

Mineralogy and Origin of Sediments From Drill Holes on the Continental Margin Off Florida

GEOLOGICAL SURVEY PROFESSIONAL PAPER 581-E

*Prepared in cooperation with the Woods Hole
Oceanographic Institution and the Joint
Oceanographic Institutions' Deep Earth
Sampling Program*



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By JOHN C. HATHAWAY, PETER F. McFARLIN, and DAVID A. ROSS

DRILLING ON THE CONTINENTAL MARGIN OFF FLORIDA

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Results of mineralogical analyses and interpretations of the origin of sediments from drill holes on the continental shelf, Florida-Hatteras Slope, and Blake Plateau

UNITED STATES DEPARTMENT OF THE INTERIOR

WALTER J. HICKEL, *Secretary*

GEOLOGICAL SURVEY

William T. Pecora, *Director*

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DRILLING ON THE
CONTINENTAL MARGIN
OFF FLORIDA

Drilling on the continental margin off Jacksonville, Fla., in 1965 was the first project undertaken by the Joint Oceanographic Institutions' Deep Earth Sampling (JOIDES) Program, sponsored by the National Science Foundation. The U.S. Geological Survey cooperated with the Oceanographic Institutions in this undertaking and is publishing the results of these investigations in a series of professional papers.

CONTENTS

	Page		Page
Abstract	E1	Origin of the sediments, by John C. Hathaway	E15
Introduction	1	Lower Tertiary sediments	15
Procedure	1	Carbonate minerals	15
General mineralogy of the cores, by John C. Hathaway and Peter F. McFarlin	4	Volcanic material	17
Carbonate minerals	4	Chert	17
Phosphates	4	Mechanism of chert emplacement	18
Silica	5	Detrital material	19
Silicates	5	Miocene sediments	20
Amorphous material	7	Carbonate minerals	20
Miscellaneous minerals	7	Silicates	20
Mineralogy of the consolidated materials	7	Phosphates	22
Mineralogy of the sand fraction, by David A. Ross	10	Detrital material	22
Introduction	10	Post-Miocene sediments	23
Methods	11	Carbonate minerals	23
Heavy fraction	13	Detrital material	23
Light fraction	14	Summary and conclusions	23
Insoluble residue	14	Selected references	24
Discussion	14		

ILLUSTRATIONS

		Page
PLATE	1. Index map, stratigraphic profile, and geologic sections showing mineralogy of the whole samples, both unconsolidated and consolidated material, and clay minerals, zeolites, and insoluble residues in unconsolidated samples in JOIDES drill holes on the continental margin off Florida	In pocket
FIGURE	1. Graph showing feldspar content of the samples	E5
	2. Graph showing zeolite content of the samples	5
	3. Geologic section showing relation between clay-size fraction and clay-mineral content of the cores	6
	4-9. Photomicrographs showing:	
	4. Cementation of foraminiferal sediment	8
	5. Dolomitized limestone	8
	6. Siliceous organisms in limestone	9
	7. Silicification of sediments	9
	8. Chert	10
	9. Zeolites	11
	10. Graph showing relationship of sand to amphiboles, epidote, and staurolite	13
	11. Graph showing relationship of weight of insoluble residue to line count of noncalcareous material	14
	12. Electron micrographs showing recrystallization of coccoliths	15
	13. Diagram showing possible mechanism for formation of chert	18

TABLES

		Page
TABLE	1. Estimates of amounts of minerals in whole samples, the clay-mineral fraction, and acetic acid-insoluble residues of the unconsolidated materials, and estimates of amounts of minerals in whole samples of the consolidated materials	E2
	2. Magnesium content of calcite in selected samples	4
	3. Mineralogical and textural data from selected samples	12
	4. Heavy-mineral composition of selected samples	13
	5. Average composition, variability, degree of homogeneity, and level of significance of samples from holes 1, 2, and 5	13

MINERALOGY AND ORIGIN OF SEDIMENTS FROM DRILL HOLES ON THE CONTINENTAL MARGIN OFF FLORIDA ¹

BY JOHN C. HATHAWAY, PETER F. McFARLIN,² and DAVID A. ROSS ³

ABSTRACT

Drill cores obtained during the Joint Oceanographic Institutions' Deep Earth Sampling Program from the continental shelf, the Florida-Hatteras Slope, and the Blake Plateau off northern Florida are composed of sediments ranging in age from Paleocene to post-Miocene. Calcite is the dominant mineral in all the cores; dolomite is almost completely restricted to the shelf and slope cores. Aragonite persists in samples as old as Oligocene, but magnesian calcite occurs only in post-Miocene samples. In general, only Miocene samples contain noncarbonate minerals in appreciable quantity. Phosphates are limited largely to the Miocene sediments. Here also, the clay minerals palygorskite, sepiolite, and montmorillonite are dominant. These clay minerals and the zeolites clinoptilolite and phillipsite in Miocene and older sediments suggest that volcanic activity was the principal source of noncarbonate deposition during much of the Tertiary. Heavy-mineral analyses suggest a southern Appalachian source for detrital materials. Terrigenous detrital material is scarce in most of the cores except for the surface samples on the continental shelf. The concentration of detrital quartz here probably resulted from reworking and winnowing by regression and transgression of the sea during the Pleistocene rather than by increased influx of terrigenous material.

Consolidated chertlike rocks consist of dominantly carbonate minerals in the nearshore holes and dominantly opaline cristobalite in the Blake Plateau holes. Reflux dolomitization by dense brines produced in evaporative lagoons in the area of the continental shelf and later incursions of fresh ground water from the Florida peninsula may have lithified sediments in the nearshore holes. Only when conditions were favorable for silicification were sediments on the Blake Plateau appreciably consolidated.

INTRODUCTION

In April and May 1965, six holes were drilled in the continental shelf, the Florida-Hatteras Slope, and the Blake Plateau off northern Florida as the first project of the Joint Oceanographic Institutions' Deep Earth Sampling Program (JOIDES). The pur-

pose of this drilling and the preliminary results were reported by the Joint Oceanographic Institutions' Deep Earth Sampling Program (1965). A discussion of some of the historical aspects of the program and a report on seismic reflection profiles along the drill holes were given by Emery and Zarudzki (1967). General descriptions of the recovered cores were given by Schlee and Gerard (1965) and by Charm, Nesteroff, and Valdes (1969). A preliminary summary of the mineralogy and stratigraphy in the drill holes was given by Hathaway and Schlee (1968). Weaver (1968) independently analyzed a different group of samples from the drill holes and summarized the mineral facies that he observed.

This paper reports the results of mineralogical analyses of about 100 samples from the six holes. The locations of these holes and a profile of the generalized stratigraphy of the area are shown on plate 1. The initial selection of 72 samples was made by John Schlee, U. S. Geological Survey, J. R. Frothingham, Woods Hole Oceanographic Institution, and R. L. Wait, U.S. Geological Survey, aboard the drilling ship *M.V. Caldrill I* at the time the cores were recovered. Most of these were unconsolidated or clay-like parts of the cores. An additional 33 samples of indurated or chertlike materials were selected later.

PROCEDURE

The samples were kept under refrigeration until their arrival in the laboratory, where they were removed from their containers, placed in small plastic boxes, and allowed to dry at room temperature. X-ray diffraction patterns were made of cuts from each of the first group of 72 samples as follows:

1. Whole sample, randomly oriented powder.
2. Clay ($<2\mu$) fraction, oriented aggregate on ceramic tile, untreated.
3. Clay ($<2\mu$) fraction, oriented aggregate on ceramic tile, treated with ethylene glycol.

¹ Contribution No. 2318 of the Woods Hole Oceanographic Institution.

² Woods Hole Oceanographic Institution, Woods Hole, Mass. Present address: Building 54, Massachusetts Institute of Technology, Cambridge, Mass. 02139.

³ Woods Hole Oceanographic Institution, Woods Hole, Mass. 02543.

Relative amounts of each mineral were estimated by comparison of intensities of diffraction maxima with each other and with external standards. Because many factors in addition to the quantity of a mineral affect its diffraction intensities, these estimates give only a general indication of the relative amounts of the various minerals present. The quantitative estimates of minerals in the samples are given in table 1.

Because in many of the samples the amount of material insoluble in acetic acid is very small, the estimates of mineral amounts in the insoluble residues are given separately in table 1 rather than being incorporated in the results for the whole sample, where they would appear only as traces.

A graphic presentation of the mineralogic information is given on plate 1. The scale of the profile for the offshore holes is half that of the nearshore holes, but the vertical spacing of the bars showing the mineralogic composition has been kept at the same scale so that the sets may be compared directly.

GENERAL MINERALOGY OF THE CORES

By JOHN C. HATHAWAY and PETER F. MCFARLIN
CARBONATE MINERALS

The dominant mineral in most of the cores is calcite. The carbonate minerals calcite, aragonite, and dolomite constitute more than 70 percent of the group of relatively unconsolidated samples examined. Hülsemann (1968) obtained calcium carbonate values that give a mean of 72.7 percent in chemical analyses of samples taken from analogous parts of the drill cores.

Aragonite was observed in cores from all the holes except hole 3, the most seaward one. This mineral occurs only in surface samples from holes 2, 4, and 6, but in samples from hole 5 it persists to a depth of about 200 meters below the sea floor in sediments as old as Oligocene. Aragonite was also observed in one sample of Miocene material from hole 1 at a depth below the sea floor of about 23 meters.

Magnesian calcite was found only in surface samples or, in the cores from hole 5, post-Miocene materials; none was observed in samples from hole 3. Table 2 lists those samples containing magnesian calcite; the amounts of $MgCO_3$ in the calcite structure are estimated by the method of Goldsmith, Graf, and Joensuu (1955). The estimates are based on the difference in peak position of the strongest calcite diffraction line ($d_{211(104)}$) from that of pure calcite. The position of the strongest line for halite served as an internal standard. The values range from 9 to 14 mole percent with a mean of 11 percent. In cores from hole 5, where more than one sample contains magnesian calcite, the $MgCO_3$ content decreases

TABLE 2.—Magnesium content of calcite in selected samples

Sample	$\Delta d_{211(104)}$	$MgCO_3$ (Mole percent)
J-1-0	0.029	10
2-0	.041	14
5-0	.039	14
35	.036	13
65	.030	10
100	.030	10
6B-0	.031	11
4-0	.026	9
4B-0	.030	10

from 13 mole percent at the surface to 10 mole percent at a depth of about 30 meters below the sea floor. The depth at which the magnesian calcite disappears has not yet been determined, but magnesian calcite is absent in a post-Miocene sample from a depth of about 61 meters in hole 5 and is absent in all Miocene and older samples.

Dolomite is distributed somewhat differently from the other carbonates. Of the 33 samples containing dolomite, 32 are from the three nearshore holes; the one additional sample is from a depth of about 15 meters in hole 3, the farthest hole from shore, but this sample contains only a trace of dolomite. The distribution of dolomite is shown on plate 1. Five of the seven samples containing more than about 30 percent dolomite are from the Miocene; the other two are from the Eocene. Samples from the Oligocene contain no more than traces of dolomite.

All dolomite in the cores showed displacements of the diffraction maxima that suggest about 10 percent excess calcium in the dolomite structure.

Some of the material identified as dolomite may contain iron in isomorphous substitution for calcium or magnesium in sufficient quantity for the material to be more correctly called ferroan dolomite. This larger iron content is suggested by indices of refraction higher than those for normal dolomite observed by John Schlee (oral commun., 1966) in thin sections of the material.

PHOSPHATES

Apatite, probably carbonate fluorapatite (francolite) (Altschuler and others, 1952; Rooney and Kerr, 1967; F. T. Manheim and R. M. Pratt, unpub. data), was observed in seven samples, five of which were of Miocene age. These samples gave X-ray diffraction patterns that indicate moderately well crystallized material, although microscopical examination reveals the very fine grain size usually observed in phosphorite. The two samples identified as non-Miocene were both recovered from positions close to Miocene boundaries. Apatite was found in samples from hole 1, about 5 meters above the Miocene-post-

Miocene boundary, and from hole 5 at the Oligocene-post-Miocene unconformity. Both occurrences may be the result of reworking of Miocene materials.

SILICA

Quartz is abundant only in two types of samples, those from the upper parts of the nearshore holes and those consisting of chertlike consolidated materials. Small amounts of quartz were found in the deeper samples from holes 2 and 5 and in the samples from offshore holes. Quartz was detected in the X-ray diffraction patterns of whole samples from hole 1 in only one sample older than Oligocene; it is a minor component even in the very small amounts of insoluble residue of the deeper samples from hole 1.

α -cristobalite occurs in one sample from the upper Eocene in hole 2. Disordered cristobalite (Flörke, 1955)⁴, was found in 12 samples, all from the Blake Plateau holes and all from the Eocene or Paleocene. Most of these samples are chertlike consolidated materials. Disordered cristobalite is the dominant non-carbonate component in all the samples but one, a lower Eocene sample from hole 6 in which quartz and disordered cristobalite are about equal in abundance.

SILICATES

Feldspar, mostly plagioclase, is nowhere more than a minor constituent of the cores. Its concentration even in the insoluble residues does not exceed 40 percent, and in all but one sample its concentration is 20 percent or less. Feldspar was detected in the X-ray diffraction patterns of whole samples only in the upper parts of the three nearshore holes. X-ray diffraction patterns of insoluble residues revealed traces of feldspar in many other samples, but principal concentrations are in Miocene and post-Miocene samples (figure 1).

Zeolites occur in 33 samples; of these, clinoptilolite alone is in 30 and phillipsite alone, in two. Both zeolites were found in one sample. No zeolites were observed in samples from hole 1. The stratigraphic distribution of the zeolites is shown in figure 2. Of the samples from which insoluble residues were obtained, all Paleocene samples and at least half the Eocene and Oligocene samples contained zeolites. Only 10 percent of the Miocene samples and none of the post-Miocene samples contained zeolites. Phillipsite is limited to samples from the Oligocene and Miocene.

⁴ The term opal includes both the crystalline material interpreted by Flörke (1955) as an intimate intermixing of cristobalite and tridymite layers, here called disordered cristobalite, and silica that is amorphous to X-rays. These two types of opal were illustrated by Swineford and Franks (1959).

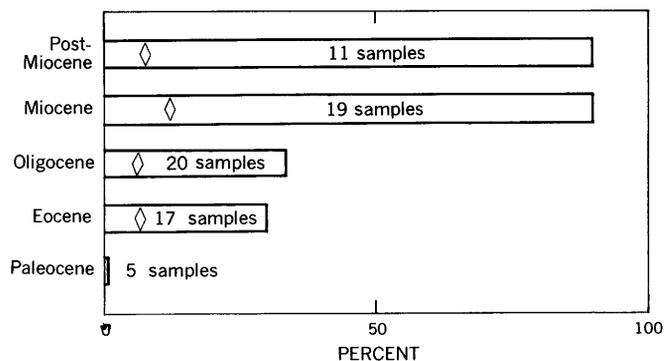


FIGURE 1.—Percentage of samples containing feldspar versus stratigraphic position, and mean feldspar content of these samples. \diamond , mean feldspar content of insoluble residues of those samples that contain feldspar. Trace amounts arbitrarily assigned values of 5 percent.

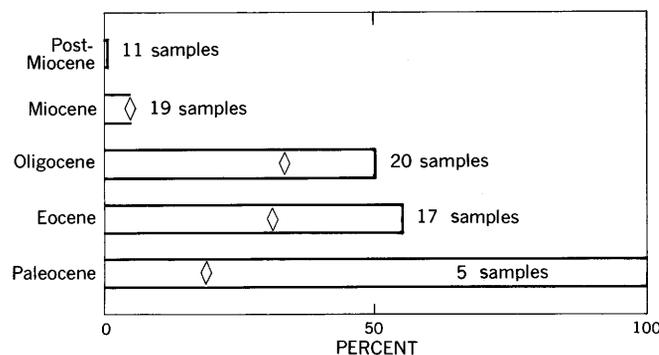


FIGURE 2.—Percentage of samples containing zeolites versus stratigraphic position, and mean zeolite content of these samples. \diamond , mean zeolite content of insoluble residues of those samples that contain zeolites. Trace amounts arbitrarily assigned values of 5 percent.

Total clay minerals in the whole samples range from traces to about 90 percent. Figure 3 shows the total clay-mineral content estimated from the X-ray diffraction pattern for each sample and the amount of material of less than 2-micron size obtained by fractionation of the sample. Agreement is poor between these amounts, mainly because some samples contain clay-size particles of nonclay minerals such as calcite, whereas others contain silt-size aggregates of clay minerals. Any inaccuracies in estimating the amounts of the clay minerals also contribute to disagreement. However, figure 3 illustrates that, except for some Miocene samples and one Oligocene sample, the amounts of clay minerals in the cores are generally small.

Montmorillonite is the principal clay mineral in most of the cores. Its largest concentration is in an

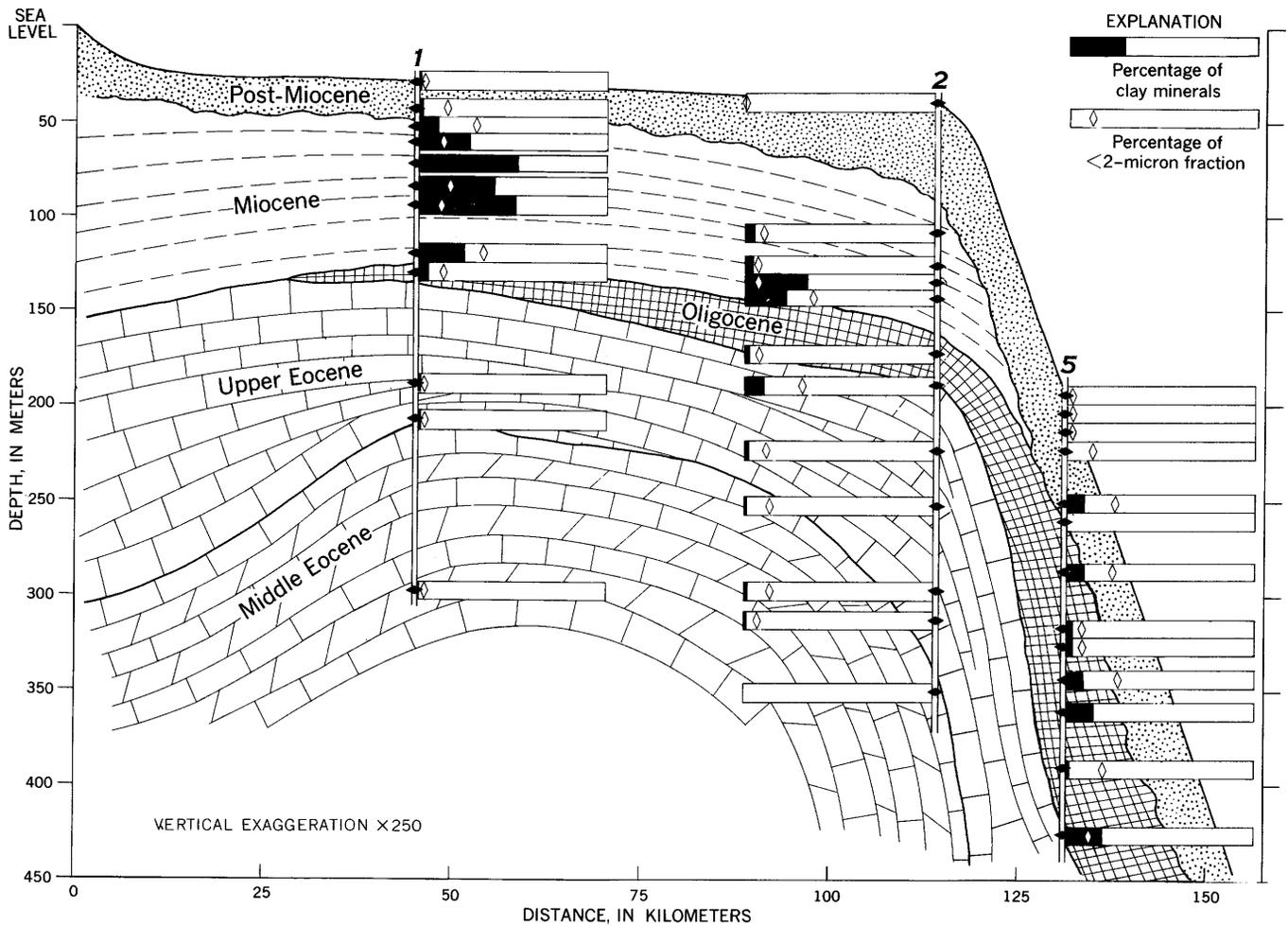


FIGURE 3.—Clay-size fraction and clay-mineral content of samples from the JOIDES drill cores.

Oligocene sample from hole 4, where it constitutes about 90 percent of the whole sample and is the only clay mineral that was detected in the sample. In none of the samples in which clay minerals were observed does it represent less than about 10 percent of the clay minerals present. The mean montmorillonite content of the clay-mineral fraction of these samples is about 60 percent.

Next in frequency of occurrence among the clay minerals is "illite."⁵ Its mean concentration in the clay-mineral fractions of the 43 samples in which it detected is about 10 percent; the maximum concentration of "illite" is about 20 percent.

⁵ The term "illite" is used in this paper to describe clay-size materials that give X-ray diffraction characteristics similar to those produced by minerals of the mica group but distinguished from the characteristics of coarser mica by relative asymmetry and diffuseness of the diffraction maxima. The usually quoted differences in potassium and water content between well-crystallized mica and illite do not enter as criteria, as no analyses were made of these constituents.

⁶ The names palygorskite and attapulgite are synonymous, but palygorskite is preferred by the authors because it has precedence (Fersman, 1913) over attapulgite (Lapparent, 1935).

Although kaolinite occurs in fewer samples than "illite," its concentration is usually greater. Kaolinite appears in 35 samples; in these, its mean concentration is about 30 percent of the clay-mineral fraction and its maximum concentration is about 60 percent. The larger amounts of kaolinite are confined to the upper parts of the three nearshore holes. Concentrations as large as about 40 percent of the clay-mineral fraction occur in samples as old as Oligocene from hole 5, whereas in the cores from holes 1 and 2 only Miocene and post-Miocene samples contain concentrations greater than 20 percent. In the cores from hole 3 on the Blake Plateau, nine of the 13 samples contain kaolinite; two Miocene samples contain about 30 percent kaolinite in the clay-mineral fraction.

Palygorskite⁶ and sepiolite appear in 17 samples and 11 samples respectively. All but two of the samples are Miocene. One Oligocene sample in hole 6

contains sepiolite, and one lower Eocene sample from hole 3 contains both palygorskite and sepiolite. The mean concentration of palygorskite in the palygorskite-bearing samples is about 25 percent of the clay-mineral fraction; the largest concentration is about 70 percent in a sample from the lower part of the Miocene of hole 1. The mean concentration of sepiolite is about 33 percent; the largest concentration, about 70 percent, is in a Miocene sample from hole 4. Sepiolite occurs with palygorskite in nine samples. In one sample the sepiolite is associated with the zeolite clinoptilolite.

Clinoptilolite was found in the clay fraction (less than 2-micron size) of 17 samples and phillipsite, in two samples. The zeolites appear principally in samples of Oligocene age or older, much as they do in the whole samples. The total amounts in the clay fraction are smaller, however, because of the tendency of the zeolites to occur as silt-size particles.

Although Weaver (1968) reported chlorite in some of the samples that he examined, none was observed in any of our samples. Its absence is noteworthy in view of the widespread occurrence of this mineral in marine sediments in general. Talc, also reported by Weaver (1968), was not observed in our samples.

AMORPHOUS MATERIAL

One Oligocene sample from hole 3 was selected for special mineralogical study at the time of re-

covery of the core because of the resemblance of the sample to volcanic ash. X-ray diffraction patterns showed this sample to be composed almost entirely of amorphous material. Examination under the petrographic microscope showed that the glassy-appearing grains were isotropic and that a few grains had shardlike surfaces. The index of refraction of the isotropic grains was 1.525. X-ray diffraction patterns of the insoluble residues of seven other samples showed amorphous material. Six of these samples are from the Oligocene, and one is from the middle Eocene. In most of these samples the amorphous constituent appears to be volcanic glass. Its concentration ranges from about 20 percent to more than 90 percent of the noncarbonate fraction.

MISCELLANEOUS MINERALS

Pyrite occurs in the insoluble residues of three Eocene samples from hole 1 and in one Oligocene and one Eocene sample from hole 5. It occurs only as trace amounts in whole samples, and its concentration does not exceed about 40 percent in the insoluble residues. Goethite was found in the insoluble residue of the surface sample from hole 4. This sample contained very little insoluble residue, so that any quantitative estimate is more uncertain than usual, but goethite appeared to constitute about 60 percent of the insoluble residue.

MINERALOGY OF THE CONSOLIDATED MATERIALS

Although many of the 33 samples of consolidated

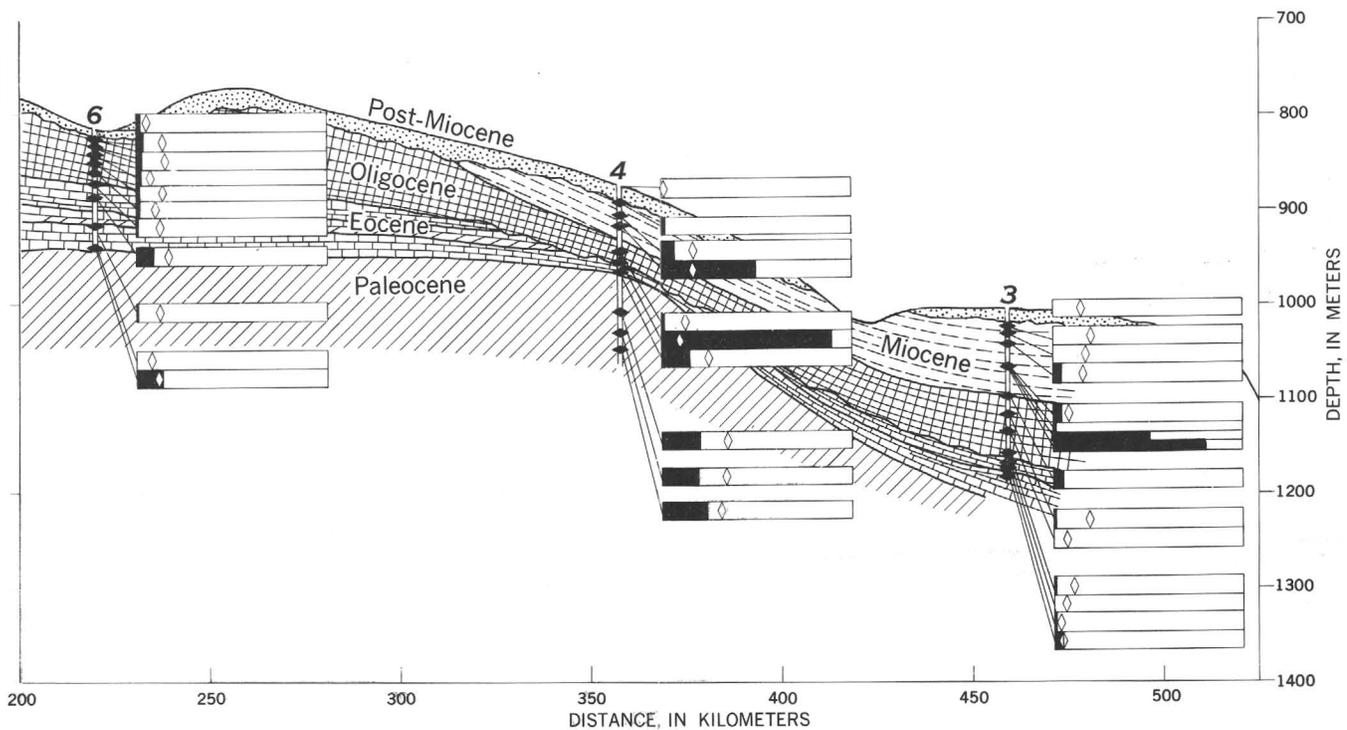
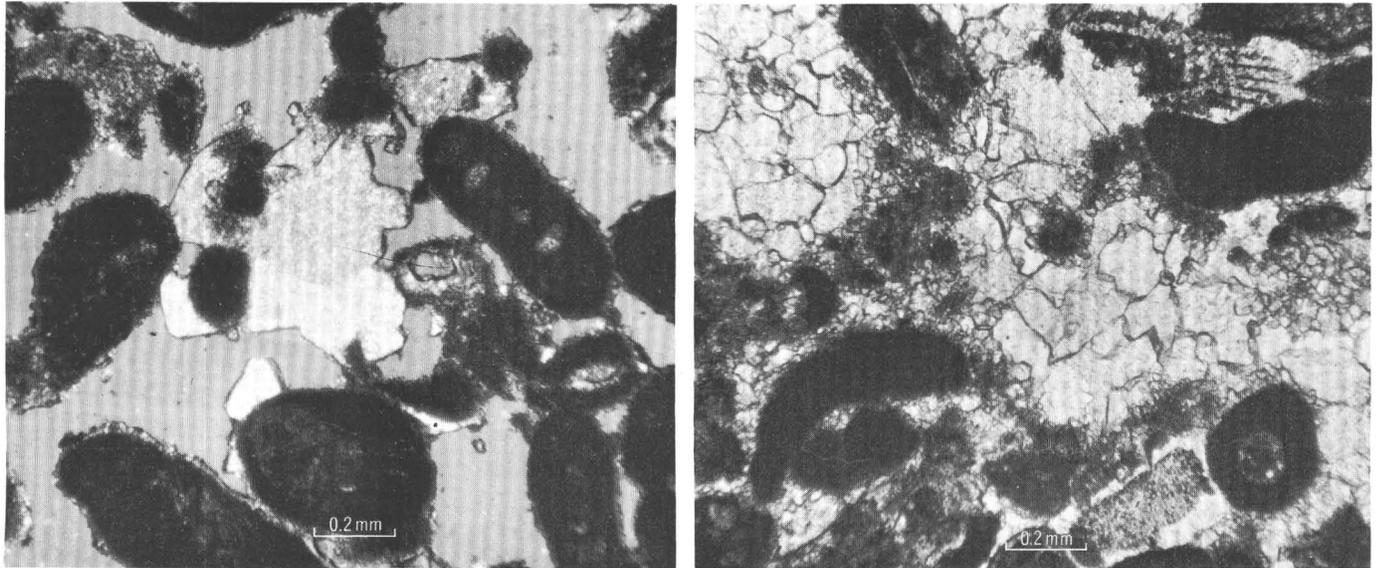


FIGURE 3.—Continued



A

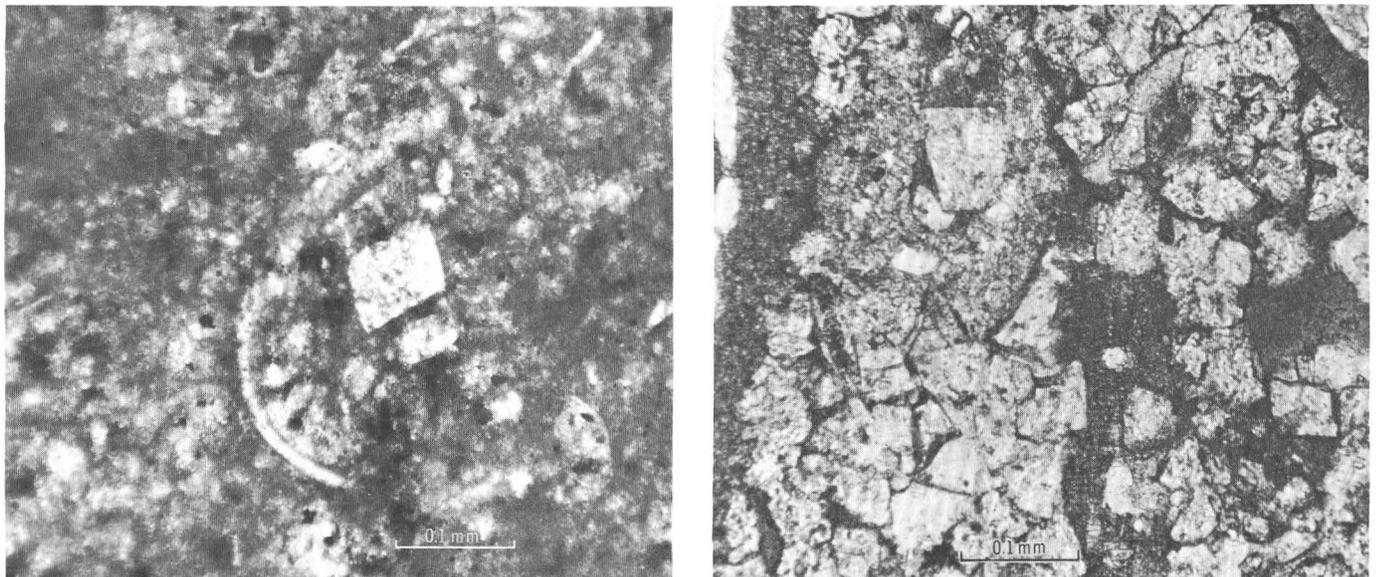
B

FIGURE 4.—Photomicrographs of thin sections showing cementation of foraminiferal sediment of middle Eocene age by calcite. *A*, Partial cementation, sample J-1-665, crossed polarizers with gypsum plate; gray areas are pore space. *B*, Thorough cementation, sample J-1-780, plain light.

or indurated materials superficially resemble cherts, none have the mineral composition of normal chert, namely, a predominance of microcrystalline quartz. Twelve of the samples contain disordered cristobalite that equals or exceeds quartz in abundance. Seventeen of the other samples are predominantly calcite,

three samples are predominantly calcium-rich dolomite, and one sample is composed principally of montmorillonite.

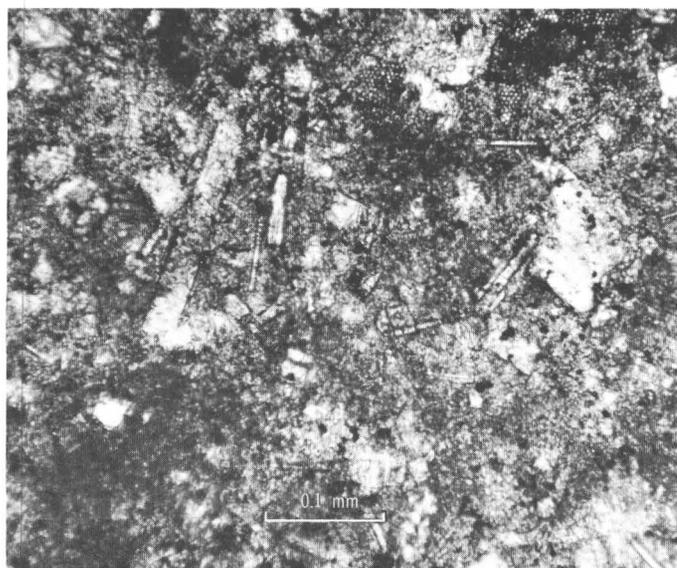
All samples that contain disordered cristobalite are from the three offshore holes, numbers 6, 4, and 3, and all are Paleocene or Eocene in age. In only



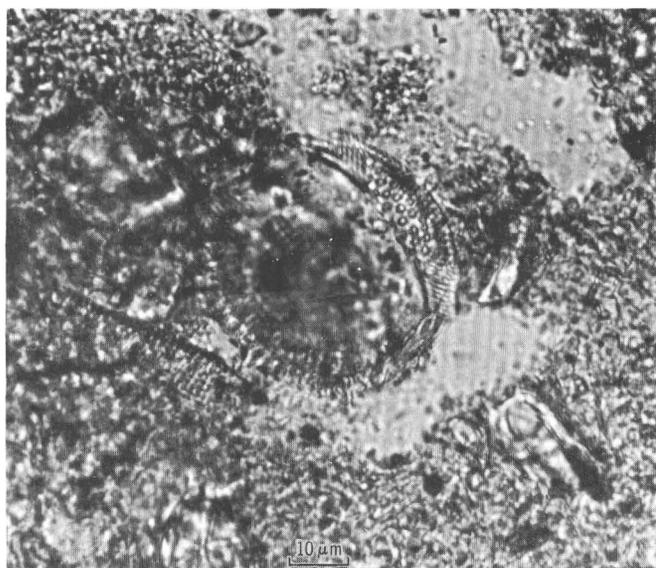
A

B

FIGURE 5.—Photomicrographs of thin sections showing dolomitization of limestones of Eocene age. *A*, Dolomite rhombs, sample J-2-775, plain light. *B*, Sample J-2-1010, plain light.



A



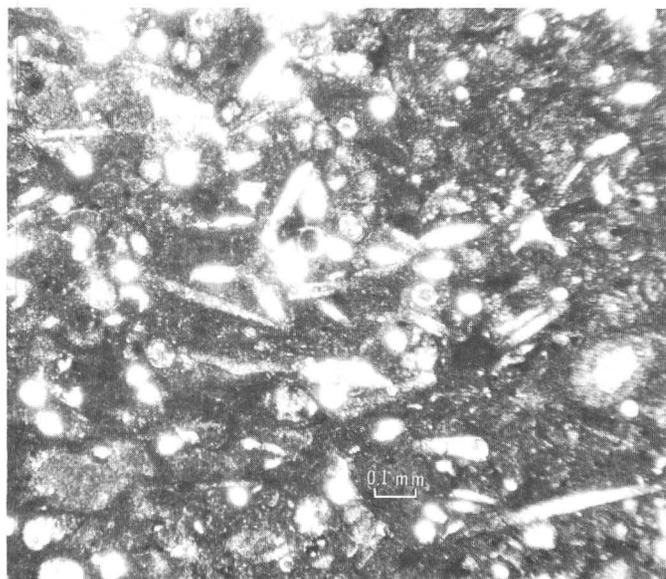
B

FIGURE 6.—Photomicrographs of thin sections showing siliceous organic remains in a limestone of Oligocene age. Sample J-5-318S, plain light. *A*, Sponge spicules and amorphous silica. *B*, Diatoms and amorphous silica.

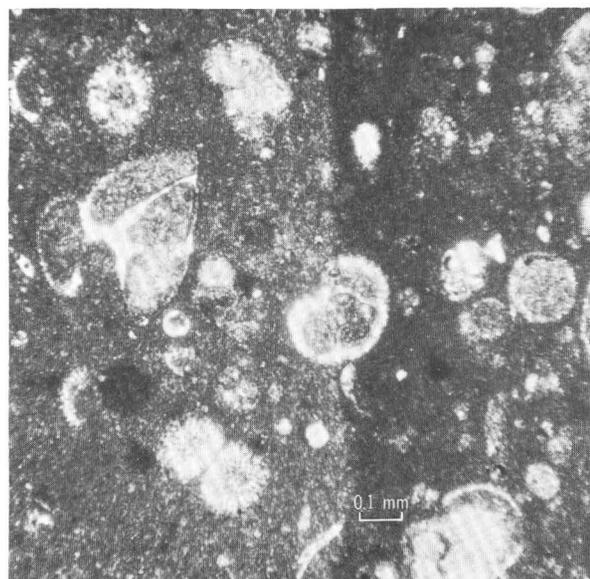
two consolidated samples from these holes is disordered cristobalite absent; one of these is the montmorillonite-rich sample of Oligocene age. The consolidated samples from holes 1, 2, and 5—the nearshore holes—contain no disordered cristobalite and seldom more than traces of quartz. Most of these

samples, however, contain at least traces of dolomite, whereas this mineral is absent in the consolidated samples from the offshore holes.

Thin sections of the samples show that much of the calcite is of biogenic origin. Figure 4 shows cementation by drusy calcite of middle Eocene



A



B

FIGURE 7.—Photomicrographs of thin sections showing silicification of sediments, plain light. *A*, Sponge spicules, Paleocene, recrystallized to quartz in matrix of disordered cristobalite, sample J-4-348. *B*, Calcareous mud, upper Eocene, replaced by silica (disordered cristobalite). Lighter colored side is replacement. About half of foraminifer in center is replaced, sample J-6-225.

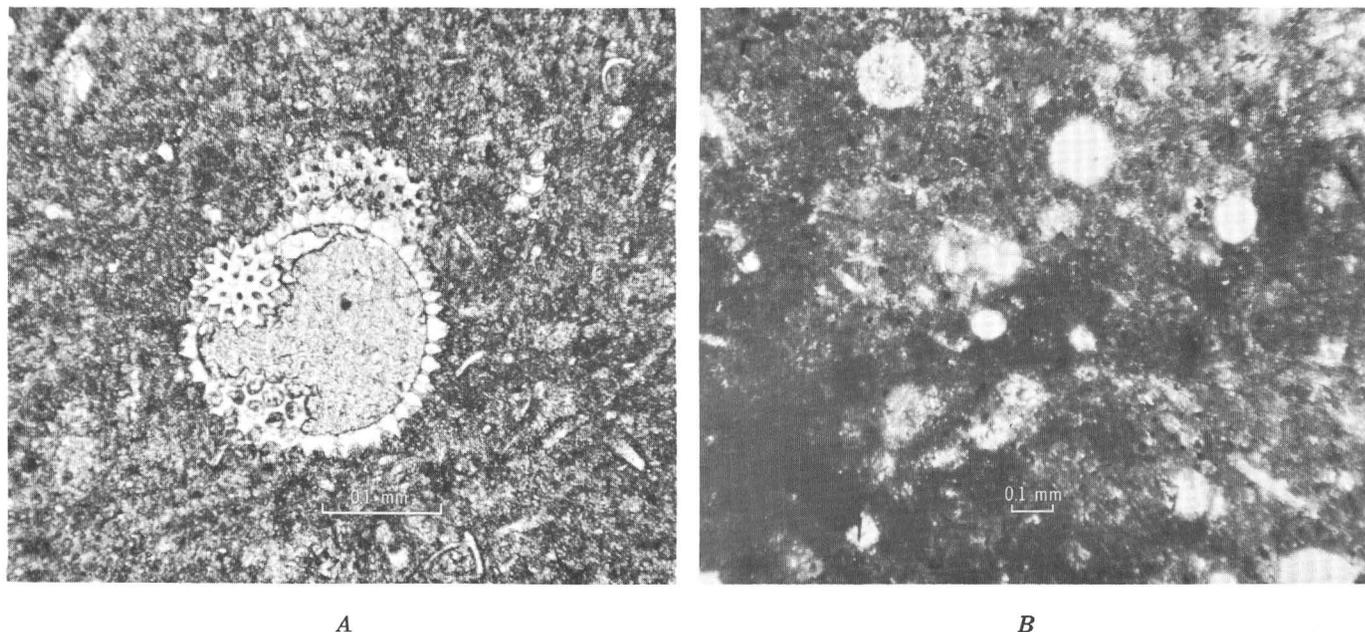


FIGURE 8.—Photomicrographs of thin sections of chert showing filling of foraminiferal chambers and replacement of foraminiferal tests by silica, plain light. *A*, Foraminiferal chambers filled with silica (disordered cristobalite), Paleocene, sample J-4-537H. *B*, Globular aggregates which may be Radiolaria or foraminiferal tests filled and replaced by silica (disordered cristobalite), Paleocene, sample J-4-517A.

foraminiferal sediment and the filling of pore space by sparry calcite. The uniform fine grain size of the foraminiferal particles suggests that recrystallization of the sediment took place before the start of cementation. The roundness of the individual grains and the absence of a matrix of carbonate mud in the interstices suggests reworking of the sediment or winnowing by relatively strong currents in the depositional environment. This type of lithification is not common to all the consolidated samples. Higher in the stratigraphic section, dolomite becomes an important constituent and may be responsible for some of the cementation (fig. 5). Many siliceous spicules and a few diatoms appear in samples from hole 5 (fig. 6). Some amorphous material accompanies the visible spicules and may account for some cementation of the samples, although in only one sample does the amorphous silica occur in sufficient quantity to be recognized in the X-ray diffractometer patterns.

Cementation by silica is clearly evident in consolidated samples from the Blake Plateau holes. There many of the spicules have recrystallized to quartz, and the silica matrix is in the form of disordered cristobalite rather than amorphous material. Figure 7 shows examples of recrystallization of spicules and replacement of calcite by silica. In figure 7B, a photomicrograph of the boundary of a chert

sample from the upper Eocene rocks from hole 6, the dark band on the calcium carbonate side of the boundary represents a zone bordering the chert. This zone resembles a watermark. It has the appearance of organic matter but its composition has not been determined. In some samples foraminiferal chambers are filled with silica. The globular aggregates observed in many of the samples may be Radiolaria or fillings of foraminiferal tests in which silica has recrystallized and replaced the original chamber walls (fig. 8).

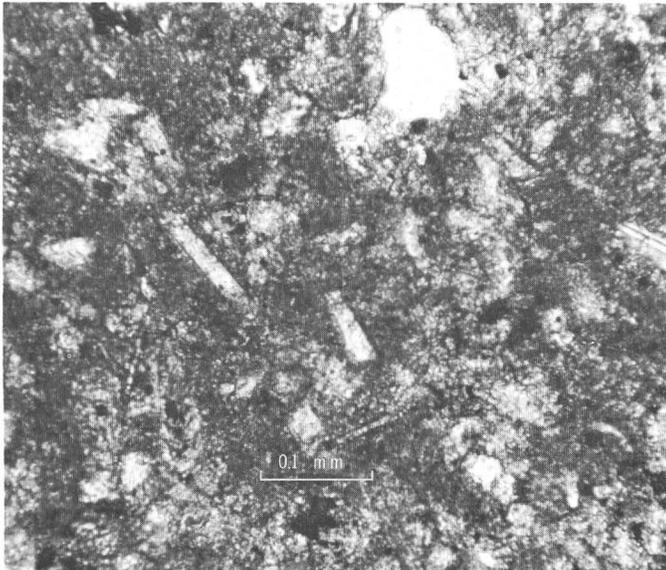
A few feldspar grains occur in some of the consolidated samples. Most are angular or nearly euhedral and are not accompanied by other minerals such as a quartz of similar grain size. Zeolites appear as lath-shaped particles both in the thin sections and in the unconsolidated samples (fig. 9). The laths of clinoptilolite range in length from about 4 microns to 100 microns. Phillipsite laths tend to be stubbier and to show pyramidal terminations on the laths (fig. 9C); the particle sizes of the phillipsite are similar to those of the clinoptilolite.

MINERALOGY OF THE SAND FRACTION

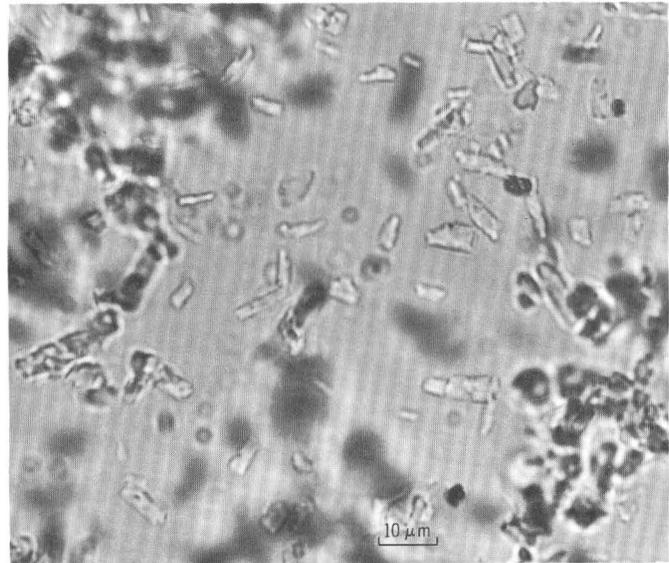
By DAVID A. ROSS

INTRODUCTION

The purpose of this section is to describe the general mineralogy of the sand fraction (2 mm to 0.062 mm) of 52 samples (table 3) from the unconsoli-



A



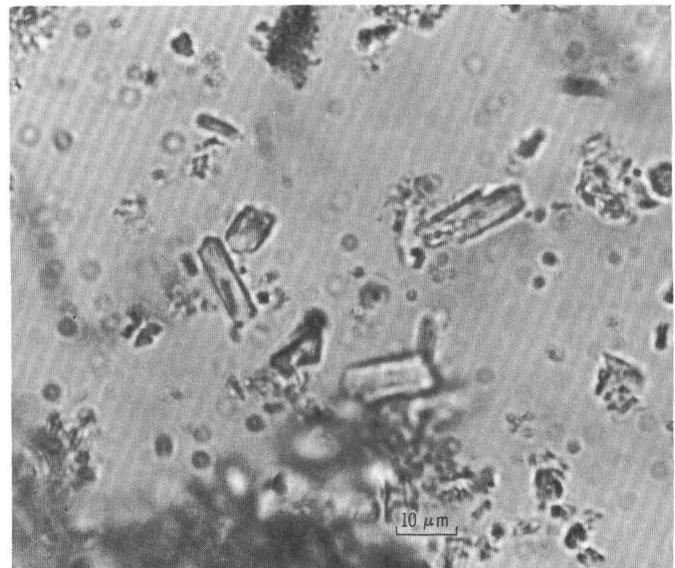
B

FIGURE 9.—Photomicrographs showing zeolites, plain light. A, Clinoptilolite in thin section, sample J-5-240. B, Clinoptilolite grains from unconsolidated sample, J-3-500. C, Phillipsite grains from unconsolidated sample, J-6-25. Note terminations on lath-shaped grains.

dated parts of the cores described in the preceding sections. Studies of the sand fraction can, in many cases, reveal important information concerning the depositional history and source of sediments. However, it should be remembered throughout this report that the sand fraction constitutes only a part, and sometimes a very small part, of the total sample.

METHODS

Sand-size material was separated from the total sample by wet sieving; in some cases disaggregation of the sample was aided by an ultrasonic vibrator. The sand was then dried and was separated, using bromoform (density 2.9 grams per cubic centimeter at 15°C), into heavy and light fractions. The light fraction after identification was treated in a 1:9 solution of hydrochloric acid to remove carbonate material. The resulting insoluble residue was examined under a binocular microscope, and where identification of light components was uncertain, X-ray diffraction techniques were used. Three hundred grains of the light fraction were counted using a line-counting method (table 3). A line count of



C

100 nonopaque grains was made using a petrographic microscope to determine the composition of the heavy minerals (table 4). The results of the analysis are presented as percentages by number, which determined by line counting, is an approximation to area or volume percent.

TABLE 3.—*Mineralogical and textural data from selected samples*

[Tr., trace; N.d., not determined. Other grains and fragments: P, phosphate; D, diatoms; M, mica; Gl, glauconite; Sp, sponge spicules; Pt, pteropods; Ag, aragonite oolites; R, Radiolaria; Ch, chert]

Sample	Quartz and feldspar grains	Rock fragments	Foraminifers	Carbonate fragments	Other grains and fragments	Terrigenous biogenous ratio	Weight Percent		
							Insoluble residue	Heavy minerals	Sand (percent)
J-1-0	81	3	Tr.	16		5.3	79.5	0.45	89.2
1-50	34	8	18	40	Tr.(P)	.7	42.6	.49	38.8
75	37	5	16	41	1(D), Tr.(M)	.7	49.2	.80	16.9
100	79	10	0	8	1(Gl), 1(M)	11.3	84.1	.34	56.1
204	59	19	6	5	5(Sp), 4(P), 1(Gl)	4.9	N.d.	<.01	
305	50	2	0	7	41(P)	1.1	39.8	.41	6.1
335	10	6	14	69	Tr.(Pt)	.2	12.7	.73	
590	3	Tr.	11	86		<.1	.4	.09	
895	2	0	Tr.	98		<.1	.4	<.01	22.1
2-0	66	4	0	17	13(Ag)	4.1	53.3	.16	97.9
223-254	27	9	36	28	Tr.(Gl)	.6	43.7	.48	24.0
290	20	2	63	15		.3	16.0	<.01	
438	7	1	31	59	1(R), Tr.(Pt)	.1	3.0	<.01	
494-504	18	2	19	58	2(D)	.3	12.3	<.01	6.3
602	2	Tr.	13	83	2(Pt)	<.1	.3	.12	32.3
845	4	0	2	94		<.1	2.0	<.01	13.2
3-0	0	0	27	73			.5	<.01	12.9
50	Tr.	0	81	19	Tr.(Pt)	<.1	<.01	<.01	11.3
100	Tr.	0	74	26		<.1	<.01	<.01	21.3
200	0	0	80	20			<.01	<.01	
300	3	0	37	60		<.1	<.01	<.01	
400	Tr.	Tr.	21	72	6(Sp), 1(R)	<.1	2.0	<.01	
500	5	Tr.	27	68		<.1	<.01	<.01	.7
527	1	0	74	25		<.1	<.01	<.01	
571	0	0	68	32			<.01	<.01	
4-0	1	Tr.	56	22	20(Pt), Tr.(R)	<.1	.2	<.01	85.3
60	Tr.	Tr.	58	31		<.1	1.2	<.01	31.7
101-120	1	Tr.	71	26	Tr.(D)	<.1	3.7	<.01	11.3
227-238	13	2	31	64	Tr.(Pt)	.2	7.1	.03	11.7
269	2	Tr.	77	20	Tr.(Sp)	<.1	3.2	<.01	6.9
438	1	Tr.	82	13	2(R), 1(Sp), Tr.(Pt)	<.1	4.2	<.01	2.5
501	2	1	53	43	Tr.(Sp, Pt, R)	<.1	18.2	<.01	.8
552	Tr.	Tr.	67	27	2(R), 2(Ch), Tr.(Sp)	<.1	51.4	<.01	.5
5-0	17	3	33	41	3(Sp), 2(Pt), Tr.(R)	.3	27.7	.13	58.8
35	13	5	5	75	2(Gl)	.2	19.1	.18	83.7
65	27	12	14	44	Tr.(R, D, Sp, P?)	.7	34.9	.48	56.8
100	13	Tr.	40	45	1(D), 1(Sp), Tr.(Pt)	.1	17.8	.08	32.7
201	19	0	53	26	1(Sp)	.2	9.6	<.01	6.8
310	22	2	20	38	4(Sp), 3(R)	.4	N.d.	<.01	1.2
438	4	0	12	84	Tr.(Pt, R)	<.1	2.0	<.01	
505	1	1	44	52	Tr.(D, R, Pt)	<.1	1.9	<.01	8.2
652	2	0	65	27	6(Sp), Tr.(Pt)	<.1	7.3	<.01	4.7
773	5	Tr.	58	36	1(R)	<.1	3.0	<.01	
6-0	0	Tr.	46	52	1(D)	<.1	.4	.32	79.7
25	4	Tr.	45	50	Tr.(D)	<.1	2.0	<.01	5.6
50	11	0	31	57	Tr.(R, D, Sp, Pt)	.1	6.0	<.01	1.5
100	3	0	30	54	7(R), 6(Sp)	<.1	10.0	<.01	1.7
158	1	1	77	30	Tr.(R)	<.1	N.d.	N.d.	
200	4	Tr.	66	30		<.1	6.2	.69	10.0
300	1	Tr.	79	19	Tr.(D, Gl)	<.1	1.4	<.01	20.4
388	2	Tr.	34	44	13(R), 4(Sp), 3(Ch)	<.1	34.4	<.01	

TABLE 4.—Heavy-mineral composition of selected samples
[Data given as percentages determined by number of grains counted]

Sample	Amphiboles	Epidote	Staurolite	Garnet	Zircon	Sillimanite	Titanite	Zoisite	Kyanite	Others
J-1-0	14	49	8	4	3	6	4	6	3	3
1-50	7	52	13	10	3	0	2	8	3	3
75	4	43	14	10	4	1	2	10	8	4
100	5	46	14	7	1	1	4	7	7	5
2-0	18	52	9	1	3	9	0	1	4	1
223-254	16	54	3	5	0	6	0	8	6	2
5-0	23	49	3	2	7	6	2	3	2	3
35	31	35	6	5	5	6	5	2	3	2
65	32	46	2	4	0	3	4	3	2	4
100	45	41	1	2	0	4	1	6	0	0

HEAVY FRACTION

Only 10 of the 52 samples had sufficient nonopaque heavy minerals for a meaningful quantitative analysis. These 10 samples were from the upper parts of the three nearshore holes (table 4). An epidote-staurolite suite is common for samples from hole 1, and an epidote-amphibole suite predominates in samples from holes 2 and 5. The 10 samples show relatively large values of the standard deviation around the mean (table 5). A chi test for homo-

Sampling and laboratory errors certainly constitute a considerable part of the variability.

Because the grain size of the analyzed samples was not determined, the effects of grain size are

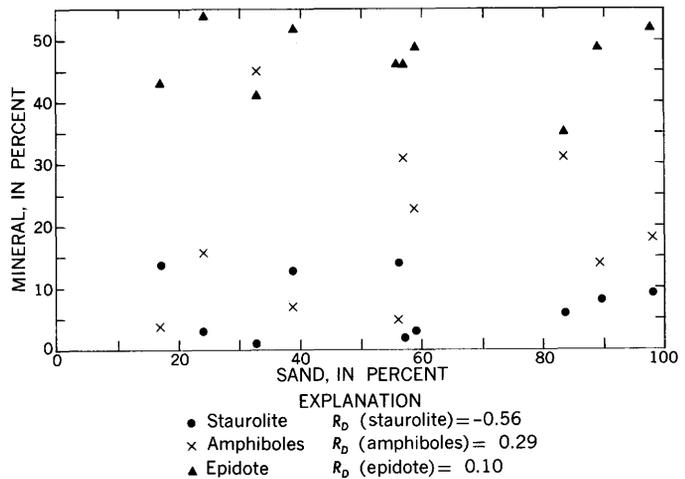


FIGURE 10.—Relationship of percentage of sand to percentage of amphiboles, epidote, and staurolite. R_D is the rank correlation coefficient. None of the correlations are significant (the hypothesis that the variables are independent is not rejected at the 0.10 significance level in any of the three cases).

TABLE 5.—Average composition, variability, degree of homogeneity, and level of significance of samples from holes 1, 2, and 5
[Mean composition (\bar{X}) data in boldface; standard deviation (σ) data in italic; χ^2 , degree of homogeneity; P , level of significance]

Hole	Amphiboles	Epidote	Staurolite	Garnet	Zircon	Sillimanite	Titanite	Zoisite	Kyanite	Others	χ^2	P	Number of Samples
1	7.5 <i>4.5</i>	47.5 <i>3.9</i>	12.3 <i>2.8</i>	7.8 <i>2.9</i>	2.8 <i>1.8</i>	2 <i>2.7</i>	3 <i>1.1</i>	7.8 <i>1.1</i>	5.3 <i>2.6</i>	3.8 <i>.9</i>	19.5	>0.250 <.100	4
2	17 <i>1.4</i>	5.3 <i>1.4</i>	6 <i>4.2</i>	3 <i>2.8</i>	1.5 <i>2.1</i>	7.5 <i>2.1</i>	0 <i>0</i>	4.5 <i>2.1</i>	5 <i>1.4</i>	1.5 <i>.7</i>	2.9	<.995	2
5	32.8 <i>9.1</i>	42.8 <i>6.1</i>	3 <i>2.1</i>	3.3 <i>1.5</i>	3 <i>3.5</i>	4.8 <i>1.5</i>	3 <i>1.8</i>	3.5 <i>1.7</i>	1.8 <i>1.3</i>	2.3 <i>1.7</i>	7.0	>.100	4
1, 2, and 5	19.5 <i>13.3</i>	46.7 <i>5.8</i>	7.3 <i>5.1</i>	5.0 <i>3.2</i>	2.6 <i>2.4</i>	3.4 <i>3.0</i>	2.3 <i>1.8</i>	5.4 <i>3.0</i>	3.8 <i>4.5</i>	2.7 <i>1.5</i>	155.6	>.001	10

geneity (Eisenhart, 1935) within selected groups shows that the variability within individual holes is considerably less than that of all the samples combined (the level of significance indicates the possibility of such a variation from homogeneity occurring).

Several reasons for sample variability are possible; they include sampling or laboratory errors, (Krumbein and Pettijohn, 1938, p. 470), mixing of different assemblages, effects of mineral size and sorting, and selective removal of unstable minerals.

unknown. The effect of size and sorting on mineral composition is generally insignificant (Van Andel, 1959). The quantities of epidote, amphiboles, and staurolite do not appear to be statistically dependent on the amount of sand present (fig. 10). The presence of several moderately unstable mineral species suggests that selective removal of unstable minerals is not an important process within these samples.

Because only 52 samples were taken over an interval of greater than 1,100 meters, it is difficult to make any detailed interpretations; however, some

general observations are evident. Only the upper parts of the three nearshore holes had sufficient quantities of heavy minerals for a meaningful quantitative determination. The weight percent of heavy minerals decreases generally with depth in each of the three nearshore holes. The heavy minerals, which constitute less than 1 percent by weight of the sand fraction of these samples, are mainly epidote, amphiboles, and staurolite. Similar assemblages have been found by Gorsline (1963) and Pilkey (1963) in surface sands of this area. The above assemblages can be considered moderately resistant (Krumbein and Pettijohn, 1938, p. 462; Pettijohn, 1957) and suggest igneous and metamorphic source rocks, probably the rocks of the southern Appalachians.

LIGHT FRACTION

Grains having a density of less than 2.9 g/cm³ dominated the sand fraction (table 3). Calcareous material, either foraminifers, pteropods, or undifferentiated carbonate fragments, was the most common constituent. Terrigenous detritus, quartz and feldspar (undifferentiated), and rock fragments are more common in samples from the upper parts of the three nearshore holes. In the samples from most of the holes, terrigenous material generally decreases and calcareous material increases with depth.

Glauconite occurred in five samples, four of which were from the three nearshore holes. Phosphate grains were found in three samples from hole 1. Their identification was confirmed by X-ray techniques. In one sample, J-1-305, phosphate as apatite constituted 41 percent (by grain count) of the sand fraction.

Foraminifers constitute a major part of the sand fraction in samples from the three offshore holes. The percentage of foraminifers is less in the Oligocene samples than in the older samples because carbonate fragments become the dominant constituent in the Oligocene sediments. Carbonate fragments are also generally more common in the post-Miocene samples.

Biogenous components other than foraminifers occur in most of the samples. Pteropods are found in about 30 percent of the samples; an especially large concentration occurs in the surface sample from hole 4. Diatoms occur in about 15 percent of the samples and are more common in samples from holes 5 and 6. Radiolarians also occur in about 15 percent of the samples, but, where present, they constitute a larger part of the sand fraction than diatoms. Sponge spicules occur in 30 percent of the samples; in several samples they constitute as much as 6 percent of the sand fraction. Aragonite oolites

were found in one sample, J-2-0, where they made up 13 percent of the sand fraction. X-ray patterns of crushed oolites showed both aragonite and quartz peaks, possibly suggesting a quartz nucleus surrounded by aragonite. This type of oolite has been found by Rusnak (1960) from a high-salinity lagoonal environment in Laguna Madre, Tex.

Chert fragments were found in two samples, J-4-552 and J-6-388, both in the Paleocene section.

INSOLUBLE RESIDUE

The light fraction, after identification, was digested in a 1:9 solution of hydrochloric acid. The remaining insoluble residue was weighed and examined. The composition of the insoluble residue generally agreed with that found from the light-fraction studies. The weight percent of insoluble residue and the "area" percent of noncalcareous material (determined by line counting) show fairly close agreement (fig. 11). Some of the causes of disagreement may be due to the presence of particles with differing density but similar sizes (for example, quartz grains and radiolarians) or very large grains which would only be counted once. The presence of many large chert grains may be the cause of disagreement in samples J-6-388 and J-4-552.

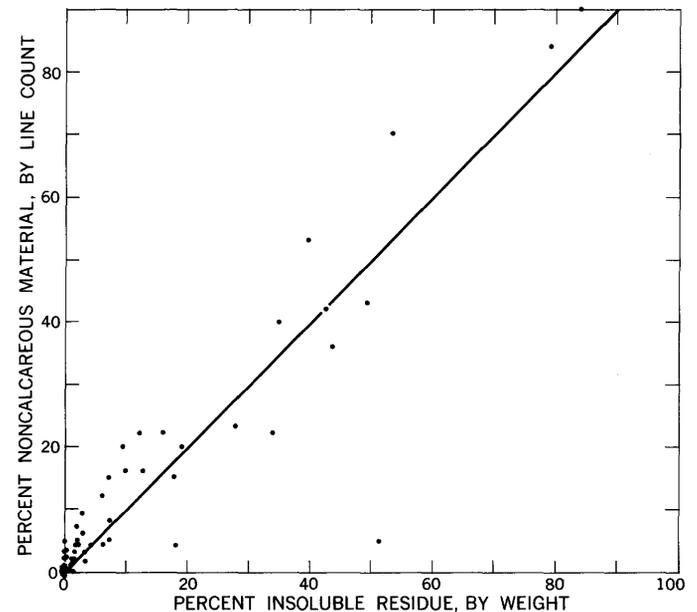


FIGURE 11.—Relationship of weight percent of insoluble residue and "area" percent of noncalcareous material as determined by line count.

DISCUSSION

The terrigenous component of the light fraction generally decreases with depth in each of the three

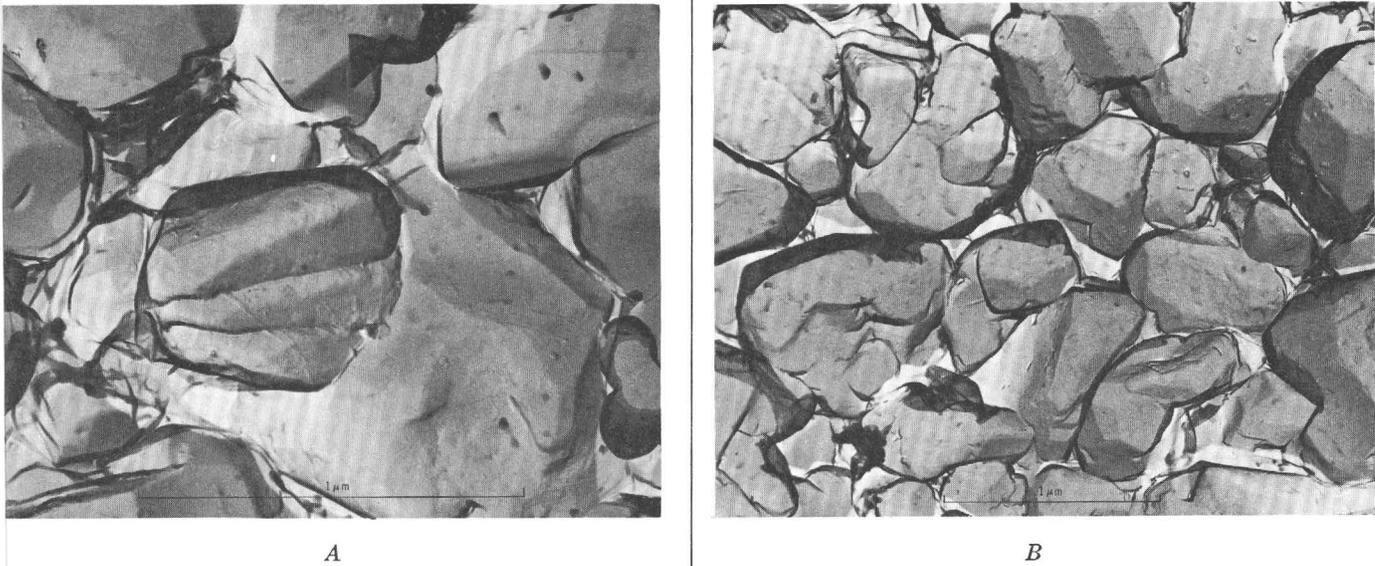


FIGURE 12.—Electron micrographs of platinum-shadowed carbon replicas showing stages in the recrystallization of coccolith fragments in samples from the lower Tertiary sediments of the Blake Plateau, sample J-3-527. Scale in micrometers (microns). *A*, Coccolith fragment. *B*, Calcite recrystallized from coccolith fragments.

nearshore holes. The biogenous fraction shows a corresponding increase. This suggests a change in the character of the sediment source in Miocene time. Whether this represents a decrease in the supply of land-derived material or increased biological productivity or both cannot be answered from these samples. Joint Oceanographic Institutions' Deep Earth Sampling Program (1965) has noted that the entire shelf section (holes 1 and 2) has benthonic foraminifers that are typical of shelf depths; this fact indicates crustal stability for the shelf area.

The sand fraction of the shelf sediments is chiefly a mixture of mostly quartz and feldspar, with smaller amounts of rock fragments, foraminifers, and carbonate material. Phosphorite is found in some of the Miocene samples. Aragonite pellets with an oolitic type of structure were found in the surface sample from hole 2.

The sand in the Blake Plateau sediments is dominantly carbonate fragments and foraminifers, with minor amounts of diatoms, sponge spicules, and radiolarians, and local concentrations of chert grains and pteropods. Little change takes place in these sediments with depth. Minor exceptions are chert grains found in the Paleocene sediments and relatively larger amounts of sponge spicules in the Oligocene. Nothing in the sand fraction from these Blake Plateau samples suggests that they were deposited in a water depth significantly different from that in which they are found.

ORIGIN OF THE SEDIMENTS

By JOHN C. HATHAWAY

LOWER TERTIARY SEDIMENTS

CARBONATE MINERALS

Most of the materials of Paleocene, Eocene, and Oligocene age that were penetrated during the drilling program are calcites of biogenic origin. Rocks of middle and late Eocene age under the shelf are similar to the Ocala Limestone and older units of the Eocene on land (Joint Oceanographic Institutions' Deep Earth Sampling Program, 1965). They differ mainly in the degree of sorting; the offshore materials contain more fine-grained interstitial material. The limestones under the shelf are composed largely of foraminiferal tests, algae, and coral debris. Beneath the Florida-Hatteras Slope the sediments are finer grained than those on the shelf. The sediments under the Blake Plateau are chiefly calcareous oozes composed of coccolithophorids and foraminiferal tests. Although these oozes are not consolidated, the individual particles of calcite have been recrystallized since the time of their deposition. Figure 12 shows a progressive transformation of coccolith fragments into calcite crystals in Paleocene and middle Eocene sediments. Why the mechanism of recrystallization has not progressed to the point of consolidation is not yet clear.

Aragonite is absent from all the samples of Oligocene and earlier age except those from hole 5, where it occurs throughout most of the Oligocene section.

Aragonite has been reported in fossils from rocks as old as the Paleozoic (Stehli, 1956; Yochelson and others, 1967), so that its persistence in Oligocene sediments is not surprising. Why aragonite should be absent from samples of similar age from the other holes becomes the question. The area of the shelf was undoubtedly exposed during times of lowered sea level during the Pleistocene. Thus, subaerial weathering and exposure to the circulation of fresh ground water may have resulted in the alteration of aragonite to calcite or the dissolution of aragonite in older sediments underlying the shelf.

Manheim (1967) demonstrated that fresh water permeates most of the sediments sampled in holes 1 and 2 and suggested that this water may discharge in depressions near the base of the Florida-Hatteras Slope. Such fresh-water circulation may account for the loss of aragonite, whether or not subaerial exposure took place. Manheim also suggested that fresh-water circulation may have extended much farther seaward under the Blake Plateau because of the higher relative hydraulic head that probably resulted from lower sea levels during the Pleistocene Epoch. However, a reason other than loss through groundwater action may account for the absence of aragonite in the sediments below the surface of the Blake Plateau. Aragonite occurs in the surface samples from holes 4 and 6 but not from hole 3. The principal, and probably the only, aragonite-bearing materials in the first two samples are petropod remains. These occur neither in the surface sample of hole 3 nor in any of the subsurface samples of all three Blake Plateau holes. Thus, the lack of aragonite may be explained simply by the absence of aragonite-secreting organisms in the environment of deposition of the Blake Plateau earlier than the Holocene.

Dolomite occurs in sediments of Eocene and Oligocene age from the three near-shore holes but not from the Blake Plateau holes. The concentration of dolomite is greatest in certain of the Eocene sediments from the two continental-shelf holes. The origin of dolomite has been a subject of much inquiry by geologists for many years, and a review of the many hypotheses for the origin of dolomite was given by Fairbridge (1957). The conclusion that dolomites are chiefly products of the replacement of limestones has been generally accepted since the work of Van Tuyl (1916), but the proposal of a workable theory that could account for the introduction of enough magnesium-bearing solutions of the proper composition to accomplish such replacement awaited the work of Adams and Rhodes (1960). Their paper presented a detailed mechanism whereby evaporation of

sea water in lagoonal environments produces dense brines with high magnesium-calcium ratios as the result of precipitation of calcium carbonate. The brines replace the underlying limestones with dolomite by seepage refluxion and provide a vehicle for the removal of the calcium thus released. The operation of such a mechanism in a present-day environment was demonstrated by Deffeyes, Lucia, and Weyl (1965) in a study of marine evaporite conditions in Bonaire in the Netherlands Antilles and recently by Bubb and Atwood (1968) in studies of artificial salt evaporation ponds in the Bahamas. Illing, Wells, and Taylor (1965) and Shinn, Ginsburg and Floyd (1965) found that dolomite can form penecontemporaneously in supratidal crusts by a similar mechanism. Lucia (1968) suggested that in an arid climate the cycle from marine to supratidal conditions is culminated by a period of reflux dolomitization and that thousands of feet of dolomite can be produced by a combination of cyclic tidal-flat sedimentation and reflux dolomitization.

The long-noted association of dolomites with evaporite sequences and with sediments of shallow-water lagoonal origin in much of the geologic column (Adams and Rhodes, 1960) and the evidence that evaporative enrichment of brines in magnesium indeed effects the replacement of calcium carbonate by dolomite suggest that dolomite forms principally in association with shallow-water lagoonal or supratidal environments.

The distance to which seepage refluxion can effect dolomitization is not known. Manheim (1967) has shown that fresh water originating on the Florida peninsula underlies the continental shelf and probably discharges on the Blake Plateau. The dense brines produced by seepage refluxion may be equally capable of migration and thus capable of dolomitization at considerable distance from the source of the brines. Migration of such brines may explain the occurrence of dolomite in the samples of Oligocene sediments from hole 5 on the Florida-Hatteras Slope, as these sediments are probably not lagoonal but slope deposits (Joint Oceanographic Institutions' Deep Earth Sampling Program, 1965). A detrital origin for the dolomite in the Oligocene samples is possible but unlikely because of the lack of shoreward increase in the amount of dolomite and the scarcity of other detrital minerals such as quartz.

Most of the Eocene sediments from the continental shelf formed in shallow water (Joint Oceanographic Institutions' Deep Earth Sampling Program, 1965); thus, episodes of supratidal or shallow lagoon evaporation might well have occurred. However, not

all dolomite-bearing samples of Eocene age are necessarily composed of shallow-water sediment. Sample J-1-525 of late Eocene age contains about 50 percent dolomite (table 1); it is composed of clear rhombs of dolomite of various sizes enclosed in a matrix of coccoliths and irregular calcite grains, 1-2 microns in diameter. Samples of similar fine-grained calcitic composition from the Blake Plateau holes contain no dolomite. This suggests that the origin of the dolomite is related not to the kind of sediment but to location. The dolomite was thus probably formed by the refluxion of dense brines formed under evaporative conditions that occurred on the shelf after, perhaps long after, the original deposition of the sediment. Absence of such conditions on the Blake Plateau prevented the formation of dolomite in that area.

VOLCANIC MATERIAL

The presence of as many as five volcanic ash beds as much as 10 cm thick (Joint Oceanographic Institutions' Deep Earth Sampling Program, 1965) and abundant montmorillonite strongly suggests that during the early Tertiary, volcanic material was the principal noncarbonate sediment deposited in the area. Clinoptilolite has commonly been observed as an alteration product of silicic volcanic ash (Deffeyes, 1959; Hathaway and Sachs, 1965), and montmorillonite is the principal clay mineral in bentonites, which result from the devitrification of volcanic ash (Ross and Hendricks, 1945; Grim, 1953, p. 361). No areas of volcanic activity during the early Tertiary near the area under study are known, but as the concentrations of the noncarbonate materials are very small in most samples (table 1) the source could have been at considerable distance. Ross (1955) has called attention to the widespread pyroclastic deposits of Tertiary age in the Gulf Coastal Plain and has suggested that these deposits might extend to Florida. Reynolds (1966) reports considerable α -cristobalite, clinoptilolite, heulandite, and montmorillonite, which, he concludes, formed by the alteration of volcanic material in the Paleocene and lower Eocene of Alabama. Similar minerals were found by Wermund and Moiola (1966) in the Meridian Sand Member of the Tallahatta Formation of Eocene age in Mississippi and Alabama. Eargle (1968) reported that indurated tuff or altered volcanic ash containing as much as 50 percent clinoptilolite and lesser amounts of opal and montmorillonite occur in the base of the Jackson Group sediments of Texas. The amount of clinoptilolite increases to the Southwest, and the amount of opal and montmorillonite decreases.

Volcanic ash is usually transported by winds. Although the surface winds of the present day in the area studied are generally easterly to southeasterly, the high-altitude winds are westerly (U.S. Weather Bureau, 1952); they could transport ash from either a Caribbean or a continental source to the west or southwest as far away as Texas or Mexico. There is no assurance that wind patterns during the early Tertiary were the same as those today; however, a considerable shift of the geographic pole would be required to alter wind directions in the upper levels of the troposphere, as these directions are similar over wide ranges of latitude. From whatever source, ash falls during times when winds were favorable produced beds such as those represented by sample J-3-360 or the montmorillonite of samples J-4-243 and J-4-251. Shallow waters and their accompanying strong currents and high production of biogenic material may have reworked, redistributed, and diluted pyroclastic material so that it is less easily recognizable in the nearshore deposits. In the deep-water areas, lack of disturbance and slow rates of carbonate deposition produced thin beds (Joint Oceanographic Institutions' Deep Earth Sampling Program, 1965) and allowed greater apparent concentrations of volcanic materials. This may explain why such materials were not observed in the lower Tertiary sediments of hole 1.

CHERT

One other type of material commonly observed in the Paleocene and Eocene was described by the Joint Oceanographic Institutions' Deep Earth Sampling Program (1965) as cryptocrystalline structureless to faintly laminated chert. These beds are composed dominantly of disordered cristobalite, the form of opal that shows some degree of crystallinity. Sponge spicules, recrystallized to quartz, constitute part of the silica in these cherts, but the opaline matrix must have entered the sediment as dissolved silica to have replaced the calcareous components (fig. 7) and to have filled interstices in the sediment.

Two principal sources for this type of silica are possible: (1) the dissolution, mobilization, and redeposition of biogenic siliceous material disseminated in the host sediment, or (2) the introduction of silica by the alteration or devitrification of volcanic ash either disseminated through the host sediment or in beds interstratified with the host sediment (Pettijohn, 1957; Cressman, 1962; Siever, 1962). Little direct evidence was observed for the first type of source. The absence of siliceous skeletal material in the surrounding sediment is inconclusive evidence, because any material dissolved and mobil-

ized would, of course, no longer be seen. Volcanic ash, on the other hand, is not composed exclusively of silica, and montmorillonite and zeolites result in many places from the alteration of volcanic ash. Silica in excess of that required to form such minerals appears in many occurrences as the disordered cristobalite form of opal.

In the insoluble residues of Paleocene samples from hole 4, disordered cristobalite and clinoptilolite bear a complementary relationship to one another; the other major constituent is montmorillonite. Microscopic examination of the sample containing the largest amount of disordered cristobalite revealed many irregular isotropic grains and some laths of clinoptilolite but no diatoms, Radiolaria, or sponge spicules. The amount of silica is insufficient to have cemented or replaced the sample to form chert, but such silica, released to solution by alteration of the volcanic ash, may have moved through the sediment to be localized and precipitated where favorable conditions existed to form chert.

The proximity of chert to material of volcanic origin does not in itself prove that the silica of the chert is derived directly from the volcanic material. Many authors (for example, Siever and Scott, 1963) have stated that markedly increased production of diatoms often follows volcanic-ash falls in the sea. Diatom frustules deposited in the sediment following the death of the plants lose their protective organic coating and begin to dissolve in the interstitial water of the sediment. Emery and Rittenberg (1952) and Siever, Beck, and Berner (1965) believe that the solution of diatoms accounts for the high dissolved-silica content, typically 50 ppm (parts per million) of interstitial water as opposed to the average of 2-4 ppm in sea water. Siever, Beck, and Berner (1965) pointed out that the dissolved-silica content of most of the interstitial water that they studied is close to the level of saturation with respect to amorphous silica at the normal temperature of the sediment. Thus, whether the immediate source of the dissolved silica is volcanic ash or biogenic material or a combination of both, the interstitial water readily receives as much silica as it can maintain in solution.

MECHANISM OF CHERT EMPLACEMENT

Emery and Rittenberg (1952) proposed a mechanism for chert deposition and replacement of calcium carbonate based on the observation that the solubility of silica decreases in the presence of some organic material. They suggested that silica is dissolved at depth in the sediment and moves toward the surface as water is expressed from the slowly

compacting sediment. Near the surface the dissolved silica encounters decaying organic matter, which would promote the deposition of silica, and low pH, which would promote the dissolution of calcite. This mechanism was shown in diagrammatic form by Siever (1962); his diagram is reproduced in figure 13.

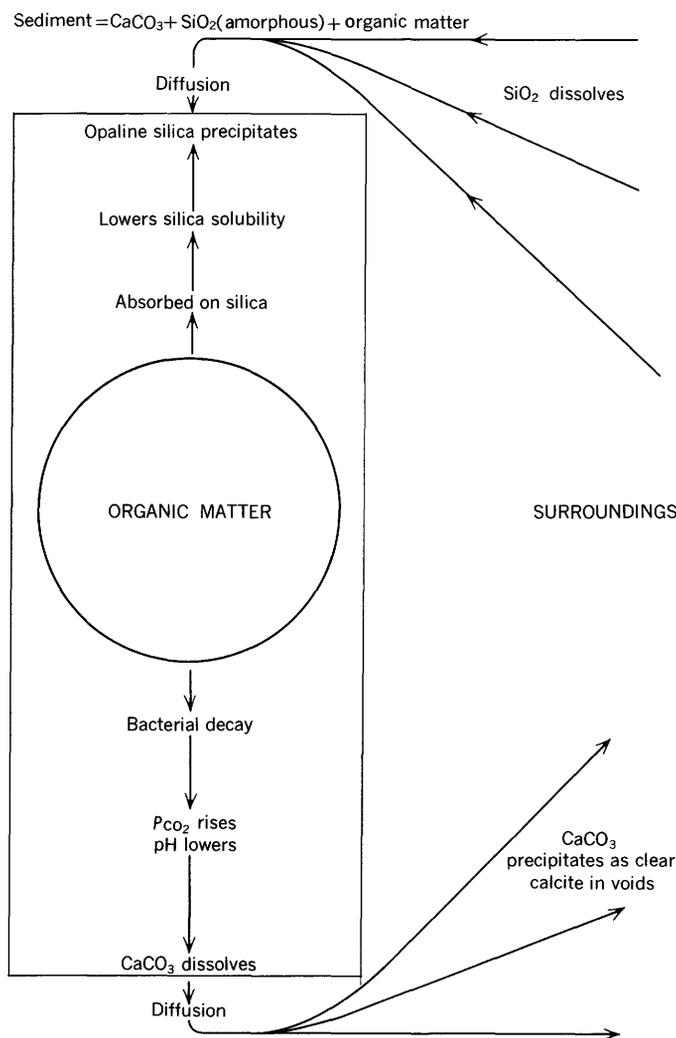


FIGURE 13.—Possible mechanism for the formation of chert in the presence of organic matter. (From Siever, 1962. Copyright by The University of Chicago Press.)

Siever noted that this mechanism would not account for postconsolidation nodules, because at this stage bacterial activity and oxidation of organic matter would have ceased. Furthermore, the localization of nodules would require local variations in pH, for which there was little evidence. Siever favored the concept that the flow of interstitial water through semipermeable beds accounts for the concentration of silica and the solution of calcium

carbonate. According to this concept, ionic strength increases below beds acting as semipermeable membranes as water expressed from the sediments by compaction moves upward. As ionic strength increases, the concentration of dissolved silica increases. Eventually the solution reaches supersaturation, and silica precipitates as chert. Unfortunately, as yet little field evidence exists that geologic materials behave as semipermeable membranes in this manner (Manheim and Horn, 1968).

The requirement in the mechanism proposed by Emery and Rittenberg that the organic matter be in the process of bacterial decay may not be necessary. Siever (1962) showed that the solubility of silica fell from about 140 ppm at 25°C to about 20 ppm at 25°C in the presence of filtered peat water at a pH of 5.2. Bacterial decay would not take place at this pH, although slight activity of actinomyces, microorganisms occupying a place between the bacteria and the fungi, would probably continue (Holger W. Jannasch, Woods Hole Oceanog. Inst., oral commun., June 1968). The organic structures in such materials are undoubtedly complex. Among them may be structures that absorb silica and lower the availability of silica to the solution much in the way that the structure of quartz apparently limits the availability of silica to the solution with which it is in contact by the absorption of an inhibiting surface cover of silicic acid (Stöber, 1967).

The dark band bordering the silica nodule shown in figure 7B may represent material that moved ahead as a front before the silicifying solutions, perhaps promoting the dissolution of the calcium carbonate. It may represent material expelled from the silicified part of the rock as gradual recrystallization of the silica took place.

Growth of the nodule probably stopped early in the history of the sediment, inasmuch as silica that has recrystallized to quartz is observed in the replaced foraminifer at the boundary of the nodule. Recrystallization to quartz is a slow process; it has not taken place in the samples of Oligocene age, nor in the matrix of the cherts of Paleocene or Eocene age, that were studied. If the growth of the nodule were a continuous process, a decrease in the amount of silica recrystallized to quartz from the interior toward the boundary of the nodule would be expected, and such a gradation was not observed; quartz is as prominent near the rim as in the interior.

It may be further speculated that the reason for the recrystallization of sponge spicules and radiolarians to quartz, where the matrix remains as disordered cristobalite, may be the relative freedom of

the undissolved siliceous skeletal material from included "foreign" material such as the very organic matter that promoted precipitation of the matrix. Any such included material may have retarded further ordering of the silica.

DETRITAL MATERIAL

Detrital minerals, other than pyroclastics, are scarce in the lower Tertiary sediments. Some montmorillonite, the small amounts of illite, and kaolinite are probably detrital. Examination of thin sections suggests that most of the quartz in these samples has recrystallized from opal. The rare feldspar grains are angular and almost euhedral and lack accompanying quartz grains. This suggests that such feldspar is of pyroclastic or authigenic rather than detrital origin.

Chen (1965) attributed the absence of detrital facies in the Eocene of Florida to the presence of the Suwannee channel crossing the area of northern Florida and southern Georgia. This channel provided a sediment trap that intercepted continental clastic material which otherwise would have been deposited on the Florida platform. This channel would have also isolated the region sampled by the drilling program. Whatever the reason, isolation continued through the Oligocene, as we observed little detrital material except in samples from the upper part of the Oligocene section from hole 5 on the Florida-Hatteras Slope. These samples contain considerably more kaolinite than samples from deeper in this hole or from rocks of Oligocene age from the other holes.

The distribution of clay minerals shown on plate 1 illustrates the similarity of the clay-mineral composition of the upper five samples of Oligocene age to the samples of post-Miocene age. The similarity extends to the mineral content of the whole samples as well. Aragonite, which is found only in post-Miocene samples from the other holes, occurs in five of the upper six samples of Oligocene age from hole 5. The possibility of contamination by material of post-Miocene age seems unlikely if the amounts of clay in the samples of Oligocene age are compared with the amounts available in the samples of post-Miocene age. For sample J-5-553 of Oligocene age to acquire its composition by contamination from material of the composition of sample J-5-201 of post-Miocene age would require about a 50 percent addition of the younger material to account for the amount of aragonite and over 100 percent addition of the younger material to account for the clay-mineral content.

The noncarbonate fraction of the upper four samples of Oligocene age contain as much as 50 percent amorphous silica. I have suggested in the discussion above that such material may indicate contribution

of volcanic ash to the sediments. Although montmorillonite would be the clay mineral usually expected from alteration of the volcanic ash, the possibility exists that this kaolinite also resulted from such alteration (Ross and others, 1929; Zen, 1959). That considerable kaolinite should occur in the clay fraction of the Oligocene sediments of hole 5 and not in sediments of like age in the other holes is puzzling, whether the kaolinite results from the alteration of volcanic ash or wash deposited as terrigenous detrital material.

MIOCENE SEDIMENTS

CARBONATE MINERALS

Calcite is the dominant carbonate mineral in Miocene sediments penetrated by the two Blake Plateau holes, 4 and 6. Here the source is fine biogenic planktonic debris, mostly foraminifers and coccoliths, similar to the source of the lower Tertiary sediments. Calcite is dominant in only a few Miocene samples from beneath the continental shelf; all but one of these samples are from hole 2. In these samples, the calcite is biogenic; foraminifers, both planktonic and benthonic, compose most of the material.

Aragonite occurs only in sample J-1-75, the only sample of Miocene sediment from hole 1 that contains calcite. This aragonite apparently occurs as fragments of very small pelecypod shells.

Dolomite is the dominant carbonate mineral in the rest of the Miocene samples from hole 1; here also are the largest concentrations of dolomite. Lesser concentrations occur in the samples from hole 2 and no dolomite occurs in the samples from the Blake Plateau holes except for a trace in the uppermost sample of Miocene sediment in hole 3.

As in the samples of Eocene sediments, the Miocene sediments from the near-shore holes also contain dolomite as clear euhedral rhombs of various sizes. The enclosing matrix differs from that of the older sediments in being composed dominantly of clay minerals rather than calcite. Seepage refluxion associated with a shallow lagoonal environment seems the most likely origin for the dolomite in the Miocene sediments. Such conditions may have been more prevalent during the early Miocene than later, inasmuch as dolomite is common in samples of the lower part of the Miocene section and scarce or absent in the upper part.

The single dolomite-bearing sample from the Blake Plateau, the uppermost sample of Miocene age from hole 3, presents a problem. If shallow-water evaporitic conditions were necessary for the formation of dolomite in this region, then this sample suggests the possibility that shallow-water conditions existed

at the outer edge of the Blake Plateau, now about 1,000 meters deep, during at least part of the Miocene or later. Unless other evidence were forthcoming, such an inference on the basis of one sample would be tenuous indeed; therefore, the possibility must be considered unlikely, and other explanations must be sought. The possibility of shipboard or laboratory mislabeling or contamination cannot be excluded, nor can the possibility of a detrital source. Delaney and others (1967) found dolomite in airborne dust collected at Barbados and traced this dolomite to African sources. Examination of deep-sea sediments downwind from these sources revealed small quantities of similar dolomite. Inasmuch as the sample from hole 3 contains only traces of dolomite, an airborne source remains a possibility; the few rhombs observed under the microscope were less than 10 microns in diameter. Waterborne detrital dolomite is unlikely as a source because of the lack of shoreward occurrences of dolomite on the plateau. Until other samples of dolomite are found in Blake Plateau sediments, the question of the origin of the dolomite in this sample must remain unanswered.

SILICATES

The noncarbonate minerals in the lower part of the Miocene section are chiefly clay minerals. In the upper part, clay minerals are less concentrated, and in samples from hole 1, quartz is the dominant mineral. Clay-mineral composition is variable; montmorillonite is the only clay mineral common to all the samples of Miocene sediments, although most contain palygorskite or sepiolite. Palygorskite is common in rocks of Miocene age in the southern Coastal Plain and is mined commercially in the Georgia-Florida State-line area (Buie and others, 1964). Both palygorskite and sepiolite have been reported in the Hawthorne Formation of Miocene age in Florida (Espenshade and Spencer, 1963; Reynolds and Goodell, 1963), Georgia (Germillon, 1965a), and South Carolina (Heron and Johnson, 1966). This paper thus extends the reported occurrences to the continental shelf and Blake Plateau areas. Sepiolite and palygorskite were also observed in some Eocene and Oligocene sediments from the Blake Plateau (pl. 1); thus, the stratigraphic range of these minerals in the southeastern United States is also extended.

Sedimentary occurrences of both palygorskite and sepiolite have been reported in rocks ranging from Carboniferous to Holocene age in other parts of the world (Rateyev and Kotelnikov, 1956; Keeling, 1956; Millot and others, 1960; Müller, 1961; Lucas and others, 1963; Bentor and others, 1963; Valiul-

lina, 1966; Siever and Kestner, 1967). Both minerals have been reported from still older rocks, but these occurrences usually represent secondary alteration or hydrothermal deposits rather than sedimentary deposits; most sedimentary occurrences of palygorskite and sepiolite are in rocks of Tertiary age. The origin of the sedimentary occurrences is not agreed upon by all investigators. Millot and his coworkers (Millot and others, 1957, 1963; Millot, 1962, 1967) favored neof ormation or authigenesis by the introduction into marine or nonmarine basins of silica derived from lateritic weathering of the source areas. Rateyev (1965) held that the formation of sepiolite requires high carbon concentration, high pH, and high SiO_2 activity or conditions associated with desiccating lakes in arid zones. Bartholomé (1966), on the other hand, proposed that the formation of sepiolite in Mesozoic and younger sediments is due to change in the oceanic geochemistry of silica brought on by increases in silica-secreting organisms.

Occurrences of sepiolite and palygorskite in both marine (Millot and others, 1957; Hathaway and Sachs, 1965; Siever and Kestner, 1967) and nonmarine (Bradley, 1930; Yarzhemskii, 1949; Millot and others, 1957; Regis, 1961) sediments indicate that either environment can be favorable for the formation of these minerals. Wollast, MacKenzie, and Bricker (1968) reported that sepiolite forms by the reaction of sea water and dissolved silica at room temperature and at a pH of 8.1, if the dissolved-silica concentration exceeds 26 ppm.

On the basis of such results, one might expect common occurrences of sepiolite in marine sediments wherever water enriched in dissolved silica entered the sea. However, MacKenzie, Garrels, Bricker, and Bickley (1967) showed that silicate minerals typical of those carried by streams to the sea exert control over the silica content of sea water by releasing silica to silica-deficient sea water and abstracting silica from silica-enriched sea water. Radiolarians and diatoms also extract and, through dissolution, release silica to sea water (Berger, 1968). The scarcity of suspended clay minerals and the presence of siliceous organisms in most ocean-surface waters probably explains the small amounts of dissolved silica (≈ 1 ppm) in many surface waters. Thus, silicate minerals at the ocean bottom would impose an upper limit (≈ 10 ppm) and biologic activity at the surface would impose a lower limit (≈ 1 ppm) on dissolved-silica content.

It is therefore unlikely that silica-enriched waters from streams draining areas of lateritic weathering

are responsible for the formation of sepiolite in the marine environment; the accompanying clay minerals would impose an upper limit to the silica content. It is also unlikely that Bartholomé's (1966) proposal is correct that increased populations of siliceous organisms were responsible for a change in the oceans' silica chemistry after Mesozoic time; these organisms would only impose lower values for dissolved silica.

A suitable source for a dissolved-silica content sufficient to form sepiolite may be volcanic ash of silica content in excess of that required to form montmorillonite. Such ash falling in water or settling to a sea floor deficient in detrital clay minerals could release silica upon alteration to montmorillonite. Reaction with the sea water, which contains the necessary magnesium (Wollast and others, 1968), would then result in the precipitation of sepiolite. Although no comparable experimental precipitation of palygorskite from sea water has been made, it might be speculated that alumina in excess of that required for the formation of montmorillonite might promote the formation of palygorskite. When the alumina was exhausted or absent, sepiolite would form.

All the Miocene sediments of the continental shelf are marine or are, at the least, shallow lagoonal. The Miocene sediments of the Blake Plateau are marine and were probably deposited at water depths similar to those of today (Joint Oceanographic Institutions' Deep Earth Sampling Program, 1965). Although some detrital minerals occur in Miocene sediments from the nearshore holes, such minerals are absent in the Miocene sediments of the Blake Plateau. A volcanic ash of suitable composition falling in this area thus would have the proper environment, under the hypothesis described above, to alter to palygorskite or sepiolite. Further evidence that volcanic ash was indeed the source of the palygorskite and sepiolite is suggested by the occurrence of these minerals with clinoptilolite in an Oligocene sediment in hole 6 and lower Eocene and Oligocene sediments in hole 3. A volcanic-ash origin for sepiolite and clinoptilolite from the Mid-Atlantic Ridge was inferred by Hathaway and Sachs (1965).

Gremillion (1965a, b) concluded that the palygorskite and sepiolite of the Miocene sediments of Florida, Georgia, and South Carolina formed from the alteration of volcanic ash in a nearshore marine environment. He cites southern Texas as the location of the volcanic activity that produced the ash, but the actual location of volcanoes is not known. The Miocene sediments of the continental shelf and

the Blake Plateau are equivalent to those studied by Gremillion and probably had the same source. Gremillion (1965a) cited the work of Bailey (1926) and Plummer (1932) on the importance of pyroclastic material in the Catahoula Tuff of Texas. Murray (1961) correlated this group with much of the Miocene section that includes the Tampa and the Hawthorn Formations, the units in the southeastern United States that contain much palygorskite and sepiolite. In south Texas, the Catahoula Tuff reaches a thickness of about 850 feet, of which about 500 feet represents pyroclastic material. The formation extends through Louisiana. Perhaps because of alteration, the pyroclastic origin of this group has not been readily recognized in Mississippi and Alabama.

Beneath the continental shelf, the Miocene is about 300 feet thick. Of this, less than about 30 percent or the equivalent of 90 feet probably represents material of volcanic origin. The rest is principally biogenic material and dolomitized limestone. Beneath the Blake Plateau, the Miocene section reaches a thickness of about 300 feet, but only a small fraction of this thickness represents non-biogenic material, considerably less than on the shelf. The large difference may be explained by the lagoonal trapping of sediment discussed under detrital minerals below. The wind directions in the upper troposphere would be conducive to the transport of fine-grained ash in an easterly direction (see discussion of lower Tertiary sediments above), and fractionation by composition because of differing physical characteristics of the glassy fragments may have been responsible for variations in mineralogic composition along the path of the fallout. Such composition differences may account for the occurrence of phillipsite in one sample of Miocene sediment from hole 4 and the lack of it in others.

PHOSPHATES

Phosphates occur mainly in sediments of Miocene age from the continental shelf, although small amounts of phosphate were detected in chemical analyses of the Miocene sediments from the Blake Plateau holes (F. T. Manheim, U.S. Geol. Survey, oral commun., June 1968). The two samples of post-Miocene materials that contain phosphate are near the lower boundary of the post-Miocene sediments, and the phosphate that they contain may well be derived from the reworking of Miocene material. The phosphate mineral in all samples is apatite, probably carbonate fluorapatite (francolite) and is probably of the same origin as the extensive phosphates of the Florida peninsula and the Coastal Plain

of the southeastern United States. What this origin may be is still a matter of controversy. McConnell (1965, 1966) favored the possibility of precipitation catalyzed by nektonic or planktonic organisms as a source of marine phosphorite, whereas Pevear (1966, 1967) favored inorganic replacement of limestone by phosphate ions in sea water as the only reasonable mechanism for phosphorite formation. McKelvey (1967) favored interstitial accretion of phosphate rather than replacement. Rooney and Keer (1967) proposed a combination of replacement and chemical precipitation for the phosphate pellets from the Miocene of North Carolina. F. T. Manheim and R. M. Pratt (unpub. data) found that replacement of carbonate sediments is the chief if not the only origin of the phosphate pavement (Pratt and McFarlin, 1966) area of the Blake Plateau.

No evidence that indicates the origin of the phosphorite was found in this study. If the origin is replacement of calcite or dolomite, such replacement probably occurred in a shallow-water evaporitic lagoon. δO^{18} values of +2.9 for dolomite and +3.2 for calcite from sample J-5-220 (Egon T. Degens, Woods Hole Oceanog. Inst., oral commun. Aug. 1968) and the occurrence of gypsum both suggest evaporitic conditions. The common occurrence of dolomite in the Miocene sediments also suggests shallow lagoonal environments conducive to reflux dolomitization. Volcanic material probably provided the source of the clay minerals accompanying the phosphorites, but no evidence suggests that volcanic ash falls promoted the formation of the phosphorite by causing the death of biological material and the subsequent release of phosphate in these materials, as proposed by Rooney and Kerr (1967) for Miocene phosphorites of North Carolina.

DETRITAL MATERIAL

Detrital quartz and feldspar, scarce in the lower Tertiary sediments, increase markedly in the Miocene sediments of the continental shelf, but not in those of the Blake Plateau. The closure of the Suwannee Channel (Chen, 1965) and the possible rise of the southern Appalachian landmass may have permitted river transport of terrigenous material to lagoons occupying the area of the continental shelf. These lagoons may have acted as sediment traps, preventing the transport of this detrital material beyond the shelf edge and thus accounting for the scarcity of detrital material on the Blake Plateau. The relatively high clay content of the Miocene continental-shelf sediments is probably the result of trapping of both detrital clay and volcanic ash that fell directly in the lagoons and later altered to clay.

Much of the detrital clay may have originated through the alteration of volcanic ash that fell on land. This inference is drawn from the high montmorillonite content relative to kaolinite, the clay mineral that would be expected if most of the detrital clay were derived from eroded soil.

It is unlikely that any of the sepiolite or palygorskite is detrital. Gremillion (1965a) pointed out the sensitivity of palygorskite to weathering, and Reynolds and Goodell (1963) observed that, in places where the Hawthorn Formation is overlain by permeable strata, sepiolite is absent, and small amounts of kaolinite appear.

POST-MIOCENE SEDIMENTS CARBONATE MINERALS

In most of the post-Miocene sediments studied, aragonite and magnesian calcite were significantly more abundant than in older rocks. The surface sample of hole 3 is an exception, as it contains only calcite. As discussed above in the section on lower Tertiary sediments, one explanation is the presence of aragonitic pteropods in the surface samples from holes 4 and 6 and their absence in the sample from hole 3. Aragonite in the post-Miocene sediments from holes 1, 2, and 5 occurs in the shells of both pteropods and small pelecypods. Pelecypods and gastropods other than pteropods are the dominant source of aragonite in samples from holes 1 and 2 and from near the surface in hole 5. Magnesian calcite probably occurs in tests of benthic foraminifers in holes 1, 2, 4, 5, and 6. Calcite occurs principally in pelecypods and their fragments near the shore. Coccolithophorids and planktonic foraminifers become the dominant source of calcite as the distance from shore increases.

Dolomite was observed in two samples dated as post-Miocene. Both samples also contain apatite and were obtained from parts of the cores close to the lower boundary of the post-Miocene sediments. The considerable reworking of Miocene sediments noted by F. T. Manheim and R. M. Pratt (unpub. data) nearby on the Blake Plateau and the disconformable contact of the post-Miocene with the subjacent sediments (Joint Oceanographic Institutions' Deep Earth Sampling Program, 1965) suggests that both the dolomite and apatite are reworked Miocene materials.

DETRITAL MATERIAL

Quartz is the major detrital mineral in the post-Miocene sediments; feldspar and clay minerals occur only in traces. The amount of detrital quartz is larger in the surface samples from hole 1 than in any other sample obtained from the cores. A smaller quantity occurs in the surface sample from hole 2, but on the

Florida-Hatteras Slope and on the Blake Plateau, detrital quartz is a trace constituent. The positions of the drill holes are south of the area of discharge of the larger rivers of the southeastern Coastal Plain and, even in the vicinity of these rivers, most of the surficial sediment is relict Pleistocene material (Emery, 1967, 1968). Thus, the large concentration of quartz sand in the surface samples of the continental shelf holes is probably due to reworking of the post-Miocene shelf sediments during regression and transgression of the sea during the Pleistocene, rather than to increased influx of terrigenous material during the Holocene. The relatively soft carbonate component of sediments would have been broken up and winnowed out, leaving the more resistant quartz sand as the surf line moved across the shelf. This mechanism may also explain why feldspar is less abundant relative to quartz in the post-Miocene sediments than in the Miocene sediments.

SUMMARY AND CONCLUSIONS

The minerals that compose the sediments of the continental margin off northern Florida are chiefly carbonates of biogenic origin. Calcite is most abundant; aragonite is common only in post-Miocene sediments. Volcanic ash probably contributed most of the noncarbonate minerals. Clay minerals, chiefly montmorillonites, are abundant only in the Miocene sediments, and here they probably formed mainly from volcanic ash. Palygorskite and sepiolite are present principally in the Miocene, but their occurrence in sediments of earlier Tertiary age and on both the Blake Plateau and continental shelf indicates that they formed in a variety of environments. This variety and the association of these minerals with the zeolite clinoptilolite in some samples suggests volcanic ash as the parent material. The occurrence of palygorskite and sepiolite in the seaward parts of the Blake Plateau in association with deep-water sediments suggests that these minerals formed in normal sea water. The composition of the parent material rather than the environment of deposition governed the clay-mineral phases that formed.

Consolidation of the sediments took place in samples from the Blake Plateau in most cases only by the formation of opaline chert. Recrystallization of coccolith fragments is common in the samples from the Blake Plateau, but such recrystallization has usually failed to progress to the point of consolidation. Cementation of biogenic carbonate debris has caused consolidation of some sediments of the continental shelf. Such cementation probably resulted from the influx of fresh artesian ground water from the Florida peninsula. Dolomitization and phosphati-

zation also consolidated some of the rocks of the shelf. The dolomite probably replaced calcite during the refluxing of dense brines from evaporative lagoons in the area of the shelf. The phosphate, limited mainly to the Miocene sediments, probably replaced carbonate minerals also, but its origin is less clear.

Terrigenous detrital materials form only a minor part of the sediments of the area. Their relatively high concentration in the post-Miocene surface sediments of the shelf is probably due to reworking and winnowing during Pleistocene regressions and transgressions of the sea.

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