute group 2 (marine).

Results

The first set of discriminant runs was intended to determine the effectiveness of each clay species in discriminating between marine and continental groups. For each test the percentages of each clay species in each of the two clay subfractions (2-0.2 μm and <0.2 μm) were considered as the variables. An additional run considered the percentages of each of the clay subfractions present as the two variables. The results of runs 1 through 8 are summarized in Table 6.

The results of the F-tests indicate that, for all variables except kaolinite, the null hypothesis of no difference was rejected at at least the 5% level of significance. The four variables which provide the most effective discrimination, as judged both by values of D^2 and E_j, are <0.2 μm clay, 2-0.2 μm illite, 2-0.2 μm mixed-layer clay, and 2-0.2 μm chlorite. To a lesser extent, the differences in <0.2 μm vermiculite, <0.2 μm montmorillonite, and 2-0.2 μm dioctahedral vermiculite

Table 6. Results of discriminant function analyses between samples of group 1 (cores VC93 and WB006), assumed to reflect a continental origin, and samples of group 2 (cores WB022, WB080, and WB095), assumed to reflect a dominantly marine origin.

Run #	Variables (1)	Mahalanobis' D^2	F (deg. of freedom)	Reject H_0? (2)
1	2-0.2 and <0.2 um ILL	7.98	27.57 (2,26)	Yes**
2	2-0.2 and <0.2 um KAO	0.80	2.77 (2,26)	No*
3	2-0.2 and <0.2 um CHL	2.90	10.01 (2,26)	Yes**
4	2-0.2 and <0.2 um DIV	1.10	3.81 (2,26)	Yes*
5	2-0.2 and <0.2 um VER	1.27	4.38 (2,26)	Yes*
6	2-0.2 and <0.2 um MON	1.12	3.86 (2,26)	Yes*
7	2-0.2 and <0.2 um MLC	3.84	13.27 (2,26)	Yes**
8	2-0.2 and <0.2 um clay	6.28	22.32 (2,27)	Yes**
9	<2 um: clay, ILL, KAO, CHL, DIV, VER, MON, MLC	16.15	10.73 (8,20)	Yes**

(1) Abbreviations:

ILL = illite
KAO = kaolinite
CHL = chlorite
DIV = dioctahedral vermiculite
MON = montmorillonite
VER = vermiculite
MLC = mixed-layer clay

(2) H_0 = hypothesis of no difference between the multivariate means of group 1 (samples from cores VC93 and WB006 and group 2 (samples from cores WB022, WB080, and WB095)

* = 5% significance level
** = 1% significance level

Run #	Variables (1)	Mahalanobis' D^2	F (deg. of freedom)	Reject H_0? (2)
10	2-0.2 um: clay, ILL, KAO, CHL, DIV, VER, MON, MLC	18.79	12.48 (8,20)	Yes**
11	<0.2 um: clay, ILL, KAO, CHL, DIV, VER, MON, MLC	15.09	10.02 (8,20)	Yes**
12	<2 um: ILL, KAO, CHL, DIV, VER, MON, MLC	4.76	3.79 (7,21)	Yes**
13	2-0.2 um: ILL, KAO, CHL, DIV, VER, MON, MLC	18.15	14.46 (7,21)	Yes**
14	<0.2 um:, ILL, KAO, CHL, DIV, VER, MON, MLC]	6.68	5.32 (7,21)	Yes**

(1) Abbreviations:

ILL = illite
KAO = kaolinite
CHL = chlorite
DIV = dioctahedral vermiculite
MON = montmorillonite
VER = vermiculite
MLC = mixed-layer clay

(2) H_0 = hypothesis of no difference between the multivariate means of group 1 (samples from cores VC93 and WB006 and group 2 (samples from cores WB022, WB080, and WB095)

* = 5% significance level
** = 1% significance level

distinguish the groups. In summary, greater abundances of illite and chlorite in the 2-0.2 µm subfractions distinguish group 2 samples from those of group 1. Group 2 samples, however, are impoverished in <0.2 µm clay, 2-0.2 µm mixed-layer clay and dioctahedral vermiculite and <0.2 µm vermiculite and montmorillonite relative to group 1 samples. These results suggest that cores VC93 and WB006 have been dominantly influenced by a fluvially-derived mineral suite, while group 2 cores indicate greater influence by shelf-derived material.

Run 9 tested the discriminatory value of each of the clay minerals as percentages of the total clay (<2 µm) in samples of each group. An additional variable considered in this run was percentage of <2 µm clay in each sample. The hypothesis of no difference was rejected at the 1% level of significance. The two variables contributing most to the discrimination are total clay, which is characteristically greater in group 1 samples, and illite, which is significantly more abundant in group 2 samples.

Runs 10 and 11 compared observations in the 2-0.2 µm and <0.2 µm subfractions separately. The hypotheses of no difference for both of the analyses were rejected at the 1% level of significance, indicating that the two groups of samples could be discriminated on characteristics of both the coarse and fine clay subfractions. For the 2-0.2 µm subfractions, greater values of illite were associated with group 2 samples, while greater abundances of mixed-layer clay and dioctahedral vermiculite marked samples of group 1. Based on the <0.2 µm values, the best separation was achieved by illite and mixed-layer clay, both of which were enriched in group 2 samples, and by vermiculite and fine clay, both of which were more abundant in group 1 samples.

To eliminate the effects of varying amounts of clay material in each sample, three final analyses were run without considering size variables. Runs 12, 13, and 14 included the clay minerals in the <2 µm, 2-0.2 µm, and <0.2 µm subfractions, respectively. Although in each case D^2 values were reduced due to the elimination of the size variable, the clay mineral variables were still effective in discriminating the two groups at the 1% level of significance. On the basis of the 2-0.2 µm subfractions, group 2 was significantly richer in illite and poorer in mixed-layer clays and dioctahedral vermiculite than group 1. Considering only the <0.2 µm subfractions, group 2 was richer in illite and mixed-layer clays and poorer in vermiculite that group 1. The analysis of the bulk clay (<2 µm) fraction showed that illite was the single most effective discriminator between group 2, in which it was most abundant, and group 1. The discriminate scores for runs 1, 12, 13, and 14 are plotted in Figure 6. These plots illustrate the ability of clay minerals, in particular illite, to distinguish between samples of continental origin (group 1) and marine origin (group 2).

To ascertain whether the fortuitous grouping of cores favorably affected the discriminant function analyses, other groupings were tested using the same methods as above. No other groupings resulted in statistically significant discriminations, suggesting that differences between groups 1 and 2 are real.

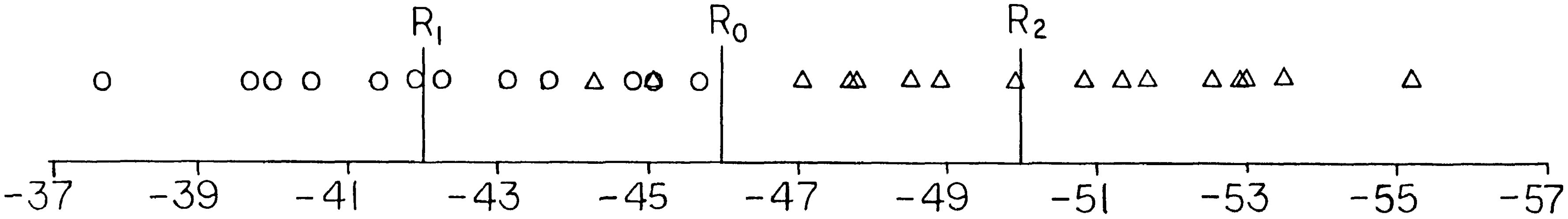
Tests for mineral size-dependency

As has been previously discussed, size-dependencies in clay minerals may significantly affect their distribution (e.g., Carson and Arcaro, 1983; Kelley, 1983) so that this effect should be considered

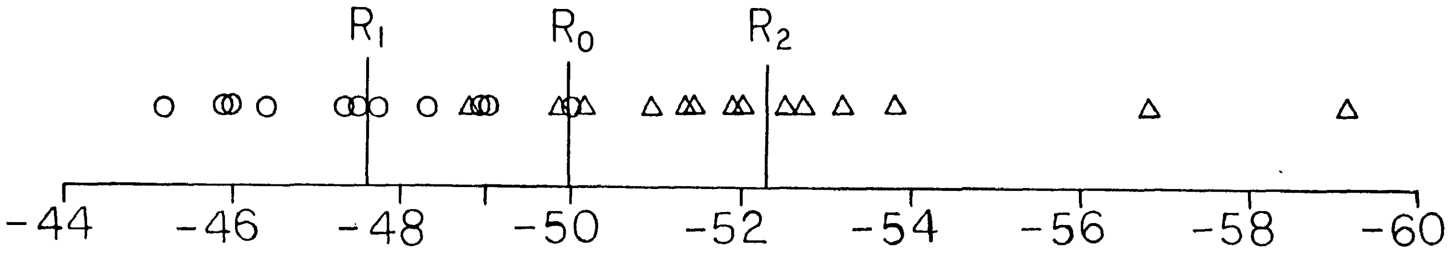
Figure 6. One-dimensional plots of the discriminant scores for runs 1, 12, 13, and 14. The plots indicate that the two groups can be discriminated relatively well on the basis of varying mineralogy of the various clay subfractions (runs 12, 13, 14). In particular, the effectiveness of illite as a mineralogic discriminator between group 1 (continental) and group 2 (marine) is demonstrated in run 1. Good discriminations show relatively few misclassified samples; correctly classified samples fall on the side of R_o closest to the appropriate multivariate mean (R_1 or R_2).

LEGEND:

R_0: DISCRIMINANT INDEX
R_1: MULTIVARIATE MEAN, GROUP 1 (CORES VC93 and WB006)
R_2: MULTIVARIATE MEAN, GROUP 2 (CORES WB022, WB080, and WB095)
○: DISCRIMINANT SCORES, GROUP 1
△: DISCRIMINANT SCORES, GROUP 2



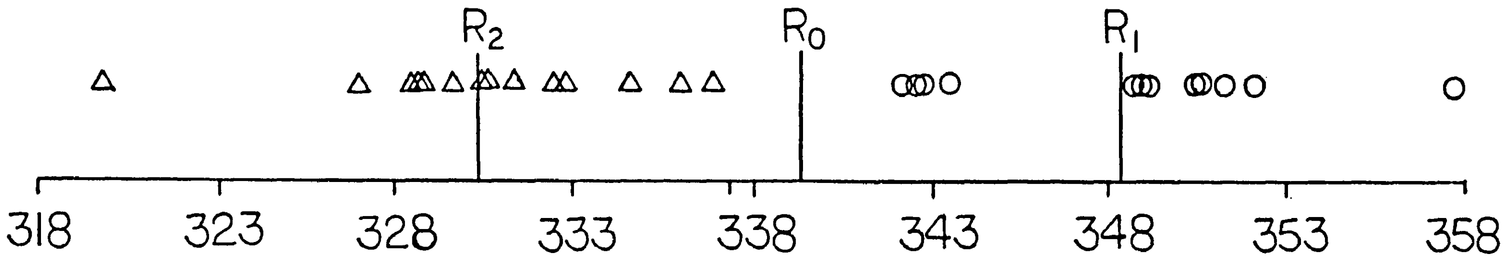
2–0.2 AND < 0.2 μM ILLITE
(RUN 1)



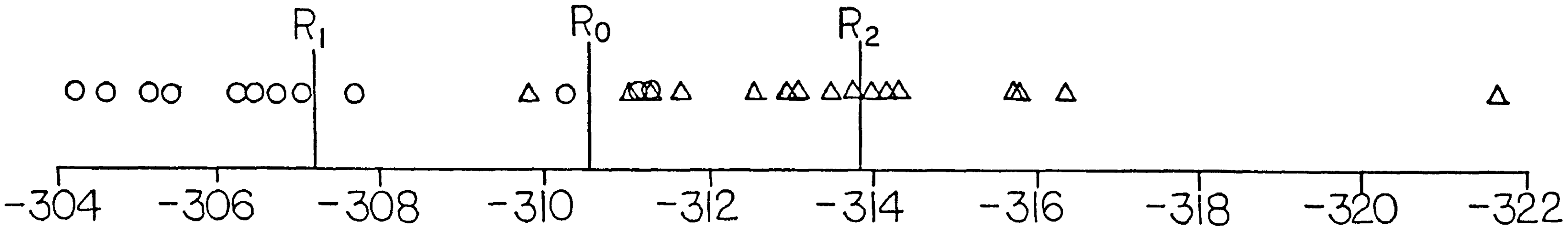
CLAY MINERALS (< 2 μM)
(RUN 12)

LEGEND:

R_0: DISCRIMINANT INDEX
R_1: MULTIVARIATE MEAN, GROUP 1 (CORES VC93 and WB006)
R_2: MULTIVARIATE MEAN, GROUP 2 (CORES WB022, WB080, and WB095)
○: DISCRIMINANT SCORES, GROUP 1
△: DISCRIMINANT SCORES, GROUP 2



CLAY MINERALS (2– 0.2 μM)
(RUN 13)



CLAY MINERALS (< 0.2 μM)
(RUN 14)

before interpretations are made (Towe, 1974). In view of the significant differences in size distribution between samples of groups 1 and 2, scatterplots and correlation statistics for each clay mineral in each clay size subfraction were generated using the SCATTERGRAM routine in the Statistical Package for the Social Sciences (SPSS) library (Nie et al., 1975). The significance of the correlations was tested using a two-tailed t-test with a null hypothesis of $R = 0$, where R is the correlation coefficient. The results of these tests appear in Table 7.

Plots of percentage of each clay species versus percentage of <2 μm clay revealed no significant correlations for any mineral when tested at the 5% level of significance. When percentages of the various clay species in the 2-0.2 μm fraction were plotted against percentages of that size subfraction for each sample, significant (5% level) correlations were indicated between illite, chlorite, dioctahedral vermiculite, and mixed-layer clay. High sample variance was reflected in the high standard errors of the estimates for illite (4.19) and mixed-layer clay (5.69). Illite and chlorite apparently increase with decreasing content of 2-0.2 μm clay, while dioctahedral vermiculite and mixed-layer clay increase with increasing quantities of this size fraction. Only one significant (5% level) correlation was noted for similar plots of <0.2 μm clay mineral percentages versus percentage of <0.2 μm clay for all samples; kaolinite showed an increase with increasing amounts of <0.2 μm clay.

Table 7. **Results of two-tailed t-tests to determine significance of correlation between mineralogy and amount of material in size class.**

Clay mineral	R	Standard error	Reject H_0? (1)
	<2 µm fractions		
Illite	-0.27	4.44	No*
Kaolinite	0.31	1.56	No*
Chlorite	-0.17	1.03	No*
Dioct. verm.	0.27	2.21	No*
Vermiculite	0.03	2.70	No*
Montmorillonite	0.04	1.25	No*
Mixed-layer clay	0.04	5.55	No*
	2-0.2 µm subfractions		
Illite	-0.54	4.19	Yes**
Kaolinite	0.06	2.61	No*
Chlorite	-0.50	0.94	Yes**
Dioct. verm.	0.36	2.37	Yes**
Vermiculite	-0.07	2.01	No*
Montmorillonite	-0.04	0.42	No*
Mixed-layer clay	0.38	5.69	Yes**
	<0.2 µm subfractions		
Illite	0.01	5.42	No*
Kaolinite	0.45	1.98	Yes**
Chlorite	-0.11	0.88	No*
Dioct. verm.	0.09	3.10	No*
Vermiculite	0.18	4.21	No*
Montmorillonite	0.12	2.02	No*
Mixed-layer clay	-0.12	7.53	No*

(1) H_0: R = 0 (no correlation)

* = 5% significance level ** = 1% significance level

VIII. DISCUSSION

The bulk (<2 um) fractions of the samples analyzed in this study reflect a composition more closely related to Feuillet and Fleischer's (1980) lower bay suite than to their James River suite. This is evidenced by relatively low kaolinite (10-15%) and high illite (35-45%) contents. Because the provenance and distribution of these species are reasonably well known, it seems likely that the continental shelf is a significant source of clay minerals in the lower bay.

Relatively homogeneous vertical distributions of the clay minerals in each of the five cores probably reflects deposition from a time averaged-invariant source. However, it is possible to identify small, but statistically significant variations in composition between two groups of cores. The first group, assumed to represent sedimentation predominantly from a continental, or riverine source, consists of cores VC93 and WB006; the second group, consisting of cores WB022, WB080, and WB095, was assumed to represent sediments derived mainly from the continental shelf. These *a priori* groupings were evaluated using a series of discriminant function analyses.

On the basis of the statistical results, it appears valid to assume a genetic relationship among the cores of group 2 based on their proximity to Thimble Shoal Channel. The samples of this group are clearly enriched in illite, which proved to contribute the most to the discriminant functions for group 2 when tested for the <2 um, 2-0.2 um, and <0.2 um subfractions. One-dimensional plots of the discriminant scores for runs 1, 12, 13, and 14 demonstrate the relatively good separations obtained from the variables considered in the analyses [Figure 6]. In particular, run 1 of Figure 6 shows that illite alone is a fairly effective discriminator between samples of group 1 (continental) and group 2 (marine). This does not imply, however, that it is the sole contributor to the discrimination.

The enrichment of illite in cores adjacent to Thimble Shoal Channel can be interpreted in terms of sources and dominant transport pathways of sediments during the late Holocene. On the basis of historical bathymetric trends, Ludwick (1981) characterized the Channel as the product of two mutually evasive tidal channels, with the landward one-third dominated by ebb flow, the seaward one-third dominated by flood flow, and the center one-third acting as a depositional "null zone." From a comparison of bottom sediment types in the area of interest, he concluded that deposition in the landward one-third of the Channel is controlled primarily by sedimentation from the ebb plume of the James River. The results of this study, however, show that sediments proximal to the Channel display mineralogic compositions which are statistically distinct from group 1 cores. If, in fact, deposition at the landward portion of the Channel has historically been dominated by the ebb plume of the river, then the mineralogy of these sediments has been so obscured by physical mixing with shelf-derived material that they are indistinguishable from the latter. Although Ludwick cited the presence of a turbid plume emanating from Hampton Roads and confined to the southern half of the bay entrance (Ludwick and Melchor, 1972), the results of this study suggest that other sources, namely shelf inputs and lateral migration of sediments in the bay, are the dominant sources of fill in Thimble Shoal Channel.

It is notable that the mineralogy of core WB095, located just seaward of the flood-dominated zone of the Channel, is similar to that of core WB022 located at the landward end. The idea that the continental shelf is a source of clay minerals in the bay is further supported by Boon et al. (1983) and Berquist (1986), who used different methods to delineate transport pathways of sandy sediment into the bay. The combined evidence strongly suggests that the shelf is a source of fine-grained sediment, as well as sand, to the lower Chesapeake Bay.

In contrast to samples of group 2, those of group 1 exhibit greater similarity to Feuillet and Fleischer's (1980) river-derived suite, which shows depletion of illite relative to seaward sediment. A slight increase in dioctahedral vermiculite relative to group 2 samples is probably also diagnostic of the river-borne suite. While the vertically homogeneous texture and mineralogic composition of core VC93 probably reflects the deposition of sediments within the so-called James River "settling basin" just west of Hampton Roads (Shideler, 1975), the depositional history of core WB006, located in the southeastern part of the river mouth, is not clear. It is possible that the composition of this core reflects some combination of fluvial deposition and inputs from shoreline erosion. In any case, the chief factor which appears to explain the mineralogic variation between group 1 and 2 is proximity to Thimble Shoal Channel, which is interpreted to act as a conduit for sediment transport from the shelf to the lower bay.

Kaolinite, typically an abundant mineral in fluvial sediments of the region (Hathaway, 1972; Feuillet and Fleischer, 1980), is relatively evenly distributed throughout all cores. This indicates that, to considerable depth, Holocene river-derived sediments have been diluted with predominantly illite-rich, shelf-derived sediments. The kaolinite values found in this study agree very well with the ~10% found by Hathaway (1972) in sediments of the shelf adjacent to Chesapeake Bay.

As has been discussed, the large error associated with estimation of the abundances of mixed-layer clays limits their utility. The general diffuse nature of all the diffraction peaks of the <0.2 µm samples may suggest that this very fine-grained material is structurally disorganized relative to 2-0.2 µm material. The fine size implies an increased surface area and reactivity with interstitial fluid. Changes at this small scale are essentially undetectable by x-ray diffraction, and would best be studied by different analytical methods.

The other clay minerals, show trends generally consistent with the assumption of two distinctive source "end-members," but are not effective discriminators for these samples. For example, dioctahedral vermiculite is a relatively good discriminator for the 2-0.2 µm fractions, showing a slight enrichment in group 1 samples consistent with a continental source. It is of little value, however, as a discriminator for the <2 µm and <0.2 µm fractions. Inasmuch as compositional trends in surficial sediments of the James River and lower bay are broadly distributed and thus detectable only over a large extent of the estuarine salinity gradient (Feuillet and Fleischer, 1980), it is to be expected that source-specific minerals of low abundance, such as montmorillonite and dioctahedral vermiculite, are of little use in this study, which presumedly concerns only a small portion of the paleosalinity gradient. This is evidenced by the low discriminant scores of these minerals in the discriminant function analyses. In addition, minerals in low abundance carry a relatively larger error in the x-ray diffraction analysis. As a result, they cannot be used with as much confidence as can illite, whose error is proportionately smaller due to its abundance.

The 2-0.2 µm and <0.2 µm subfractions each exhibit disparate mineralogic compositions, reflecting chiefly the modal size distributions of the dominant species. Illite, the most abundant species, composes 39-57% of the 2-0.2 µm subfractions but only 12-28% of the <0.2 µm subfractions. Chlorite, although low in abundance, is concentrated in the 2-0.2 µm subfraction, reflecting a relatively large modal size. Montmorillonite and vermiculite display a mode in the <0.2 µm subfractions, but kaolinite and dioctahedral vermiculite are variable over both subfractions. The results of the size-dependency correlations are interpreted to reflect predominantly the modal size distributions of the dominant species; there is little evidence in these results to indicate that clay mineral distributions are significantly influenced by size-selective sorting. This interpretation is substantiated by the fact that core groups 1 and 2 each display similar within-group mineralogy but considerably different textures. For example, the modal textures of samples from cores WB022, WB080, and WB095 are clay, sand, and silt, respectively; all three, however, display similar compositions. It is concluded, therefore, that mineralogy is essentially independent of texture in these samples.

The present results qualitatively agree with the trends found by Carson and Arcaro (1983), showing relative decreases in illite and chlorite, and an increase in montmorillonite with decreasing size. The approximately equal abundances of kaolinite in both the coarse and fine clay subfractions may indicate an intermediate or variable size range for this mineral. Few size data are available for vermiculites so that comparisons with other studies can not be made. However, results from this study suggest a wide range of sizes for dioctahedral vermiculite and a relatively smaller range for vermiculite.

IX. SUMMARY AND CONCLUSIONS

The overall clay mineral composition of the <2 μm fractions of thirty samples from five cores in the lower Chesapeake Bay-James River estuary ranges from 26-45% illite, 8-14% kaolinite, 3-7% chlorite, 6-16% dioctahedral vermiculite, 4-17% vermiculite, 2-8% montmorillonite, and 14-38% mixed-layer clays. These values are in good agreement with previous results on surficial sediments in the region. Based on comparison with these previous studies, the late Holocene clay mineral suite shows enrichment in illite and depletion in kaolinite relative to James River sediments. This suggests that the mineralogic composition of lower bay sediments has been greatly influenced by transport of sediment from the continental shelf. It can be concluded that the source and transport pathway of fine-grained sediment roughly parallel those of sand-sized material.

The results of a series of discriminant function analyses showed that samples from cores proximal to Thimble Shoal Channel are effectively distinguished from samples coming from the distal cores by the relative abundance of illite. Samples from the region of the Channel, an important conduit for tidally-mediated sediment transport from the shelf to the bay, are enriched in illite by approximately 6% in the <0.2 μm and bulk <2 μm fractions, and 8% in the 2-0.2 μm fraction relative to the samples from cores distal to the Channel. Therefore, illite is the single most effective indicator of the input of clay minerals from the shelf.

The compositional similarity of the three cores adjacent to Thimble Shoal Channel implies that, contrary to Ludwick's (1981) conclusion, sedimentation in this area is dominated by inputs from the shelf, and perhaps, from lateral migration or bay-floor erosion; there is no mineralogic evidence which suggests that the James River is the dominant source of this sediment.

None of the five cores in the study showed significant vertical variations in clay distribution, suggesting that the sources and transport pathways of the sediments have not significantly varied throughout the late Holocene.

Clay mineral distributions are not apparently influenced by size-selective sorting, as evidenced by the similar mineralogies but disparate textures of cores WB022, WB080, and WB095. The very different mineralogies of the 2-0.2 μm and <0.2 μm subfractions chiefly reflect the modal sizes of the clay minerals. The dominant mechanism of distribution of the clay minerals is physical mixing by circulation, in agreement with Feuillet and Fleischer (1980).

While it is sometimes difficult to obtain substantial sections of fine-grained sediment in the lower bay, particularly in the mouth of the James River estuary where sand predominates, the ability to distinguish subtle variations in clay mineral composition is useful in determining the relative influences of landward and seaward sediment transport through time. This distinction is particularly relevant considering the characteristic spatial variability of estuarine facies (e.g., Nichols and Biggs, 1985; Howard and Frey, 1986). The results of this study provide evidence that variable sedimentary textures may still not obscure useful mineralogic information.

Suggestions for future research

This study provides a basis for a more detailed, integrated program of analyzing clay mineral distributions in subsurface sediments in the lower Chesapeake Bay. In order to more closely examine end-member sources and transport pathways of clay minerals in the bay, it would be necessary to sample cores along a transect spanning a substantial portion of the Holocene paleosalinity gradient. Such a scheme, perhaps in conjunction with chemical studies, would enable the determination of the landward limit of marine-derived clays, and an evaluation of changes in distribution patterns related to the continuing Holocene transgression.

To determine possible lateral variations of clay minerals in the lower bay, it would be necessary to sample a grid of cores. Possible lateral influences on clay mineral distribution which should be evaluated include transport of material from the upper bay as well as inputs from shoreline erosion. This approach should consider the fact that more than two end-member sources may affect the observed clay mineral distribution in the lower bay. It would be interesting to determine whether clay mineral distributions in the sandy estuary mouth, which was not adequately sampled in this study, are consistent with the analysis presented here.

Given the proven utility of heavy minerals in delineating sources and pathways of Holocene sands in the Chesapeake Bay, it is anticipated that the present methods and results can be applied to similar studies involving fine-grained sediments. The mutual study of mineralogic variations in fine- and coarse-grained sediments can be a useful approach to integrative studies of estuarine stratigraphy and sedimentation.

APPENDIX

Core locations and descriptions

[Adapted from Hobbs et al. (1984) and Swean (1986)]

Core VC93

Date coring completed: 9 May 1983

Location: latitude/longitude: 36° 57.18′ N, 76° 25.35′ W

Virginia state coordinates: 232,267.00 N, 2,607,016.00 E

Water depth: 50.1 ft (15.3 m) MSL

Penetration: 20.0 ft (6.1 m)

Recovery: 15.0 ft (4.6 m)

Interval	Description	Sampled at:
0.0-6.0 ft (0.0-1.8 m)	Highly plastic silty clay with traces of fine sand and peat.	2.0 ft (0.6 m) 4.6 ft (1.4 m)
6.0-19.6 ft (1.8-6.0 m)	Clayey silt, highly plastic, with traces of fine sand and shell fragments.	7.2 ft (2.2 m) 9.8 ft (3.0 m) 12.5 ft (3.8 m) 15.1 ft (4.6 m) 17.7 ft (5.4 m)

Core WB006

Date coring completed: 5 February 1981

Location: latitude/longitude: 36^{o} 58.41′ N, 76^{o} 14.20′ W

Virginia state coordinates: 240,997.04 N, 2,661,128.31 E

Water depth: 26.0 ft (7.9 m) MSL

Penetration: 20.6 ft (6.3 m)

Recovery: 17.6 ft (5.4 m)

Interval	Description	Sampled at:
0.0-1.1 ft (0.0-0.3 m)	Highly plastic, clayey medium to coarse sand	1.3 ft (0.4 m)
1.1-12.8 ft (0.3-3.9 m)	Highly plastic clay	3.9 ft (1.2 m) 6.6 ft (2.0 m) 9.2 ft (2.8 m) 11.8 ft (3.6 m)
12.8-14.1 ft	Highly plastic, clayey medium to	

(3.9-4.3 m)	coarse iron-stained sand
14.1-17.2 ft (4.3-5.2 m)	Coarse iron-stained sand with clay pods)

Core WB022

Date coring completed: 25 July 1980

Location: latitude/longitude: 36° 59.51′ N, 76° 11.30′ W

Virginia state coordinates: 248,011.91 N, 2,675,080.44 E

Water depth: 53.0 ft (16.2 m) MSL

Penetration: 20.0 ft (6.1 m)

Recovery: 17.0 ft (5.2 m)

Interval	Description	Sampled at:
0.0-16.5 ft (0.0-5.0 m)	Highly plastic clay	2.0 ft (0.6 m) 4.6 ft (1.4 m) 7.2 ft (2.2 m) 9.8 ft (3.0 m) 12.5 ft (3.8 m) 15.1 ft (4.6 m)

Core WB080

Date coring completed: February 1982

Location: latitude/longitude: 37° 00.58′ N, 76° 14.80′ W

Virginia state coordinates: 254,090.90 N, 2,657,893.56 E

Water depth: 63.0 ft (19.2 m) MSL

Penetration: 40.0 ft (12.2 m)

Recovery: 25.8 ft (7.9 m)

Interval	Description	Sampled at:
0.0-5.6 (0.0-1.7 m)	Micaceous sandy silt grading to clayey silt with shell fragments; scattered fine sand	2.0 ft (0.6 m) 4.9 ft (1.5 m)
5.6-10.6 (1.7-3.2 m)	Clayey silt with fine shell fragments	7.9 ft (2.4 m)
10.6-15.7 (3.2-4.8 m)	Fine sandy clayey silt with fine shell fragments	10.8 ft (3.3 m) 13.8 ft (4.2 m)

15.7-20.7 (4.8-6.3 m)	Very fine sandy clayey silt grading to silty clay	16.7 ft (5.1 m) 19.7 ft (6.0 m)
20.7-22.7 (6.3-6.9 m)	Silty clay grading to sandy clay	
22.7-25.8 (6.9-7.9 m)	Medium sand, silt, and clay grading to sand and silt with wood fragments; clay ball	

Core WB095

Date coring completed: February 1982

Location: latitude/longitude: 36° 57.35′ N, 76° 03.87′ W

Virginia state coordinates: 235,818.72 N, 2,711,574.01 E

Water depth: 37.0 ft (11.3 m) MSL

Penetration: 36.0 ft (11.0 m)

Recovery: 37.0 ft (11.3 m)

Interval	Description	Sampled at:
0.0-2.0 (0.0-0.6 m)	Silty medium sand grading to clayey sand with shell fragments; pebble	2.0 ft (0.6 m)
2.0-6.4 (0.6-2.0 m)	Highly plastic clay with shell fragments	3.0 ft (0.9 m) 4.9 ft (1.5 m)
6.4-10.1 (2.0-3.1 m)	Highly plastic clay with scattered fine wood fragments	6.9 ft (2.1 m) 8.9 ft (2.7 m)

10.1-11.4 (3.1-3.5 m)	Peat
11.4-15.8 (3.5-4.8 m)	Clayey peat grading into fibrous peat grading into medium sandy peat
15.8-16.4 (4.8-5.0 m)	Gravel, sand, and silt with organic material
16.4-16.7 (5.0-5.1 m)	Micaceous clayey silt with some organic material and sand
16.7-26.9 (5.1-8.2 m)	Micaceous clayey silt of low to medium plasticity
26.9-37.0 (8.2-11.3 m)	Micaceous clayey silt with shell fragments; low to medium plasticity

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