Environment of Calcium Carbonate Deposition West of Andros Island Bahamas

---

GEOLOGICAL SURVEY PROFESSIONAL PAPER 350

U.S. DEPARTMENT OF THE INTERIOR
March 3, 1849

Environment of Calcium Carbonate Deposition West of Andros Island Bahamas

By PRESTON E. CLOUD, JR.

With sections on Mechanical Characteristics of the Sediments, *by* Paul D. Blackmon; Microbiology and Biochemistry of Sediments and Overlying Water, *by* Frederick D. Sisler; Chemical Analyses of the Water, *by* Henry Kramer; The Problem of Calcium Determination in Sea Water, *by* James H. Carpenter; Experimental Consolidation of Calcium Carbonate Sediment, *by* Eugene C. Robertson, Lynn R. Sykes, and Marcia Newell

GEOLOGICAL SURVEY PROFESSIONAL PAPER 350

A study of the sediments, waters, general ecology, precipitation mechanisms, and early diagenesis in an environment considered comparable to those in which some ancient aphanitic and pelletal limestones originated

U.S. DEPARTMENT OF THE INTERIOR
March 3, 1849

UNITED STATES GOVERNMENT PRINTING OFFICE, WASHINGTON : 1962

UNITED STATES DEPARTMENT OF THE INTERIOR

STEWART L. UDALL, *Secretary*

GEOLOGICAL SURVEY

Thomas B. Nolan, *Director*

The U.S. Geological Survey Library has cataloged this publication as follows:

Cloud, Preston Ercelle, 1912–

Environment of calcium carbonate deposition west of Andros Island, Bahamas. With sections on Mechanical characteristics of the sediments, by Paul D. Blackmon; Microbiology and biochemistry of sediments and overlying water, by Frederick D. Sisler; Chemical analyses of the water, by Henry Kramer; The problem on calcium determination in sea water, by James H. Carpenter; Experimental consolidation of calcium carbonate sediment, by Eugene C. Robertson, Lynn R. Sykes and Marcia Newell. Washington, U.S. Govt. Print. Off., 1961.

Cloud, Preston Ercelle, 1912– Environment of calcium carbonate deposition west of Andros Island, Bahamas. 1961. (Card 2)

vi, 138 p. illus., map, diagrs., tables. 29 cm. (U.S. Geological Survey. Professional paper 350)

Bibliography: p. 126–131.)

1. Calcium carbonate. 2. Sedimentation and deposition—Andros (Island) 3. Sedimentation and deposition—Bahamas. I. Title. II. Title: Calcium carbonate deposition west of Andros Island, Bahamas. (Series)

For sale by the Superintendent of Documents, U.S. Government Printing Office
Washington 25, D.C. - Price $1.50 (paper cover)

CONTENTS

ILLUSTRATIONS

[Plates 1-10 follow index]

TABLES

ENVIRONMENT OF CALCIUM CARBONATE DEPOSITION WEST OF ANDROS ISLAND, BAHAMAS

By Preston E. Cloud, Jr.

ABSTRACT

Recent calcareous sediments west of Andros Island resemble those from which some widespread aphanitic and pelletal limestones were formed in the past. These limemuds and pelletal limesands are accumulating beneath subtropical water of salinity averaging greater than 39 parts per thousand and rising locally to 46 parts per thousand over 13,000 square kilometers (5,000 sq mi) of shallow banks in the lee of this 170-kilometer-long island-complex. Opposing surface currents that flow around the island and from the Straits of Florida retard exchange between bank and ocean waters, and a high rate of evaporation brings about unusual concentrations of the dissolved solids. Increasing salinity, in combination with elevated temperature and other factors, facilitates a high rate of calcium carbonate withdrawal. Sufficient residual current remains moreover, to insure renewal of bank water at a rate permitting continued, seasonally accelerated, loss of $CaCO_3$ without introducing subsequent evaporation products, Effects are especially marked in the northern half of the area, where a prong of hypersaline water persists between opposing masses of more normal water to the northeast and southwest. Here the ratios to chloride of calcium and alkalinity (reflecting CO_3^{--} concentration) fall with increasing salinity across the bank toward Andros Island. This concurrent loss of Ca^{++} and CO_3^{--} ions, in nearly equal combining ratios and under essentially uniform and normal pH and Eh (8.1 and +0.35 volts), signifies local withdrawal of calcium carbonate for local reasons. It does not, however, identify the mechanics by which this withdrawal takes place.

Average size distribution of sediments beneath this water is about 40 percent clay, 14 percent silt, and 46 percent sand. Clay minerals and quartz are rare, and the terms clay, silt, and sand here refer to grain size only. About half the sand fraction is ovoid fecal pellets of calcium carbonate with average diameters of 0.2 by 0.5 mm; the other half is divided between skeletal calcium carbonate and miscellaneous aggregates of fecal and skeletal origin. These pelletal aragonite muds and muddy pelletal limesands grade locally to nearly pure limemuds and pellet sands. Genuine, concentrically laminated ooids were identified at only one site, although many pellets have a hard, polished surface. Water averages 64 percent by volume of the upper 60 cm of fresh, wet pelletal limemud. Specific gravity of the oven-dried whole sediment averages 2.78, fresh wet mud 1.66.

Analyses by Blackmon reveal that more than 95 percent of the clay fraction and more than half the silt consists of needles and laths of aragonite a few microns long, or of aggregates of such needles. Only 6 to 12 percent of the total sediment is calcite. Magnesium content of the calcite is either high (11–19 mole percent) or low (0–5 mole percent). Low-magnesian calcite is most abundant toward shore and in bottom core samples that reached bedrock. High-magnesian calcite increases offshore and is probably all skeletal. In the sediments from the Straits of Florida both total magnesium and total calcite increase westward toward Florida, owing to the more numerous calcitic tests of plankton in that direction. The magnesium is apparently all in solid solution—no dolomite was found in either bank or straits sediments. Silica amounts to less than 1 percent of the total bank sediment. It tends to vary parallel to low-magnesian calcite. The commonest clay minerals of both bank and straits are kaolinite and hydrous mica ("illite"). Chlorite occurs persistently but in trivial quantity in the bank sediments; none was found, however, in sediments from the Straits of Florida. Montmorillonite is abundant in the straits, mainly filling the tests of Foraminifera, and therefore presumably authigenic, but it was not found on the banks.

Although the biotas are not very diverse, the total biomass and variety is greater than has generally been reported, especially that part of it which remains in the sediments or emerges only at night. The most distinctive elements are marine angiosperms, codiacean and dasycladacean algae, sponges, annelids, tunicates, and white mud-burrowing fish and crustaceans. The turtle "grass" *Thalassia* and algae are the primary food source, and their remnants are rare beneath normal root or holdfast depth. Calcareous codiacean and dasycladacean algae, shelly mollusks that feed on plants or plant detritus, and Foraminifera would be the principal fossils in such a deposit. The burrlike calcareous dermal spicules of didemnid tunicates are a distinctive minor element of the finer silt fraction.

Bacteria in the bank muds were found by Sisler to reach local concentrations as great as 10^{10} individuals per gram, wet weight, of sediment, and to have an abundance inversely related to grain size of the sediment. They decompose organic matter, take up oxygen, and evolve carbon dioxide, hydrogen, and perhaps other gases. Such reactions presumably bring about the reduction of pH and Eh and the increase of total alkalinity observed in the interstitial environment. Falling pH and rising alkalinity cause excess bicarbonate ions and increase of calcium in the interstitial solutions. All effects contribute to the striking contrast and apparently large degree of chemical independence observed on opposite sides of the sediment-water interface. Bacterial separation of the hydrogen isotopes in the laboratory emphasizes the need for further study of microbiological and biogeochemical factors in the segregation of rare elements, and in hydrocarbon genesis.

A floor of porous calcitic limestone lies beneath the aragonitic sediments at depths as much as 3 meters or more. The radiocarbon age range of 12,000 to 21,000 years found for these rocks is probably younger than that of sedimentation. Radiocarbon data more reliably indicate that the top 2 meters of wet aragonitic bank sediment represent 2,500 years of accumulation, at an average rate of 0.8 mm per year. The deepest sediment penetrated (3 meters), therefore, was presumably deposited about

3,800 years ago, and a rate of about 0.38 mm per year is indicated for the formation of aphanitic and pelletal limestones under similar conditions and relation to sea level, assuming compaction and lithification.

Approximate, rapid-method analyses of the dissolved solids in surface and bottom waters by Kramer and associates brought out no consistent differences between these waters but did delineate marked areal variations across the banks. Analyses of high accuracy were made only for critical samples and elements. One result of the chemical work was to confirm that, even in waters from which it has been precipitated, calcium in the sea may be determined more consistently and accurately from Wattenberg's ratio (Ca^{++}mg-atom/l$=\frac{1}{2}$ alkalinity me/l$\times$ 0.465 Cl^{-}mg/l) than from usual quick methods of analysis.

Aragonite needles precipitated experimentally from sea water resemble both those found in the raw sediment and those of known algal origin. Minor differences are inconclusive. The range in temperature and salinity of the bank water is believed to be consistent with the formation of the sedimentary needles at equlibrium with it as regards analytical oxygen isotope ratios. Addition of bacteria and bacterial nutrients did not enhance the capacity of sea water to precipitate $CaCO_3$.

Experimental consolidation of the sediment was produced by Robertson, Sykes, and Newell under varying conditions of pressure, temperature, time, composition and concentration of fluid and solid fractions, particle size, and permeability of supporting cylinder. Change from a consolidated but readily disaggregated aragonite sediment to a calcite rock was directly proportional to temperature, pressure, and time. The effects of water-vapor pressure and dissolved salts have not yet been evaluated.

The problem of origin of the sediment is reviewed, and an attempt is made to quantify possible contributing mechanisms. Transport from Andros Island is estimated as responsible for perhaps 5 percent of the total sediment. Another 20 percent is identified as of skeletal origin, mainly algal. The remaining 75 percent is believed due to chemical precipitation, with subsequent intensive organic pelleting of the clay and silt fractions. The difference between $CaCO_3$ removal indicated by independent estimates of Ca^{++} and CO_3^{--} loss across the banks implies that effects of bacterial origin could account for not more than 15 of this 75 percent, or none at all. The regularity, and some particulars, of the decrease from approximately twofold supersaturation in aragonite of waters at the bank edge toward a state of quasi-equilibrium over the inner bank favors a fairly systematic mechanism for the remaining 60 to 75 percent. The proposed mechanism calls on the combined physicochemical effects of temperature increase, evaporation, and evasion of CO_2 to the atmosphere. It allows also for secondary biochemical effects such as photosynthetic CO_2 uptake.

Data obtained also have a bearing on calcium carbonate equilibrium relations. For either activity product constant (K_{CaCO_3}) or the empirically determined apparent solubility product constant (K'_{CaCO_3}), it is important to know whether figures cited apply to aragonite or to calcite. The most recent independently duplicated values for K'_{CaCO_3} at 25° C, 36 parts per thousand salinity, and atmospheric pressure are 1.14×10^{-6} for aragonite, and 0.61×10^{-6} for calcite.

When the accepted K' values are compared with activity products computed from the same basic data, it becomes evident that although the best empirical results are internally consistent and have a real comparative value, they are quantitatively unsatisfactory. The minimal value obtained for $aCa^{++}\times aCO_3^{--}$ (aragonite) over the inner banks was 7.8×10^{-9}, which is more than 2 orders of magnitude below the K' values but in reasonably good agreement with Latimer's value $K_{CaCO_3\ (\mathrm{aragonite})}=6.9\times10^{-9}$ at 25° C and one atmosphere pressure. Computation from the cited values of K'_{CaCO_3} for aragonite and for calcite gives a standard free-energy difference of -360 calories per mole as compared to -300 from present activity computations and -270 to -334 calories per mole from recent experimental data. Finally, calculated supersaturation in $CaCO_3$ at the bank edge is significantly less with regard to K than with regard to K'.

Solubility and free energy relations are called upon to explain the particular mineralogic form assumed by a given $CaCO_3$ precipitate, in accordance with Ostwald's rule of successive reactions. Inasmuch as the computed solubility and activity product constants for different polymorphs are at different ionic concentrations, it is thermodynamically predictable that degree of supersaturation of the parent solution should influence the mineralogic form of the precipitate, and the experimental and field data are consistent with this prediction. Aragonite is the expectable initial precipitate from solutions supersaturated for both calcite and aragonite (but not for vaterite), because its formation involves the smaller energy loss; only calcite can form between the saturation points for calcite and aragonite. Attainment of supersaturation reaching the aragonite field seems to be favored by various kinetic and biologic factors, chief among which is increasing ionic strength of the solution, with accompanying reduction of ionic activities up through the range of sea-water concentration. Once formed, such aragonite will apparently maintain its crystallographic integrity as long as it remains in contact with a fluid at a concentration resembling that from which precipitated, or is dry sealed. It alters to calcite at different rates following exposure to solutions undersaturated for aragonite, or to the moist atmosphere.

INTRODUCTION

SCOPE AND ORGANIZATION OF STUDY

Few geological problems more broadly affect our daily lives than the origin and diagenesis of the carbonate sediments. Limestone and dolomite the world over are familiar host rocks for oil and ore bodies, providers of structural and geochemical index levels, last resting places for myriads of fossils, and the subjects of major engineering efforts and problems. They are staples of the industrial world, whose trace element content or physical properties may make the difference between success or failure of costly ventures. Few problems, either, pique more facets of the geological curiosity or provide subject for more spirited discussion than those of the carbonate sediments and rocks.

It is not surprising, therefore, that studies of the emerged carbonate rocks have been avidly pursued. Even the storied tropical reefs have had fairly continuing attention. But the signal modern sedimentary province known to contain unconsolidated counterparts of the widely distributed (and genetically complex) pelletal, aphanitic, and oolitic limestones has only recently begun to receive the renewed attention it deserves. This is the Floridian-Bahaman carbonate province (fig. 1), next door to one of the world's largest

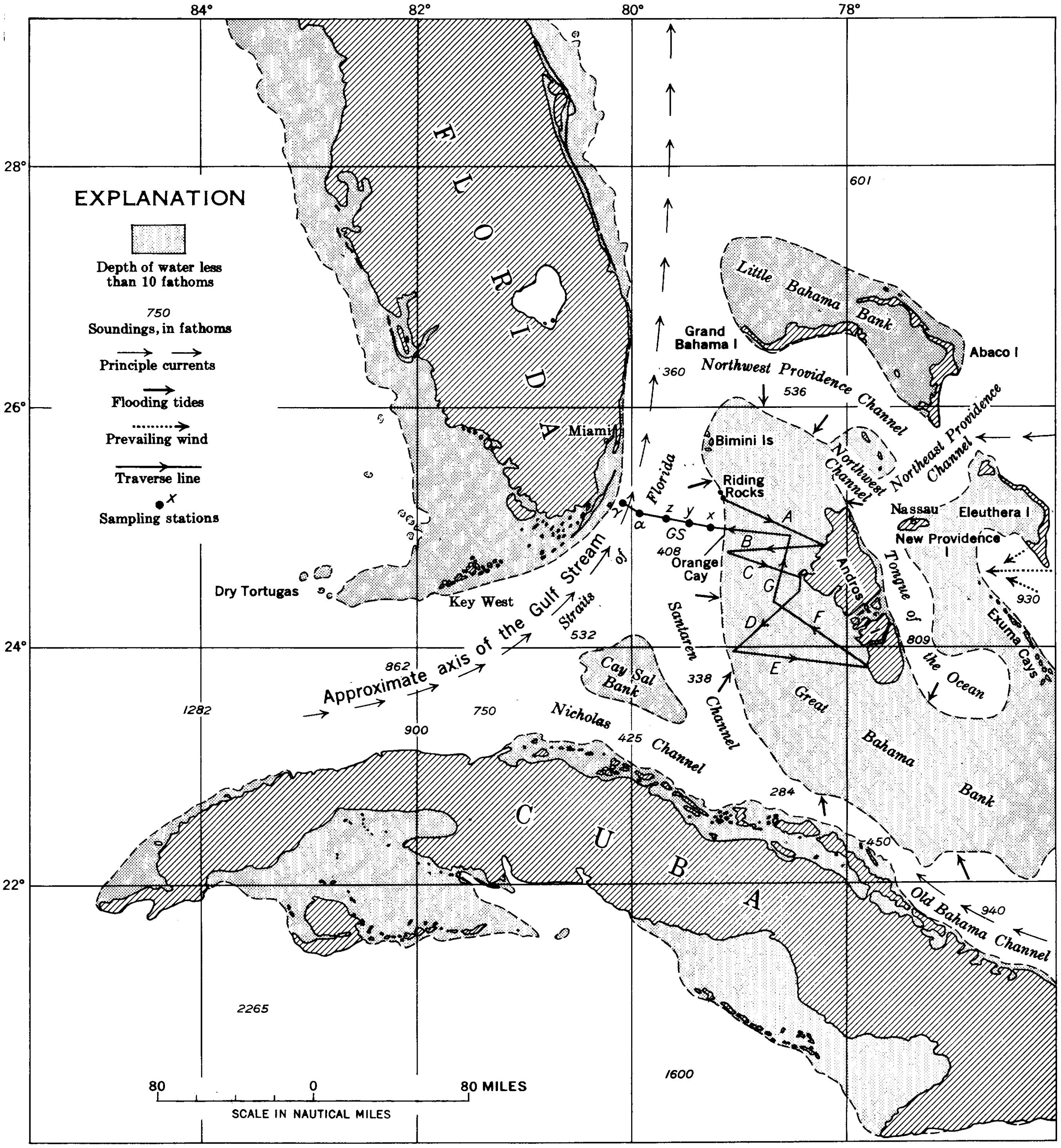


FIGURE 1.—Index map, showing traverses made.

per capita concentrations of geologists and oceanographers and the subject of excellent background studies by earlier workers. Within this large shoal-water region, the present study concentrates on that part between Andros Island and the Straits of Florida, an area almost half the size of Belgium. This unusual area comprises some 13,000 square kilometers of water less than 10 meters deep, and the principal known site of aragonite-needle accumulation.

The objectives of the present work were simply to study the origin and early diagenesis of sediments corresponding to one apparently widespread type of aphanitic and pelletal limestone, with the hope of better defining some facets of the general problem and perhaps contributing to its solution.

The work evolved through four main steps. The first was to characterize in a broad way the sediments and the environments in which they are being deposited and undergoing early alteration. Alternative hypotheses of origin then grew out of preliminary analysis and interpretation of the field evidence and previous publications. Next a program of laboratory studies was undertaken to refine the characterization and to try to quantify apparent trends against a background of field data. A final effort sought experimental testing and quantification of inferred mechanisms, supplementation of field data at critical points, and analytical data of greater precision.

Much the same sequence is followed in the report. It is always hard to consolidate diverse and complex matter into logical wholes, and this method at least provides a pathway roughly parallel to the study described.

FIELDWORK AND SAMPLE HANDLING

Most of the fieldwork was done during the latter half of May 1955. Because of good weather, the excellent help of R. B. Neuman and Richard Rezak, and the prodigious seamanship and industry of our skipper Jariilo Walter it was possible to do a great deal of work in a short time. Field observations and analyses were made, and water, sediment, and biologic samples were taken, at 57 stations along traverses on the banks and 5 across the Straits of Florida. After a year of laboratory studies on these samples, it seemed necessary to have more field data on special phases of the work and to get large sediment and water samples for experiments and more accurate analysis. On a return trip with F. D. Sisler in mid-June 1956 special attention was given to obtaining the needed additional samples, to estimating algal populations and volumes, to finding the principal pellet makers, and to bacteriological and productivity studies in place and on fresh samples. Samples of the air at and above the surface of the sea were also taken at this time. The tireless efforts of skipper Koo Walter and the faithful help of James Double assured accomplishment of principal objectives, despite operational difficulties that required some curtailment of plans.

Work at sea was carried out aboard University of Miami Marine Laboratory vessels MV *Physalia* in 1955 and *Aphrodite* in 1956. The *Physalia*, a 25.5-meter-long converted Coast Guard cutter with a 1.7-meter draft and a 900-mile range, was equipped with A-frame and boom for handling coring apparatus, necessary winches, refrigerators, deck laboratory, and recoding fathometer. It was well suited for the work. The *Aphrodite* was a 12-meter-long short-range cabin cruiser with a 1.2-meter draft, not well suited for the work it was called upon to perform but usable and helpful to have when expected transportation failed to materialize.

Aerial reconnaissance of western Andros Island and the banks westward from it was made in 1955 in a small Grumman amphibian. The pilot, Leonard M. Thompson, of Nassau, has known the region since childhood and has been on the interior lakes with survey parties.

Observations of and manual collections at the bottom were made by Cloud at all except the straits stations, utilizing self-contained underwater breathing apparatus. Underwater photographs for later study were taken with 16-mm and 35-mm cameras in waterproof housings. Cores taken in 1955 were obtained with a modified Kullenberg-type piston coring device (pl. 1*E*) loaned by the Chesapeake Bay Institute through the courtesy of D. W. Pritchard and operated by J. Walter and Neuman. At stations where the layer of sediment was too thin to support the core barrel, samples were taken by hand, in a tin can. Biological samples were also taken by hand and canned or bottled in formalin or alcohol. The handling of biological and water samples on deck was mainly by Rezak. Ashore or in very shallow water, cores were taken with plastic tubes and a gripping device designed and loaned by Robert Ginsburg (pl. 1*F*).

In 1956, cores at sea were taken by simply pushing 1.2-meter lengths of plastic tubing directly into the bottom by hand. As in Ginsburg's method, a rubber stopper on a line was used as a piston. Full penetration and good recovery was obtained in all instances. Recovery and manipulation might have been improved by a gasket (such as a chamois wrapper) around the stopper, and a core retainer of some sort. From this experience it seems that the difficulty of using the standard piston-corer in shallow water would be obviated in the area studied by simply easing the weighted core barrel into the bottom.

All sediment and water samples were taken in duplicate, one set for on-the-spot analyses and records, the second set to be preserved for later study.

Shipboard analyses were made while running between stations by Cloud and Rezak. Surface and bottom water was tested for hydrogen ion concentration (pH), oxidation-reduction potential (Eh), alkalinity in milliequivalents per liter (A me/l), and chloride in grams per liter (Cl^- g /l), using standard potentiometric and colorimetric titration techniques. Specific gravity and salinity were estimated with hydrometers by the method and with equipment described by the U.S. Coast and

Geodetic Survey (1941, p. 83–88). Cores were tested for pH, Eh, and interstitial water properties. The Eh reading was taken with the sediment beneath a layer of recently boiled water (to exclude oxygen), but the sediment was not mixed with the water. The meter needle was allowed to drift as far as it would go in reasonable time in a negative direction. Readings were taken at the point where the drift changed to a positive direction or became imperceptibly slow.

On the 1955 trip, the top and bottom 35 cm of all cores, and the middles of some, were immediately refrigerated in their plastic liners. Water for chemical analysis was passed through millipore filters to exclude particles larger than 0.45 micron and refrigerated in screw-top polyethylene bottles. Surface and bottom waters were separated, in completely filled containers, mostly of 210-ml but some of 500-ml capacity. All refrigerated samples were placed in wet ice promptly on arrival at Miami (dry ice was avoided to obviate introduction of excess CO_2) and flown in the same ice to Washington, D.C., where they were promptly transferred to cold storage. They were kept undisturbed in cold storage or refrigeration until studied.

Although the 1955 water samples were adequate for approximate analyses to detect mass variations, they were apparently not large enough for the laboratory methods available for accurate analyses except for pH, alkalinity, and a few elements; nor was sufficient sample left after analysis for independent check and definitive experiment. In 1955 therefore, 4-liter samples were obtained at 2 check stations, and 80-liter samples at 2 more. It was impracticable to filter or refrigerate these on the spot, but they were rushed to Washington, D.C., in semidarkness, (to inhibit biological activity), and samples for analysis were filtered within 5 to 7 days of collecting and refrigerated until analysis.

The laboratory treatment of samples is discussed in the applicable sections.

The original field designations are used throughout all discussions. Thus *GS* (for Gulf Stream) is retained to designate samples from the Straits of Florida; surface water is from the surface of the sea; top sediments are from the surface of the sea bottom; and bottom sediments are from the bottom of the core.

Linear and areal measurements are given in the metric system except for distances and travel rates at sea which are, according to practice, in nautical miles and knots. Depth of water is given in meters except on accompanying maps, where fathoms are used in accordance with nautical practice.

PREVIOUS WORK

Although the region (fig.1) has only recently begun to receive the emphasis it deserves from the viewpoint of sedimentary, diagenetic, and ecologic processes, geologists are by no means uninformed about the Bahamas and their implications for the carbonate problem. Even the British nautical surveys of 1836 and 1848 (on which the current hydrographic charts are based) call attention to the sandy ridges and bores of the bank edges, note areas of soft mud, and record streaks of white water, presumably comparable to the whitings of the present report.

Then in 1891 J. I. Northrop wrote of the famous ocean holes, of root casts in limestone (see also Shattuck and others, 1905, pl. 3, fig. 2), of evidence for recent sea-level changes, and of the soft limemuds along the western shore of Andros Island.

Later, Alexander Agassiz described the general oceanographic setting of the Bahamas and provided many profiles and sketches of specific features (1895). He sailed across the area of present study twice—from Santaren Channel eastward to the bights at the middle of Andros Island, north up the west coast of Andros Island to its western apex, and then back west to Orange Cay and finally north to the Bimini Islands (Agassiz, 1895, p. 50–64). Agassiz drew particular attention to the white calcium carbonate muds near shore "resembling plaster of Paris which has just been mixed for settling." He noted also that the sediment became looser and more granular toward the bank edge and described some of the accompanying biotal changes, including a subsequently unconfirmed "flourishing" growth of astrean and meandrine corals on north-south "bars" between Orange Cay and Riding Rocks (1895, p. 56–57). Agassiz (1895, p. 52–54) attributed the "white marl" to attrition of supposed eolian sediment along the coast and inside Andros Island, an explanation now known to be inadequate. He ascribed (probably correctly) the numerous vertical holes in the sediment to shrimp.

Then, in 1905 the Bahama Expedition of the Geographical Society of Baltimore issued a comprehensive, extensively and well-illustrated general source book on the Bahama Islands under the editorship of G. B. Shattuck. Shattuck and B. L. Miller did the geology in this report. It also includes a section on paleontology and the nonmarine mollusks by Dall. Chapters by others deal with tides, magnetic observations, climate, upper atmosphere, soils, vegetation, insects, birds and terrestrial vertebrates, fishes, sanitation, and history. Shattuck and Miller state (*in* Shattuck and others, 1905, p. 13) that the "lakes, ponds, and marshes" found on the larger islands are "usually undrained" and contain brackish water. They report that many are shallow but some are deep and connect with the ocean. They conclude (p. 15) that the lake deposits are generally so thin over fossiliferous marine beds "that the substratum of the Bahamas, throughout at least the northern part of the archipelago, was marine." It is reported in the soils chapter (C. N. Mooney *in* Shattuck and others, 1905, p. 170–172) that white marl covers the western half of Andros, to "a depth of from 1 to 3 feet," and that it is "often covered partially or wholly by salt or brackish waters." Partial analyses to percent oxides of a "typical sample" give, besides CaO, 3.22 SiO_2, 2.85 MgO, 0.123 P_2O_5, and 0.306 K_2O.

Shattuck and Miller state categorically (1905, p. 16) that the bank sediment is "derived chiefly from the erosion of coral reefs." This view, however, withered in the face of growing appreciation of the volumetric insignificance of living reefs and true reef rock in the region. Like Agassiz, these authors made no reference to Dall's earlier suggestion (*in* Dall and Harris, 1892, p. 101) of a chemical origin for similar deposits behind the Floridian reefs.

Somewhat later Vaughan, with his usual energy, moved temporarily into the Bahaman scene, and together with A. G. Mayor drew several associates into the problem. The resulting publications by Vaughan (1914a, 1914b, 1917, 1918, 1924), Drew (1911, 1912, 1913, 1914), Lipman (1924, 1929 a, b), Goldman (1926), Bramlette (1926, parts), and Thorp (1936, 1939) will be referred to as appropriate in later discussion. These papers are more generally known than the older ones, and it is sufficient here to say that they are important background for the present work.

Also stimulated by A. G. Mayor, R. M. Field organized and led an "International Expedition to the Bahamas," the results of which were summarized by Field and others in 1931. A brief paper by Hess (1933) and the important works of Black (1933a, 1933b) and Bavendamm (1932) were further results of this expedition.

The works of de Laubenfels (1936) and Taylor (1928) are the basic references for the sponges and algae of the region, respectively. Various handbooks issued since the late 1920's by the New York Academy of Sciencies and comprising its "Scientfic Survey of Porto Rico and the Virgin Islands" cover other biotal elements and are referred to specifically as appropriate.

Signs of renewed interest on the part of geologists came with a deep test to 4,488 meters by the Bahamas (Superior) Oil Co. at Stafford Creek on Andros Island in 1946–47 (Eardley, 1951, p. 573). Rich's imaginative airplane-window reverie (1948) followed, and commercial production of oil in Florida assured attention to the whole province. Under a grant from Humble Oil Co., Newell (1955) and collaborators (1951, 1957, 1959; Squires, 1958) began studies in the Fresh Creek area, then transferred activities to the Lerner Marine Laboratory of the American Museum of Natural History at Bimini, along the northwestern bank margin. Work, meanwhile, was underway by the British Bahamian Oil Development, and reports by Lee (1951) and Illing (1954) presented publishable results of that endeavor, the work by Illing being of special interest to geologists. Current activity in the region, commercial and otherwise, is at a high level (for example, Wassall and Dalton, 1959).

With all this activity it seems surprising that the only previous systematic effort to quantify and interpret chemical gradients in the field in the known area of aragonite muds was as an adjunct to sponge fishery investigation. It would be difficult to place too high a value on the significance of this splendid study by C. L. Smith (1940, 1941) for the geology of the carbonate sediments. His careful documentation, meticulous reasoning, and advance in theory also helped greatly in developing a fruitful plan of study for the present work.

ACKNOWLEDGMENTS

This work was made possible through the immediate favorable response and continuing sympathetic interest of W. H. Bradley, who was Chief Geologist during the life of the project. It had also the wholehearted and continuing help of many other Survey colleagues. In addition to those who are not authors of separate sections, or appropriately credited elsewhere, I must mention especially John Hathaway, Earl Ingerson, Dorothy Carroll, Meyer Rubin, A. M. Pommer, Irving Freidman, Leonard Shapiro, W. W. Brannock, Charles Milton, Ed Chao, Paul Barton, Irving May, and R. M. Garrels. The frequent generous help and wise counsel of John Hathaway in particular calls for acknowledgment. He prepared all the electron micrographs and contributed in countless other ways to the development of the materials and ideas included. Garrels and Barton also contributed materially to this work through their criticisms of the chemical sections of the text in draft and their advice, encouragement, and help with the computations.

In the laboratory, also, this project had, at various times, the very helpful assistance of Harry Starkey, Marcia Newell, and James Patten. Starkey carefully performed all the tedious and difficult mechanical analyses and helped effectively with many other details. Miss Newell provided welcome general assistance to all phases of the laboratory work, especially the bacteriology and geophysical work. Patten assisted with the batch-water evaporation experiments.

Richard Rezak, R. B. Neuman, and Capt. Jariilo Walter were largely responsible for the success of the

1955 fieldwork. Rezak performed the majority of the shipboard analyses, and Neuman and Walter took and cared for the cores. Help also was received with core handling from Donald Stewart in 1955 and from James Double in 1956.

From their work leading toward publication of a separate report on the Foraminifera, Ruth Todd and Doris Low have provided information on occurrence of the principal foraminiferal species; and Miss Low undertook the onerous responsibility of typing, checking, and processing the often complicated pages of this report. Kenneth Lohman studied selected samples for diatoms in the midst of heavy pressure from other work. Biological determinations have also been provided by specialists of the U.S. National Museum and other organizations as indicated on tables 3, 10, and 11. The fishes were identified by Leonard Schultz, of the U.S. National Museum, and plankton collections were reported on by David L. O'Berry, of the University of Miami Marine Laboratory. As usual, Frederick M. Bayer has been a constantly available and generous source of information and advice on ecological subjects.

Arrangements for work at Andros Town in 1955 were made by Kay Norton and Arne Lindroth of the Wenner-Gren Foundation. At Andros Town much courteous help was received from Gunnar Lindstrøm, Kenneth Sundin, and Misse Peterson.

Both in 1955 and in 1956, F. G. Walton Smith and Hilary Moore came to the rescue at the crucial moment with marine equipment from the University of Miami Marine Laboratory. To them and to G. E. Voss, of the Marine Laboratory, and Robert Ginsburg, of Shell Development Corp., I am warmly grateful for many favors and much useful advice. To Farrington Daniels I am also grateful for taking time out from a very busy period in Washington, D.C., for discussion of the precipitation problem and for subsequent helpful correspondence.

An emergency grant of $785 from the Geological Society of America permitted F. D. Sisler's employment for critically needed bacteriological work until arrangements could be completed for his assignment to the U.S. Geological Survey. The Department of Geology, U.S. National Museum, generously provided laboratory space and facilities for his work for the duration of this project.

Most of the collaborating authors have read and criticized all sections of the report, and D. L. Graf and R. S. Boardman critiqued the entire report. Helpful review of individual sections was made by F. S. Grimaldi, John Lyman, E. W. Roedder, George Switzer, and Claude ZoBell.

But for the earlier ground-breaking work of C. L. Smith, of Liverpool University, the present study would have been impossible in anything like its present form. I am also obliged to him for the previously unpublished data presented in figure 41.

BROAD FEATURES OF THE ENVIRONMENT

REGIONAL SETTING

Unusual though its sedimentary and ecologic characteristics may be, a region of hypersaline tropical shoal water twice the size of Switzerland and isolated from important terrestrial influences cannot be dismissed as a freak occurrence. That is the setting of the Bahama Banks (fig. 1)—a total area of 80,000 square kilometers, a major scene of calcium carbonate sedimentation, and a probable modern representative of a type of environmental complex that is believed to have been widespread at times in the remote past. Oceanic channels such as separate this region from Florida and Cuba also divide and deeply indent the banks themselves. The only land consists of occasional islands and keys along the bank edges, also made of calcium carbonate and mostly of trivial size.

The ultimate origin of these deep channels and shoal banks is a mystery concerning which there is little evidence and wide difference of opinion (Hess, 1933; Lee, 1951, p. 656; Newell, 1955, p. 314; Newell and Rigby, 1957, p. 19–24). It is known only that a pile of carbonate sediments at least 4,488 meters thick (Stafford Creek well) has been accumulating intermittently since Late Cretaceous or earlier and that elongate unfilled or superimposed gaps, such as the Tongue of the Ocean, extend downward as much as 2,000 meters from its surface. General depth ranges are indicated on figure 1, and Agassiz (1895) gives a number of profiles across the trenches. There are no obvious present limitations on conjecture as to how this relief came about, except that provision must be made for generally continuing subsidence of the shoal-water bank sediments and for approximate isostatic equilibrium of the whole. Critical evidence might be obtained by bedrock sampling along the steep channel walls.

If the few samples available from the Tongue of the Ocean (Thorp, 1936, p. 89; Drew, 1912, p. 141) and the Straits of Florida (present work; Agassiz, 1888, p. 286–287) are typical, the deep bottom sediments around the banks are primarily *Globigerina* and pteropod ooze having a large silt and clay fraction of aragonite needles, coccoliths, discoasters, and rhabdoliths, and (Newell and Rigby, 1957, p. 61) local transported skeletal debris from shallow water. Thus, even at depths up to 2,000 meters, these waters are apparently saturated with $CaCO_3$; and where they spill across the banks, they lose it rapidly to the sediments. The nature and rate of this loss in the area west of Andros Island is the central problem of the present report. Those factors that affect water movement and chemistry, organic activity, and exchange between sea and land are, therefore, of particular interest here.

Wind, tide, current, and topography are the principal influences on water movement across the banks (figs. 1, 2; table 1). The location of the Bahamas near the southwestern edge of the Bermuda High and the northern edge of the trade-wind belt assures a prevailing easterly wind throughout the year (Fassig *in* Shattuck and others, 1905, p. 118). The main oceanic surface current is thus a general westerly drift (C. L. Smith, 1940, p. 152). The direction of flooding across the banks, however, is affected by local current systems in such a way as to produce opposing forces that tend to cancel out. Andros Island and the banks east of it, for instance, deflect the regional westerly drift. Intermittent countercurrents along the margins of the Gulf Stream (or Florida Current) and other channel currents tend to retard and reorient bank onflow from these sources. Weak tidal currents tend to be radially oriented on and off the banks. The wind itself (C. L. Smith, 1940, p. 152–156, 161–162) apparently has a determining influence on the strength and direction of residual water movement.

TABLE 1.—*Temperature, humidity, rainfall, and tide at Nassau and Cat Cay*

[Tide from U.S. Coast and Geodetic Survey tide tables for 1955; other data from averages over 4 or more years before 1904, from Fassig (*in* Shattuck and others, 1905, p. 114–120)]

	Nassau	Cat Cay
Air temperature (in °C):		
Mean annual	25.0	
Mean annual min	21.7	
Mean annual max	28.3	
Absolute min	11.7 (February)	18.9 (January)
Absolute max	36.7 (June)	32.8 (August)
Mean of hottest month	28.3 (August)	
Mean of coldest month	21.7 (February)	
Humidity (percent):		
Daily mean	78	
Mean monthly min	75 (August)	
Mean monthly max	82 (January)	
Rainfall:		
Yearly average in cm (in.)	126 (49)	113 (44)
Average of rainiest month (August) in cm (in.)	23 (9)	
Average of least rainy month (March) in cm (in.)	2.5 (1)	
Average days with rain per year	152	
Tide in m. (ft.):		
Mean	.80 (2.6)	.74 (2.4)
Spring	.95 (3.1)	.86 (2.8)

From March or April through August, the prevailing wind is east or southeast (Fassig *in* Shattuck and others, 1905, p. 119; C. L. Smith, 1940, p. 155). In September it begins to shift northward, and from October or November into February or March it is northeast or east, abetted by some direct northerly winds. Westerly winds are rare through most of the year.

The resultant effect, from April or earlier to September or later, is a general drift of water around the north and south ends of Andros Island, largely counterbalanced by overflow from the western channels and by tidal influences. Residual currents are sluggish, and persistent evaporation creates high concentrations of dissolved solids, especially in the area westward from the north half of Andros. Peak salinities in this area presumably reflect opposition to the weak general southwesterly drift by heavier onflow from the southwest where converging currents meet and force water over the banks. A marked local effect is produced by tidal flowage through the Bights.

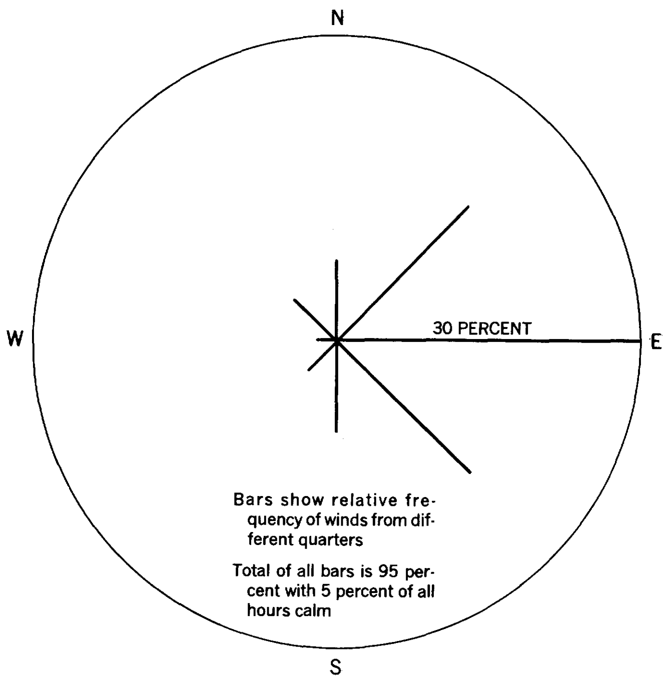


FIGURE 2.—Wind directions at Nassau.

Deterioration of the high-salinity pattern takes place during the winter months, but salinities as high as 38 parts per thousand may be observed as late as December (C. L. Smith, 1940, p. 162, fig. 49), after the seasonal northeasterly and northerly winds have abated. Presumably, therefore, the general salinity configuration persists in some degree throughout the year with 7 or 8 months of high concentration.

The area has been characterized as sparse in kinds and numbers of animals and plants (Field and others, 1931, p. 769), and C. L. Smith showed (1940, p. 165–166) that mineral nutrients are virtually absent in the upper 100 meters of Providence Channel, northeast of Andros Island. Studies of the phytoplankton by Mann (1935) led to the conclusion (p. 122) that "in all the Bahama-Florida samples * * * diatoms are strikingly few in number, imperfectly silicified, and frequently of misshapen form," although his list of species is six pages long and he notes that *Mastogloria* is "very abundant" in the Floridian samples.

From limited data (table 2), however, it seems that phosphate is much higher in bank and Straits of Florida waters than in Providence Channel to the northeast. In fact, some of the analyses of local surface waters compare favorably with those recorded for areas of high biological productivity, and the deep water of the Straits of Florida has a very high phosphate content (table 2). The deep water at station *GSα*, however, probably includes phosphate from sediments. Bsharah (1957, p. 208–220) shows a similar year-round variation of mineral nutrients with depth in the Straits of Florida, a more reasonable high inorganic-phosphate value of 2.6 microgram-atoms per liter, and a late summer through winter nitrate-phosphate increase that trails a summer and fall expansion of a phytoplankton that is dominated by dwarf forms. Tows for plankton made as a part of the present study also show a low density of the forms usually retained on a 20-mesh net.

TABLE 2.—*Reported inorganic phosphate content of bank waters west of Andros Island, compared with other waters (microgram-atoms per liter)* [1]

Place	Station reading	Minimum	Maximum
Bank proper (sta. *It'*, June 1956)		0.10	0.30
Bank edge (sta. *A1'*, June 1956)	0.37		
Bank maximum (approx. analysis, sta. *B8*, May 1955)	1.55		
Florida Straits surface, 40 miles west of bank edge, May 1955 (sta. *GSα*)	.81		
Florida Straits 650 m., 40 miles west of bank edge, May 1955 (sta. *GSα*)	[2] S.71		
Florida Straits surface, 4 miles west of bank edge (Bsharah, 1957, fig. 10)		Trace	.35
Florida Straits 650 m., 4 miles west of bank edge (Bsharah, 1957, fig. 10)		.70	2.40
Providence Channel surface, December 1938 (C. L. Smith, 1940, p. 166)	Trace		
Providence Channel 650 m., December 1938 (C. L. Smith, 1940, fig. 51)	.04		
English Channel seasonal (Sverdrup and others, 1942, figs. 63–64)		.03	.77
Friday Harbor, Wash., seasonal (Sverdrup and others, 1942, fig. 62)		1.25	2.00
Gulf of Maine upper 60 m., seasonal (Sverdrup and others, 1942, table 54)		.60	1.03
Gulf of Maine 180–240 m., seasonal (Sverdrup and others, 1942, table 54)		1.22	1.61

[1] The standard reporting unit is μg-atoms /l of PO_4-P, but the samples from Andros Island and Florida Straits were reported simply as P. This was calculated as PO_4-P for comparison with other data. The method employed gives inorganic P only. In addition millipore filtration presumably removed organic and particulate P.

[2] High reading probably in part due to phosphate introduced from disturbed sediment, as water sampled was from top of core barrel in contact with sediment and was not collected in a standard water sampler.

In fact, observed density of benthonic species and of bacteria, oxygen productivity tests, and nutrient analyses all support the view that the bank area somehow maintains a higher level of productivity than might be expected from previous reports (until Newell and others, 1959). Dry-weight analyses by Mrs. Elizabeth Murphy, of the U.S. Department of Agriculture, show 1.162 percent nitrogen and 0.014 percent phosphorus in a composite algal sample and 0.850 percent nitrogen, 0.025 percent phosphorus in a sample of the even more abundant turtle "grass" from 1956 station *It'*. Mineral nutrients are therefore present and are being utilized to maintain an aberrant but reasonably prosperous biota.

The western part of Andros Island is mainly water (pl. 1*A*, *B*), and there is extensive communication between land and sea through a broad belt of mangrove swamps and many tidal inlets. Rarely is there any question, though, about where the sea leaves off and the island starts (pl. 1*C*, *D*; pl. 2*D*), and mixing of their deposits seems to be limited. The lakes are apparently mainly shallow and undrained, with thin calcareous deposits over marine country rock (pl. 1*A*–*C*) (Shattuck and others, 1905, p. 13). Tidal inlets are ordinarily clear, to judge from their black color on aerial photographs (pl. 1*D*), and the one that leads to the lake at station *D1a* on Williams Island was transparently clear in May 1955. Bars of mud across their mouths (C. L. Smith, 1940, p. 149) indicate no great seaward transfer of material, and the salinity of the bank water shows little or no diminution along the shore such as should result from dilution by outflowing water. The strength of the prevailing residual currents is not conducive to volumetrically great or frequent movement of bank water eastward overland beyond the normal high-tide flooding of the marginal mangrove swamps, where sediments are held in place by leathery algal mats. Inspection of the mollusks found in sediment samples along shore and across the banks (table 3), to be sure, shows mixing of marine, brackish-water, and land shells along the beach; but none of the distinctive land or mangrove swamp shells and few intertidal or brackish-water types were found at any great distance seaward.

BANK WATER

Observations of the waters and sediments west of Andros Island in May 1955 were made at stations roughly 6 nautical miles apart along 7 traverses spaced over an area of about 13,000 square kilometers. Cores were obtained and studied at 47 of the 55 bank stations occupied; hand samples of the sediments were taken at all others; and water analyses and bottom observations (pl. 2) were made at all. These data were supplemented by studies of 1 traverse, consisting of 5 stations, across the Straits of Florida to the west. Several stations were also occupied in the bights, lakes, and mangrove swamps.

Field observations at most stations included temperature, density (specific gravity), titration chlorosity, titration alkalinity, pH, and Eh of both surface and bottom waters. As many as possible of the same observations, except density, were made of interstitial water from the top layer of sediments and on the top and bottom of a duplicate core sample. First approximation of salinity, from hydrometric density (U.S. Coast and Geodetic Survey, 1941), was helpful in

TABLE 3. *Distribution of mollusks observed in sediment samples from west of Andros Island*

[Asterisk (*) indicates samples identified by Dr. Harald Rehder; others are from comparison with Rehder's determinations. a, indicates abundant; c, indicates common; X, indicates present; cf, indicates probably present]

	Station, location or distance from shore, and stratigraphic depth																						
	*E9a,** mangrove swamp, top	*A11*, 100 yd, top	*C7a,** beach	*C7*, ¼ mile, top	*D1,** ½ mile, surface rock	*E9,** 1 mile, rock beneath sediment	*C6,** 4 miles, 2 in.	*B1*, 5 miles, 1 in.	*D2*, 7 miles, 1 in.	*C5*, 8 miles, top	*F2,** 12 miles, 6 in.	*C4*, 16 miles	*G1*, 17 miles, top	*D4*, 20 miles, top	*F4*, 20 miles, top	*C3*, 22 miles, top	*G3,** 22 miles, 7 in.	*F7*, 25 miles, top	*D5,** 26 miles, 4 in.	*F5*, 26 miles, 5 in.	*A4*, 40 miles, 2 in.	*D9*, 59 miles, top	*20/1*, South Bight, top
Land snails:																							
Cerion sp			X																				
Helicina convexa rawsoni Pfeiffer			X																				
Opisthosiphon vaughani Bartsch			X																				
Polygyra microdonta (Deshayes)			c																				
Mangrove swamp snails:																							
Batillaria (*Lampanella*) *minima* Gmelin [1]	a	c	a	X																			
Land and brackish-water snails, shore margins:																							
Truncatella bilabiata Pfeiffer			X																				
Intertidal and brackish water snails:																							
Bulla cf. *B. occidentalis* Adams			X								X												
Cerithidea costata (da Costa)	c		c		X																		
Modulus modulus (Linné) also fresh water			X			X		c									X						
Shallow marine snails:																							
Cerithium algicola Adams		X		X		X	c	a	c	X	X	X	c	X	X	X	c	X	c	c	X		X
cf. *C. floridanum* Mörch							X																
variabile Adams			X																				
sp			X																				
Conus stearnsii Conrad						X										X	X						
Crassispira ostrearum (Stearns)																	X						
Murex (*Chicoreus*) *florifer* Reeve					X																		
Nassarius sp																	X						
Prunum apicinum (Menke)						X						X					X						
Vermicularia spirata (Philippi)																	X	X					
Shallow marine clams:																							
Aequipecten gibbus (Linné)									cf.								X		X		cf.		
cf. *A. muscosus* (Wood)																	X						
Anadara notabilis Röding																cf.	X		X				
Chione cancellata (Linné)		X		X	X	c		X	X		X		c				X						X
Donax sp									X					X								X	
Laevicardium cf. *L. laevigatum*											X						X						
Lucina (*Bellucina*) *amianthus* Dall						a											X						
Phacoides pennsylvanicus (Linné)						c	X										X						
(*Lucinisca*) *nassula* (Conrad)																	X						
Trigonocardia antillarum (d'Orbigny)		?			X												X						?
(*Americardia*) *medium* (Linné)														cf.			X						
Venerid, unidet., small smooth sp		X						X					c				X						

[1] Kornicker and Purdy (1957) seem to imply that this snail also lives in a normal shallow-marine environment, but living records from the present study are all from mangrove swamps or immediately bordering intertidal water.

guiding fieldwork. However, the salinity and chlorinity of the illustrations and discussions in this paper are the standard salinity and chlorinity of international oceanographic description (Sverdrup and others, 1942, p. 51–52), converted to parts per thousand (°/₀₀) from grams per liter (g/l) of chloride ion determined by silver nitrate titration at field temperature. Conventional chlorosity, which is g/l of Cl^- at 20°C is not dealt with in this report.

Average properties of the principal water types are summarized from approximate analyses and compared with "normal" and reference water in table 4. Table 5 gives the condensed basic data from analyses by Henry Kramer and associates (table 25), arranged in groups according to geographic location and alkalinity. Calcium and magnesium values in the averaged columns of table 4, and in table 5, show an anomalous relation to chloride; this was found on checking to be due to a systematic error of about −10 percent for Ca and +4 percent for Mg (determined by difference from Ca) in the visual titration with versene (ethylenediaminetetraacetic acid, EDTA). Calcium and magnesium values in table 4 to the right of the column " 'normal' sea water" are believed to be accurate within 0.2 percent.

Those features of the water chemistry appropriate to an understanding of the origin of the sediments are considered in detail at the places where they apply; and the problem of calcium determination in sea water is critically discussed in a later section by James Carpenter. Here it will suffice to discuss briefly only those properties which are of interest in characterizing the water mass.

TABLE 4.—*Average properties of principal water types west of Andros Island, May 1955,*[a] *compared with "normal" sea water and analyses of 1956 reference waters*

	Straits of Florida		All bank stations (surface plus bottom)	Bank edge (sta. *A1, B8, D8, D9, E1, E2*		Bank stations of alkalinity—			Tidal lake on Williams Island (sta. *D1a*)	Bights, east side (sta. 19/x and 20/y)	"Normal" sea water[b]	Sta. *A1′*, 1956, surface	Sta. *It′*, marginal, 1956, surface	Sta. *It′*, whiting, 1956, surface	Method of analysis of samples in the preceding three columns
	Surface	Bottom		Surface	Bottom	>2.2	2.0–2.2	>2.0							
Number of stations	5	5	56	6	6	11	26	19	1	2	composite	1	1	1	
T ° C.:															
field	27.9	22.6	28.4	27.8	27.8	28.1	28.4	28.5	27.0	28.1	20.0	28.0	29.5	29.5	
laboratory	27.2	27.7	28.0	28.5	28.6	28.1	27.9	28.1	31.0	28.0		26.6	26.6	26.6	
pH	8.04	7.83	8.08	8.14	8.17	8.16	8.10	8.02	8.10	8.20	8.25±	8.20	8.04	8.10	Potentiometric.
Eh volts	+0.31	+0.33	+0.32	+0.31	+0.33	+0.35	+0.33	+0.27	+0.30	+0.40	-------------	+0.38	+0.40	+0.40	Potentiometric.
Specific gravity:															
field *T*	1.0239	1.0252	1.0270	1.0252	1.0252	1.0253	1.0269	1.0283	1.0297	1.0264	1.0224(28°)	1.0239	1.0281	1.0282	
20° C	1.0260	1.0259	1.0294	1.0273	1.0273	1.0275	1.0292	1.0307	1.0317	1.0286	1.0246	1.0260	1.0308	1.0309	
Dissolved solids:[i]															
sum ‰	37.05	36.66	41.82	38.53	38.93	39.18	41.53	43.75	47.34	38.25	35.94	3702	43.16	43.14	
chlorinity ratio	36.09	35.58	40.82	37.74	38.14	38.38	40.53	42.63	46.33	37.38	35.15	36.17	41.94	42.00	
Salinity ‰	35.93	35.43	40.64	37.57	37.97	38.21	40.35	42.45	46.13	37.22	35.00	36.00	41.76	41.82	Chlorinity ×1.805+.03
Chlorinity[c] (Cl) ‰	19.89	19.61	22.50	20.80	21.02	21.15	22.34	23.50	25.54	20.60	19.37	19.93	23.12	23.15	Cl mg/l÷SG.
Cl[c] mg/l	20,360	20,100	23,110	21,320	21,550	21,690	22,940	24,170	26,300	21,150	19,800	20,410	23,770	23,800	Gravimetric.
A_t[a] mg/l	148	160	127	147	145	139	128	116	120	123	148	149	149	123	Potentiometric titration.
SO_4 mg/l	2,908	2,860	3,230	2,977	3,006	3,006	3,200	3,396	3,580	2,985	2,762	2,892	3,364	3,414	Gravimetric.
Na mg/l	11,300	11,240	12,730	11,620	11,760	11,860	12,650	13,340	14,350	11,600	11,010	11,330	[d] 13,350	13,190	Gravimetric as uranyl acetate.
Mg mg/l	[e] 1,524	[e] 1,484	[e] 1,734	[e] 1,612	[e] 1,618	[e] 1,625	[e] 1,719	[e] 1,817	[e] 1,970	[e] 1,560	1,327	1,400	1,566	[f] 1,649	Gravimetric as $Mg_2P_2O_7$
Ca mg/l	[e] 388	[e] 394	[e] 430	[e] 417	[e] 415	[e] 415	[e] 427	[e] 443	[e] 480	[e] 405	420	[g] 435	477	[h] 490	$(NH_4)_2C_2O_4$ triple precipitate corrected for Sr.
K mg/l	410	406	462	425	426	430	458	485	530	415	396	402	475	468	Flame photometer.
Sr mg/l	6.9	7.8	7.7	5.2	5.7	6.9	7.9	7.9	---------	7.2	7.9	5.0	5.2	5.3	Oxalate separation flame determination.
B mg/l	3.9	4.4	4.8	4.4	4.5	4.5	4.6	5.2	6.4	4.5	4.0	4.5	5.5	5.5	Potentiometric titration.
P mg/l	0.025	0.270	<0.010–0.048	<0.010–0.048	<0.010–0.033	<0.010–0.044	<0.010–0.044	<0.010–0.023	---------	<0.010	-------------	0.011	0.003	0.009	Al precipitation and colorimetric determination.
SiO_2 mg/l	0.8	2.0	2.0	1.4	1.3	1.4	1.7	2.8	7.4	1.0	-------------	---------	---------	---------	
Cl^-[a] me/l	574.22	566.88	651.79	601.29	607.78	611.73	646.98	681.67	741.74	596.50	558.42	575.63	670.38	671.24	
A_t me/l	2.43	2.62	2.08	2.41	2.38	2.28	2.10	1.91	1.96	2.02	2.43	2.44	2.44	2.02	
SO_4^{--} me/l	60.54	59.55	67.24	61.98	62.58	62.58	66.62	70.70	74.54	62.15	57.51	60.21	70.04	71.08	
Principal anions me/l	637.19	629.05	721.11	665.68	672.74	676.59	715.70	754.68	818.24	660.67	618.36	638.28	742.86	744.34	
Na^+ me/l	491.37	488.76	553.55	505.28	511.37	515.72	550.07	580.08	623.99	504.41	478.76	492.67	580.51	573.55	
Mg^{++} me/l	125.43	122.14	142.72	132.67	133.16	133.74	141.48	149.55	162.14	128.40	109.22	115.13	128.78	135.60	
Ca^{++} me/l	19.36	19.66	21.46	20.81	20.71	20.71	21.30	22.10	23.95	20.21	20.96	21.71	23.80	24.45	
K^+ me/l	10.49	10.38	11.82	10.87	10.90	11.00	11.71	12.40	13.56	10.61	10.13	10.28	12.15	11.97	
Sr^{++} me/l	.16	.18	.18	.12	.13	.16	.18	.18	---------	.16	.18	.11	.12	.12	
B^{+++} me/l	1.08	1.22	1.33	1.22	1.25	1.25	1.27	1.44	1.77	1.25	1.11	1.24	1.52	1.52	
Principal cations me/l	647.89	642.34	731.06	670.97	677.52	682.58	726.01	765.75	825.41	665.04	620.36	641.14	746.88	747.21	

[a] Straits of Florida pH are nighttime values, at the surface they should be about 8.2 to 8.3 during the day. Eh, pH, and specific gravity are field values; chlorine and alkalinity are averages of accepted field and laboratory determinations; salinity equals 0.03+1.805×chlorinity; all other values are from laboratory determinations given in table 25. A_t (titration alkalinity) approximates HCO_3 as conventionally reported.

[b] After Sverdrup and others (1946, p. 173) and Rubey (1951, p. 1126); recalculated to rounded mg/l at 28°C with minor recombination for comparison with waters to left, and with correction for new Ca and Sr values. The difference of 2 me/l between anions and cations is attributable to 1.11 me/l boron plus 0.89 me/l conversional discrepancy. It provides a more realistic comparison with reported analytical imbalances in real waters to leave the "normal" figures unbalanced than to adjust them into conformity. The reader will recognize, also, that most of the analytical data, and the converted data for "normal" sea water are given to more places than are significant. This is simply the way the new data were recorded, and it seems better to leave them that way in the tables, and to treat comparative data in the same manner.

[c] Includes bromine, fluorine, and iodine.

[d] Value probably too high; should analyze 13,200 if Cl correct.

[e] Ca from visual versene titration runs about 10 percent too low and Mg by difference from Ca correspondingly about 4 percent high.

[f] Value probably too high; should analyze 1,590 if Cl correct.

[g] Carpenter value by ion-exchange photometric titration 433.4.

[h] Carpenter value by ion-exchange photometric titration 490.8.

[i] Total dissolved solids given as arithmetic sum of averages, and also computed from Lyman-Fleming equation: Σ ‰ =0.073+1.8110 chlorinity (Sverdrup and others, 1946, p. 172).

TABLE 5.—*Data for computation of average water properties*

[pH, Eh, and specific gravity are field values; Cl mg/l, chlorinity, and alkalinity are averages of accepted field and laboratory determinations; salinity equals 0.03+1.805×chlorinity; all other values are from laboratory determinations given in table 25. Ca values are about 10 percent too low, and Mg values about 4 percent too high, as explained in text]

Station	Field T°C	pH	Lab. T°C	Eh (volts)	Hydrometric specific gravity		Salinity (°/oo)	Chlorinity (Cl °/oo)	Cl mg/l	Titration alkalinity (A_t me/l)	SO_4 (mg/l)	Na (mg/l)	Mg (mg/l)	Ca (mg/l)	K (mg/l)	Sr (mg/l)	B (mg/l)	P (mg/l)	SiO_2 (mg/l)
					Field T	20° C													
BANK STATIONS																			
Alkalinity >2.2 (11 stations)																			
A1	27.25	8.10	30.0	+0.44	1.0239	1.0259	36.69	20.31	20,800	2.35	2,930	11,600	1,580	420	400	4.9	4.5	0.016	1.5
2	28.50	8.12	28.5	.45	1.0248	1.0271	38.08	21.08	21,600	------	3,000	11,800	1,620	400	430	7.8	4.7	------	.8
B8	27.75	8.10	30.0	.18	1.0251	1.0272	37.79	20.89	21,400	2.42	2,970	11,500	1,620	410	420	4.0	4.6	.040	.8
D7	28.75	8.20	28.0	.24	1.0258	1.0283	38.57	21.35	21,900	2.34	3,090	12,100	1,660	420	450	7.7	4.7	<.010	.9
8	28.50	8.20	27.0	.24	1.0255	1.0279	37.86	20.96	21,500	2.40	2,950	11,900	1,620	410	430	6.5	4.4	------	------
9	27.25	8.15	30.0	.27	1.0242	1.0263	36.87	20.41	20,900	2.40	2,930	11,400	1,580	410	410	3.9	4.2	.018	1.6
E1	28.00	8.18	25.8	.42	1.0256	1.0279	38.75	21.45	22,000	2.38	3,070	12,000	1,650	420	450	7.7	4.2	<.010	3.3
2	28.00	8.20	29.0	.38	1.0259	1.0282	38.73	21.44	22,000	------	3,130	11,900	1,630	430	430	9.0	4.8	<.010	.5
3	28.25	8.15	25.5	.39	1.0257	1.0281	39.64	21.94	22,500	2.42	3,070	12,000	1,660	420	440	7.7	4.4	<.010	3.7
4	28.25	8.12	27.8	.40	1.0252	1.0276	38.40	21.26	21,800	2.34	3,120	12,000	1,630	410	430	7.9	4.4	------	.4
5	28.50	8.18	28.2	.46	1.0258	1.0282	39.09	21.64	22,200	------	3,110	12,300	1,630	410	440	8.6	4.5	<.010	.5
Sum	309.00	89.70	309.8	3.87	11.2775	11.3027	420.47	232.63	238,600	19.050	33,070	130,500	17,880	4,560	4,730	75.7	49.4	------	14.0
Average	28.09	8.16	28.10	+.35	1.0253	1.0275	38.21	21.15	21,690	2.28	3,006	11,860	1,625	415	430	6.9	4.5	<0.010-0.044	1.4
Alkalinity 2.0–2.2 (26 stations)																			
A3	28.75	8.18	30.0	+0.47	1.0258	1.0283	39.79	22.03	22,600	2.11	3,140	12,400	1,690	430	440	6.1	4.7	0.016	0.9
4	28.75	8.18	28.5	.31	1.0260	1.0285	39.61	21.93	22,500	2.05	3,110	12,400	1,650	420	450	7.4	4.7	<.010	.7
5	29.00	8.18	29.5	.32	1.0265	1.0291	40.12	22.21	22,800	2.12	3,180	12,600	1,690	420	460	9.4	4.9	------	.9
6	28.75	8.15	26.0	.26	1.0269	1.0294	41.51	22.98	23,600	2.07	3,210	12,800	1,760	430	460	6.6	5.2	.019	1.2
7	28.50	8.12	30.0	.32	1.0276	1.0300	41.13	22.77	23,400	2.06	3,320	12,700	1,800	440	460	8.8	5.0	.044	1.7
8	28.00	8.00	------	.46	1.0273	1.0296	39.04	21.61	22,200	2.06	------	------	------	------	------	------	------	------	------
B7	28.75	8.10	28.0	.20	1.0278	1.0302	41.65	23.06	23,700	2.08	3,250	13,100	1,760	480	470	8.6	5.3	<.010	------
C4	28.50	7.95	------	.29	1.0274	1.0299	40.79	22.58	23,200	2.00	------	------	------	------	------	------	------	------	------
5	28.00	7.95	28.0	.26	1.0271	1.0294	41.15	22.78	23,400	2.04	3,250	12,900	1,720	440	460	7.5	5.4	<.010	1.1
D3	28.00	8.05	27.0	.30	1.0270	1.0293	40.99	22.69	23,300	------	3,240	12,800	1,710	440	450	6.9	5.1	------	------
4	28.00	8.08	29.5	.22	1.0263	1.0286	39.78	22.02	22,600	------	3,210	12,600	1,680	420	450	7.5	4.3	<.010	.8
5	28.50	8.10	27.0	.22	1.0259	1.0283	38.91	21.54	22,100	2.07	3,020	12,100	1,650	430	430	6.3	5.0	------	------
6	28.75	8.05	31.0	.21	1.0261	1.0286	39.43	21.83	22,400	2.12	3,060	12,500	1,720	430	450	------	5.9	------	7.0
E6	28.75	8.175	27.8	.42	1.0259	1.0284	38.57	21.35	21,900	2.18	3,170	12,000	1,660	400	450	8.0	5.2	<.010	.7
7	28.75	8.10	27.5	.45	1.0263	1.0288	39.25	21.73	22,300	2.13	3,180	12,300	1,700	410	450	9.3	4.6	.016	.6
8	28.00	8.10	27.0	.34	1.0285	1.0308	42.84	23.72	24,400	2.12	3,300	13,600	1,820	450	480	8.6	5.2	------	------
9	28.25	8.10	27.0	.37	1.0290	1.0314	43.89	24.30	25,000	------	3,370	13,500	1,860	440	490	9.7	5.9	<.010	1.3
9a	27.00	8.20	27.0	.29	1.0301	1.0320	43.48	24.07	24,800	2.13	3,410	13,900	1,880	460	500	7.6	5.5	------	------
F1	28.00	8.10	27.8	.34	1.0266	1.0289	39.23	21.72	22,300	2.14	3,120	12,400	1,690	400	450	7.6	4.6	<.010	.8
2	28.25	8.18	28.0	.38	1.0272	1.0296	40.10	22.20	22,800	2.13	3,280	12,900	1,720	450	460	7.4	5.1	<.010	.9
3	28.25	8.20	26.5	.39	1.0269	1.0293	40.46	22.40	23,000	2.11	3,200	12,700	1,690	430	460	8.6	4.8	<.010	.8
4	28.50	8.05	27.0	.38	1.0260	1.0284	39.96	22.12	22,700	2.13	3,180	12,500	1,720	420	460	9.2	4.9	.020	1.2
5	29.00	8.10	27.0	.39	1.0259	1.0285	39.61	21.93	22,500	2.16	3,220	12,200	1,650	400	450	8.4	4.0	<.010	3.7
6	29.00	8.05	27.5	.36	1.0259	1.0285	39.61	21.93	22,500	2.16	3,120	12,100	1,710	400	450	6.3	4.4	.023	4.6
7	28.75	8.05	28.2	.30	1.0261	1.0286	38.91	21.54	22,100	2.06	3,150	12,300	1,650	410	450	8.2	4.7	<.010	3.5
G1	28.75	8.00	26.5	.26	1.0261	1.0286	39.43	21.83	22,400	------	3,120	12,300	1,680	400	460	7.7	4.8	------	------
Sum	739.50	210.50	669.3	8.61	26.6982	26.7610	1,049.24	580.87	596,500	46.23	76,810	303,600	41,260	10,250	10,990	181.7	109.2	------	32.4
Average	28.44	8.10	27.88	+0.33	1.0269	1.0292	40.35	22.34	22,940	2.10	3,200	12,650	1,719	427	458	7.9	4.6	<0.010–0.044	1.7
Alkalinity <2.0 (19 stations)																			
A9	28.00	8.00	26.0	+0.26	1.0268	1.0291	40.10	22.20	22,800	------	3,180	12,700	1,770	420	460	6.9	4.4	------	------
10	28.25	8.00	30.0	.30	1.0270	1.0294	41.69	23.08	23,700	1.88	3,270	12,800	1,740	420	470	9.8	5.1	<0.010	0.9
11	29.00	8.10	27.0	.31	1.0288	1.0313	43.53	24.10	24,800	1.87	3,510	13,600	1,860	450	490	8.7	5.3	< .010	.9
B1	29.00	7.95	26.5	.34	1.0281	1.0306	42.34	23.44	24,100	------	3,460	13,400	1,800	430	480	8.1	5.8	------	------
2	29.00	8.00	26.8	.28	1.0283	1.0308	43.21	23.92	24,600	1.91	3,400	13,600	1,810	450	480	8.2	5.2	------	------
3	28.00	8.00	31.0	.32	1.0296	1.0318	45.61	25.25	26,000	1.78	3,580	13,800	1,960	490	530	------	5.5	------	4.4
4	28.00	8.00	27.0	.22	1.0285	1.0307	42.68	23.63	24,300	1.84	3,360	13,100	1,810	440	480	9.8	5.2	<.010	.9
5	28.75	8.05	31.0	.22	1.0286	1.0310	42.50	23.53	24,200	1.85	3,500	13,600	1,870	460	480	------	6.0	------	5.0
6	29.00	8.10	26.5	.20	1.0281	1.0306	41.64	23.05	23,700	1.95	3,450	13,200	1,750	450	470	7.5	4.6	------	------
C1	29.00	8.00	28.5	.30	1.0275	1.0300	41.65	23.06	23,700	1.97	3,330	13,100	1,760	430	460	8.0	------	<.010	.6
2	29.00	8.05	29.5	.21	1.0278	1.0303	41.65	23.06	23,700	1.96	3,360	13,300	1,780	420	470	9.7	5.0	<.010	.9
3	29.00	8.08	28.2	.20	1.0277	1.0302	41.31	22.87	23,500	1.93	3,380	13,300	1,750	420	480	7.9	4.8	<.010	.5
6	28.00	7.95	31.0	.24	1.0278	1.0300	41.83	23.16	23,800	1.98	3,280	13,000	1,800	450	470	------	5.8	------	4.3
7	29.25	8.00	31.0	.30	1.0309	1.0336	46.60	25.80	26,600	1.78	3,650	14,600	2,040	500	550	------	6.3	------	7.4

D1	27.25	8.00	27.0	.24	1.0304	1.0324	44.18	24.46	25,200	1.98	3,560	14,200	1,890	450	500	7.9	6.1		
2	27.75	8.02	26.0	.26	1.0283	1.0303	41.64	23.05	23,700		3,280	13,100	1,800	440	470	6.3	4.6	.012	.9
G2	28.25	8.02	27.5	.34	1.0273	1.0296	40.44	22.39	23,000	1.98	3,210	12,600	1,730	420	470	6.4	4.9	<.010	4.3
3	28.25	7.95	27.5	.35	1.0280	1.0302	41.64	23.05	23,700	1.90	3,300	13,000	1,780	430	480	6.8	4.9	.023	4.4
4	28.75	8.10	25.8	.31	1.0289	1.0313	42.48	23.52	24,200	1.94	3,460	13,400	1,820	440	520	6.2	4.8	<.010	4.4
Sum	541.50	152.37	533.8	5.20	19.5384	19.5832	806.72	446.62	459,300	30.50	64,520	253,400	34,520	8,410	9,210	118.2	94.3		39.8
Average	28.39	8.02	28.09	+0.27	1.0284	1.0307	42.45	23.50	24,170	1.91	3,396	13,340	1,817	443	485	7.9	5.2	<0.010-0.023	2.8
Grand total	1,590.00	452.57	1,512.9	17.68	57.5141	57.6469	2,276.43	1,260.12	1,294,400	95.78	174,400	687,500	93,660	23,220	24,930	375.6	252.9		86.2
Grand average	28.39	8.08	28.02	+0.32	1.0271	1.0294	40.64	22.50	23,110	2.08	3,230	12,730	1,734	430	462	7.7	4.8	<0.010-0.044	2.0

BANK-EDGE STATIONS

Surface

A1	27.00	8.10		+0.43															
B8	27.50	8.10	30.0	.19	1.0240	1.0265	37.05	20.51	21,000	2.43	2,890	11,300	1,580	400	420	4.3	4.5	0.048	0.5
D8	28.50	8.20		.23	1.0253	1.0277	37.52	20.77	21,300	2.44									
D9	27.50	8.10	30.0	.27	1.0242	1.0263	36.33	20.11	20,600	2.38	2,870	11,400	1,570	410	400	2.3	4.1	.025	1.2
E1	28.00	8.15	25.0	.40	1.0258	1.0280	38.39	21.25	21,800	2.39	3,020	11,900	1,670	430	450		4.0	<.010	3.3
E2	28.00	8.20	29.0	.32	1.0259	1.0281	38.57	21.35	21,900	2.40	3,130	11,900	1,630	430	430	9.0	4.8	<.010	.5
Sum	166.50	48.85	114.0	1.84	5.1252	5.1366	187.86	103.99	106,600	12.04	11,910	46,500	6,450	1,670	1,700	15.6	17.4		5.5
Average	27.75	8.14	28.5	+0.31	1.0251	1.0273	37.57	20.80	21,320	2.41	2,977	11,620	1,612	417	425	5.2	4.4	<0.010-0.048	1.4

Bottom

A1	27.50	8.10	30.0	+0.45	1.0238	1.0259	36.71	20.32	20,800	2.34	2,930	11,600	1,580	420	400	4.9	4.5	0.016	1.5
B8	28.00	8.10	30.0	.18	1.0255	1.0277	38.22	21.16	21,700	2.40	3,050	11,800	1,660	420	430	3.7	4.8	.033	1.3
D8	28.50	8.20	27.0	.25	1.0256	1.0280	38.04	21.06	21,600	2.38	2,950	11,900	1,620	410	430	6.5	4.4		
D9	27.00	8.20	30.0		1.0244	1.0263	36.85	20.40	20,900	2.42	2,980	11,400	1,590	420	430	5.5	4.2	.012	1.1
E1	28.00	8.20	26.5	.44	1.0256	1.0278	38.93	21.55	22,100	2.36	3,120	12,100	1,640	400	440	7.7	4.5		
E2	28.00	8.20		.44	1.0260	1.0282	39.09	21.64	22,200										
Sum	167.00	49.00	143.0	1.76	6.1509	6.1639	227.84	126.13	129,300	11.90	15,030	58,800	8,090	2,070	2,130	28.3	22.4		3.9
Average	27.83	8.17	28.60	+0.33	1.0251	1.0273	37.97	21.02	21,550	2.38	3,006	11,760	1,618	415	426	5.7	4.5	<0.010—0.033	1.3

STRAITS OF FLORIDA

Surface

GSx	29.50	8.05	26.5	+0.37	1.0234	1.0262	36.18	20.03	20,500	2.46	2,930	11,300	1,550	390	420	7.1	4.0		
GSy	27.50	8.00	26.5	.30	1.0240	1.0261	36.17	20.02	20,500	2.39	2,890	11,400	1,510	400	410	7.4	3.3		
GSZ	28.00	8.00	26.5	.28	1.0235	1.0257	35.67	19.74	20,200	2.43	2,910	11,100	1,550	380	400	6.7	4.2		
Gsα	27.00	8,10	30.0	.29	1.0239	1.0258	35.64	19.73	20,200	2.49	2,950	11,400	1,490	390	400	6.5	4.0	0.025	0.8
Gsγ	27.50	8.05	26.5	.33	1.0239	1.0260	35.99	19.92	20,400	2.37	2,860	11,300	1,520	380	420	6.9	4.1		
Sum	139.50	40.20	136.0	1.57	5.1187	5.1298	179.65	99.44	101,800	12.14	14,540	56,500	7,620	1,940	2,050	34.6	19.6		
Average	27.90	8.04	27.20	+0.31	1.0238	1.0260	35.93	19.89	20,360	2.43	2,908	11,300	1,524	388	410	6.9	3.9	.025	.8

Bottom

GSx	25.00	7.80	26.5	+0.33	1.0239	1.0263	35.64	19.73	20,200	2.38	2,880	11,200	1,500	400	410	7.2	4.2		
GSy	22.50	7.80	26.5	.29	1.0254	1.0261	35.59	19.70	20,200	2.65	2,860	11,300	1,470	420	420	8.4	4.8		
GSz	21.00	7.70	26.5	.34	1.0250	1.0253	35.95	19.90	20,400	2.83	2,860	11,400	1,440	380	400	7.2	4.0		
gs	21.50	8.00	30.0	.42	1.0245	1.0249	35.62	19.72	20,200	2.52	2,840	11,100	1,490	370	400	9.0	4.1	0.270	1.8
GS	23.00	7.85	29.0	.29	1.0260	1.0268	34.32	19.00	19,500	2.73	2,860	11,200	1,520	400	400	8.1	4.7		3.2
Sum	113.00	39.15	138.5	1.67	5.1248	5.1294	177.12	98.05	100,500	13.11	14,300	56,200	7,420	1,970	2,030	38.9	21.8		4.0
Average	22.60	7.83	27.70	+0.33	1.0250	1.0258	35.43	19.61	20,100	2.62	2,860	11,240	1,484	394	406	7.8	4.4	.270	2.0

BIGHTS—SURFACE AND BOTTOM

19/X	28.0	8.30	27.0	+0.43	1.0257	1.0279	36.63	20.28	20,800	2.13	2,890	11,500	1,550	400	410	7.0	4.3	<0.010	1.1
20/1	28.2	8.10	29.0	.36	1.0270	1.0293	37.81	20.93	21,500	1.90	3,080	11,700	1,570	410	420	7.3	4.7	< .010	.9
Sum	56.2	8.40	56.0	.79	2.0527	2.0572	74.44	41.21	42,300	4.03	5,970	23,200	3,120	810	830	14.3	9.0		2.0
Average	28.1	8.20	28.00	+0.40	1.0264	1.0286	37.22	20.60	21,150	2.02	2,985	11,600	1,560	405	415	7.2	4.5	< .010	1.0

SALINITY AND ALKALINITY

Figures 3 to 5 show that the area west of Andros Island was the scene of elevated salinity, and chlorinity, not only in May 1955, but also in April 1939, and September 1938. This reflects the persistent sluggish water movement inferable from wind, current, and tidal patterns. In May 1955 minimum salinity was 36 to 37°/oo along the bank edge and in the adjacent straits. Over the bank this increased to generally over 39°/oo (that of the Red Sea), to a midbank peak of 45.5°/oo, and to a maximum of 46.5°/oo along shore at the western apex of Andros Island. Moreover, the sites of peak salinity in 1938, 1939, and 1955 are in the same general area of stagnation—toward the central part of the bank waters north from the western apex of Andros Island and locally along the shore. The most conspicuous feature of the pattern is the westward extending prong of hypersaline water that appears, when contoured, as if it were being squeezed between the opposing masses of more nearly normal water which reach across the bank from the northeast and southwest.

From Dittmar's ratios based on analyses of 77 water samples collected on the first *Challenger* Expedition (1872–76) and from subsequent research (Sverdrup and others, 1942, pp. 166, 196), oceanographers have come to rely on the chloride content of the sea as an index to other ions present. Of special interest in the present work is the ionic complex referred to as alkalinity, consisting of various weak anions, which may behave as weak acids or Brønsted bases, according to whether they yield or take up protons (H^+ ions). Alkalinity is most commonly expressed in milliequivalents per liter of hydrogen ion required to balance out these substances, as determined from titration with 0.02 normal HCl or H_2SO_4 to a sharp break in the potentiometric curve at pH 4.5. In normal sea water this titration alkalinity varies directly as 0.123×chlorinity (or 0.12×chlorosity), and this ratio was confirmed for the Straits of Florida by the present work. Over the bank itself, however, alkalinity varies inversely as chloride and salinity (fig. 6), indicating a condition that runs counter to simple concentration effects. Apparently the anions which determine alkalinity are being lost across the bank, and chief among these is bicarbonate (HCO_3^-). As this is the mother ion of carbonate (CO_3^{--}), with 2 negative charges (2 excess electrons), it is presumably being withdrawn in some way in combination with something that carries 1 or 2 positive charges; and, as will be shown later, the same water undergoes a parallel and nearly equivalent loss of the divalent calcium cation.

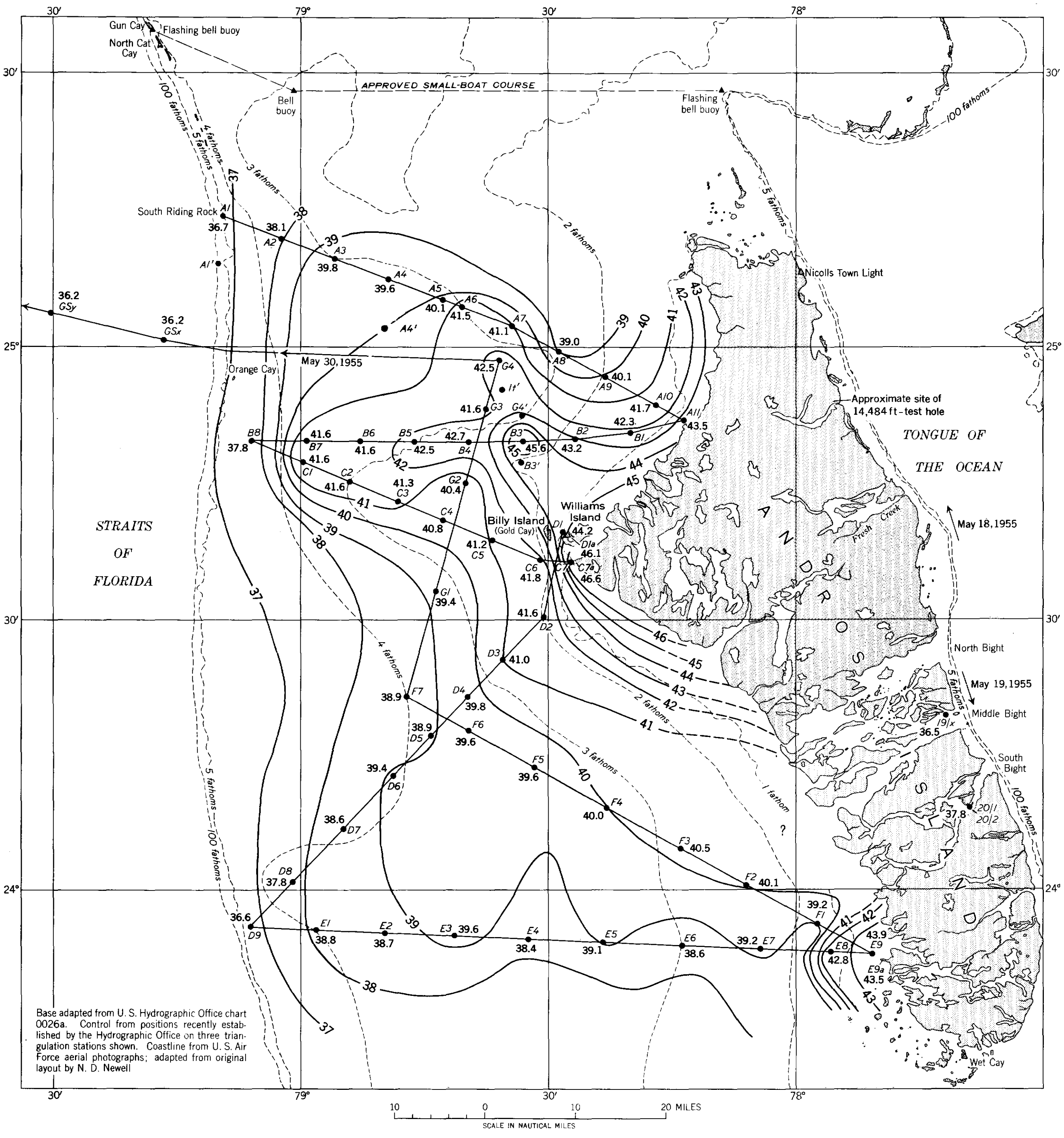
TEMPERATURE, pH, AND Eh

The calcium carbonate system is also affected by the temperature and hydrogen ion activity of the water. Temperature affects the total CO_2 that can be held in solution, and thereby partial pressure of CO_2, pH, and alkalinity. Hydrogen ion activity (aH), inversely expressed as pH ($\log_{10}$ of reciprocal of aH) and affected by many factors other than temperature, is an index to the relative concentration of the alkalinity components in the well-buffered marine waters. These relations are expressively diagrammed by Sverdrup and others (1942, fig. 40) and are very simply shown by Harvey (1955, fig. 63), whose diagram is reproduced as present figure 7. This indicates that, owing to loss of H^+ by HCO_3^- ions, the CO_3^{--} component of alkalinity increases rapidly with increasing pH (decreasing H^+) from zero at pH 7. It assumes that other factors remain equal, which they never quite do, but deviations of other components over their observed range in the sea affect only degree and not direction of change. Another important index, oxidation-reduction potential (Eh), expresses, among other things, the balance between O_2 and CO_2 in the system measured.

The temperature of the shallow waters west of Andros Island is strongly dependent on that of the air. In the late spring of both 1955 and 1956, it averaged about 28.5° C, falling to 27° in the shallower parts at night and rising to 29.5° during a hot day. The average temperature at 5 late evening and night stations across the Straits of Florida was 28°; so there is little variation from straits surface water to bank water at this time of year. Records published by C. L. Smith (1940, p. 156–158) show that waters in Middle Bight reach a maximal early morning average of 29.7° C in August and a minimal average of 21.6° in December, trailed by an average oceanic high of 28° to 29° in October and a minimal oceanic average near 23° about February. Air temperatures in the area may rise as high or 36.7° C (table 1).

The pH shows a slight general decline from about 8.15 at the bank edge to 8.02 at bank stations of lowest alkalinity. Because Straits of Florida stations were all read at night, they are lower for the surface waters than daytime readings would be, owing to photosynthetic withdrawal of CO_2 during daylight hours. The straits averages read are 8.07 for surface waters and 7.83 for bottom waters.

Oxidation-reduction potentials of the water averaged about +0.3 volts as read on the banks in 1955. Lowest Eh was found at sites of low pH, but values were everywhere relatively high positive, in both surface and



EXPLANATION

——— 38 ———

Line of equal salinity, in parts per thousand, based on international chlorinity ratio $S = 0.03 + 1.805 \times Cl$ ‰

Values are generally consistent with and more regular than total dissolved solids or hydrometric salinity determinations tabulated under stations. Chlorinity values employed are average of field and laboratory, surface and bottom waters

----- *3 fathoms* -----

Generalized bathymetric contour, based on fathograms and spot soundings along lines of traverse, May 1955

—●*B6*—●*B5*—

Line of traverse, showing location of May 1955 sample stations; traverse is in direction of increasing numbers. Check stations *A1′*, *A4′*, *B3′*, *G4′*, and *It′* occupied June 1956

● *20/1*

Bight station

May 19, 1955 ⟶

Location, direction, and date of plankton tow

FIGURE 3.—Areal differences in salinity west of Andros Island, May 1955.

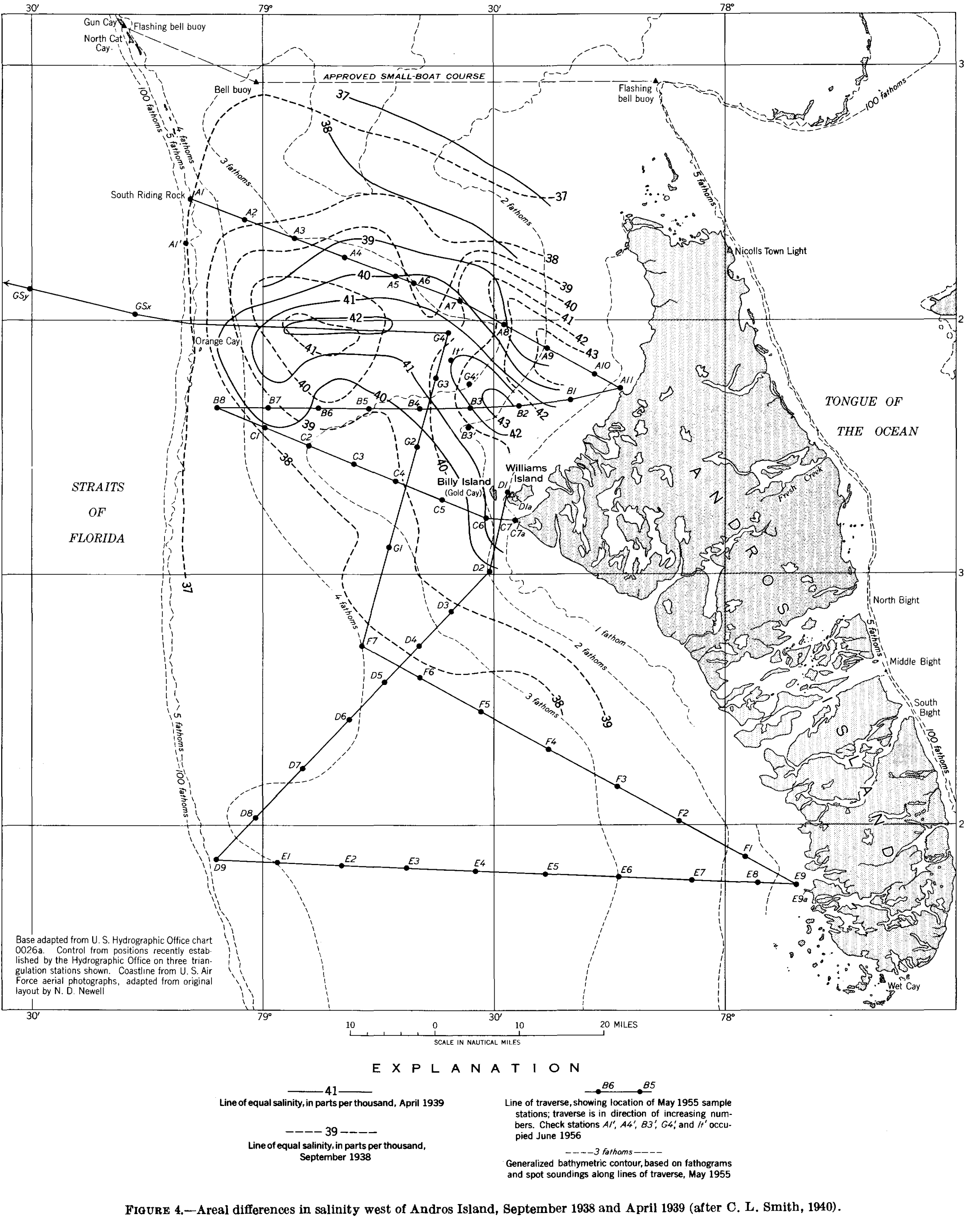
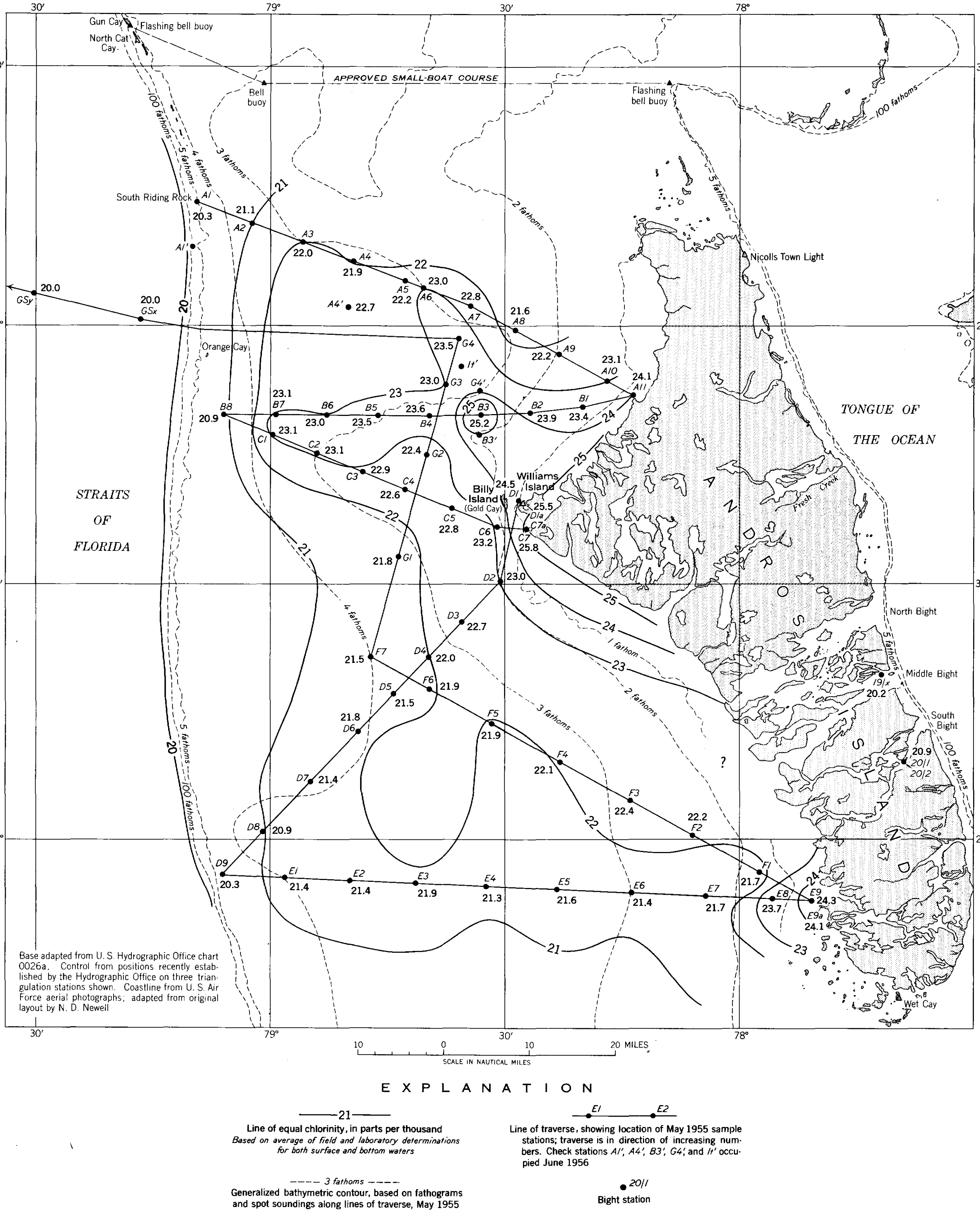


FIGURE 4.—Areal differences in salinity west of Andros Island, September 1938 and April 1939 (after C. L. Smith, 1940).



Base adapted from U. S. Hydrographic Office chart 0026a. Control from positions recently established by the Hydrographic Office on three triangulation stations shown. Coastline from U. S. Air Force aerial photographs; adapted from original layout by N. D. Newell

EXPLANATION

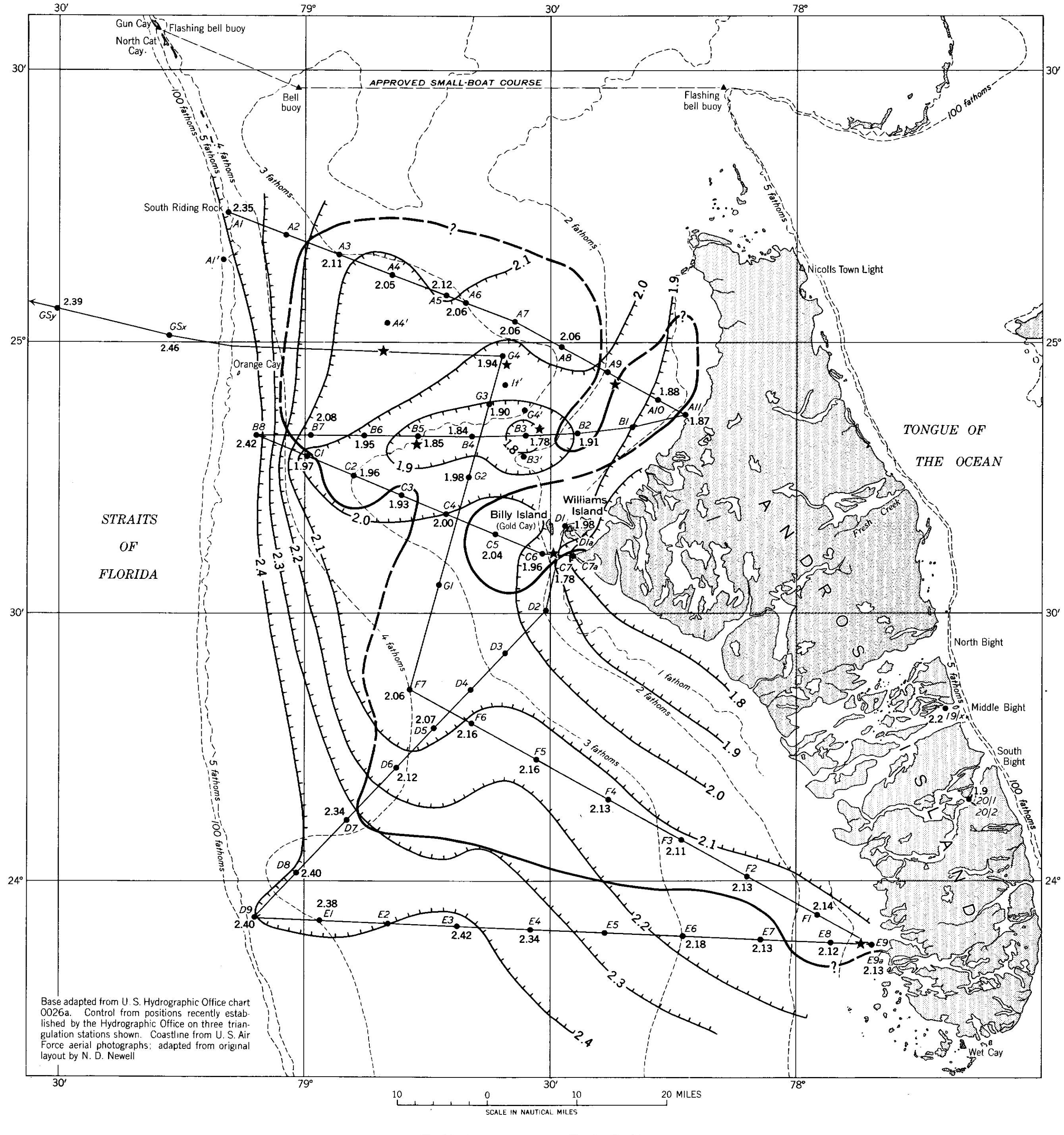
——21—— Line of equal chlorinity, in parts per thousand
Based on average of field and laboratory determinations for both surface and bottom waters

—●E1——●E2 Line of traverse, showing location of May 1955 sample stations; traverse is in direction of increasing numbers. Check stations A1′, A4′, B3′, G4′, and It′ occupied June 1956

---- *3 fathoms* ---- Generalized bathymetric contour, based on fathograms and spot soundings along lines of traverse, May 1955

● *20/1* Bight station

FIGURE 5.—Areal differences in chlorinity west of Andros Island, May 1955.



EXPLANATION

2.2

Contours showing titration alkalinity in milliequivalents per liter

Average of surface and bottom values at the 45 stations where accepted field and laboratory determinations agree within 3 percent. Interval 0.1 milliequivalents per liter Contours hachured on side of decreasing alkalinity

Line enclosing negative and low positive (<0.1v) field values of top sediment Eh

★

Salinity highs 1938-55

Values exceed 41 parts per thousand

– – – – 3 fathoms – – – –

Generalized bathymetric contour, based on fathograms and spot soundings along lines of traverse, May 1955

B6 B5

Line of traverse, showing location of May 1955 sample stations; traverse is in direction of increasing numbers. Check stations *A1′*, *A4′*, *B3′*, *G4′*, and *It′* occupied June 1956

● *20/1*

Bight station

FIGURE 6.—Areal differences in alkalinity of water and oxidation-reduction potential (Eh) of sediment west of Andros Island, May 1955.

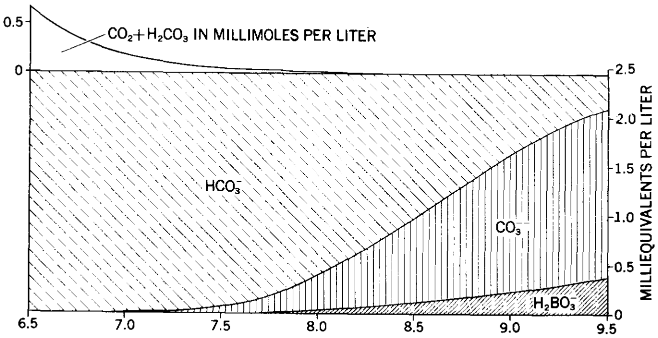


FIGURE 7.—Change in alkalinity components of sea water with changing pH.

bottom waters. Readings were steady with little or no needle drift, indicating well-poised conditions.

The possible significance of these values will be considered in an interpretative section.

DIURNAL AND DEPTH VARIATIONS

Systematic study of diurnal changes in the water chemistry was not undertaken during the fieldwork here reported and the few observations made add little to previous knowledge. As has been found elsewhere, pH trended downward at night. Eh seemed to show a slight but irregular tendency to rise at night, as pH fell. However, as Eh varies with O_2 and pH inversely with CO_2, Eh and pH would be expected to rise and fall together, as implied by areal relations.

Although systematic variation with depth was not expected in these shallow waters, surface and bottom samples were nevertheless separated and analyzed separately. The results confirmed the absence of significant variation, and analyses of surface and bottom waters over the banks are treated as essentially duplicate analyses. Only at the bank margins was there a suggestion that the bottom waters are a little saltier and heavier than the local surface water (table 4), possibly indicating basal outflow there.

WHITINGS

A striking feature of the waters west of Andros Island is the occurrence of isolated small areas of milk-white water locally known as whitings (pl. 2*B–C*). It is surprising to see such contrasts with the surrounding sea in an area where the water is everywhere somewhat opalescent from suspended matter, and where there is no boat traffic to disturb the bottom. These whitings are, in fact, so distinctive and interesting a feature of the bank waters that it is worth considering them in some detail, even though they cover only a small fraction of the total bank area at any given time.

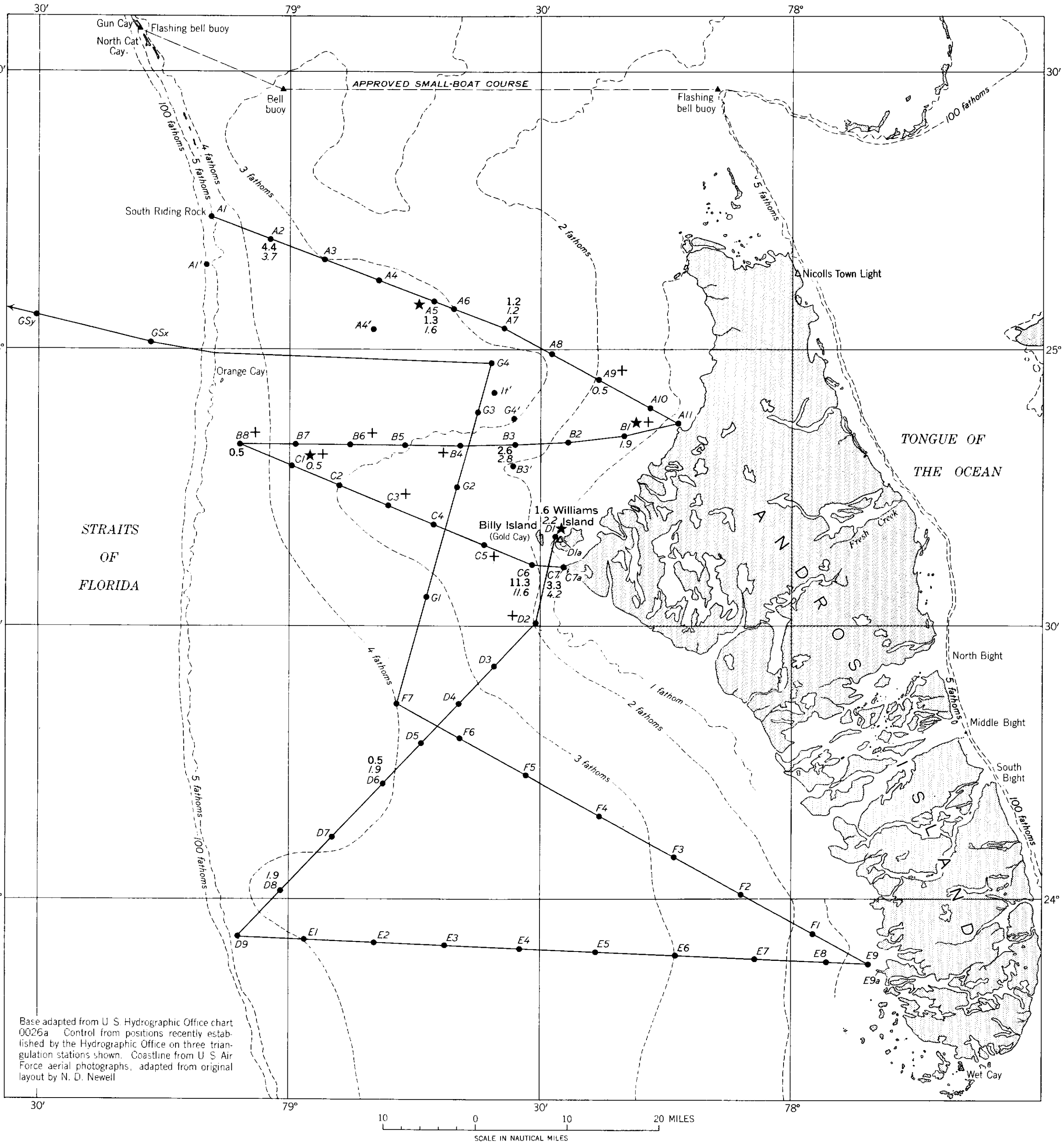
Whitings can evidently originate in different ways. We made them many times by stirring up the bottom with the *Physalia*'s propeller or by dragging anchor. Underwater springs, gas outbursts from bottom sediments, or unusual local meterologic conditions might produce identical effects. Very similar appearing clouds of sediment are stirred up by schools of bottom feeding fish, such as the mullet that produce the "fish muds" of Florida Bay (Ginsburg, 1956, p. 2398). Chemical precipitation from supersaturated water might also start at centers of nucleation or CO_2 evasion which would appear at first as whitings, then gradually spread and dissipate. Even bare-topped underwater dunes (pl. 2*A*) surrounded by darker vegetated bottom or appreciably deeper water simulate the appearance of whitings from a distance. The examination of individual whitings is needed to determine in any given area what features they may share in common and wherein they differ.

Three whitings were studied in the field, station spacing and course being altered slightly from plan to intercept them. The first two, at stations *A6* and *C6* were observed in 1955; the third, at station *It'* in 1956. At *A6* the *Physalia* was anchored at the center of a small whiting, but before preparations were completed to enter it, it had drifted away with a slight current to the south. An underwater inspection of the drifting margin showed the water to be unusually milky from suspended matter but revealed no local turbulence or bottom disturbance.

At station *C6*, anchor was set in the path of observed drift of a north to south elongated whiting about 1.6 km long, and 0.4 km wide. Suspension with free diving apparatus beneath its center gave the sensation of weightless fixity in the middle of a sunlit cloud bank. It was impossible, without resting motionless, to detect buoyancy and drift, or to tell up from down or sideways. The brilliant lighting was so dispersed that a hand, invisible at armslength, had to be kept extended to grope for bottom and avoid collision on surfacing. No fish were seen (or felt) nor was any other evidence of bottom disturbance found. The material in suspension was collected on a millipore filter and found on microscopic examination to consist entirely of aragonite needles (pl. 4*A*). The amount was equivalent to 11.5 milligrams per liter of water, which greatly exceeds any other value for suspended material left after rejection of those found to include Foraminifera or other extraneous objects (fig. 8).

Local squalls and barometric changes observed over the banks in May 1955 did not cause noticeable differences in the amount of suspended sediment in the water, although close attention was given to the possibility that they might.

The whiting observed at station *It'* in 1956 was come upon while we were attempting an approximate relocation of station *G4* of the previous year. The murkiest part of this north to south elongated whiting was about



EXPLANATION

4.4
3.7
Upright figure indicates milligrams per liter $CaCO_3$ in surface water; inclined figure indicates same data for bottom water

●
Stations where values were obtained by titrating Ca and Mg in acidified wash, subtracting Ca due to evaporation, as computed from Ca/Mg ratios of station water, and converting to $CaCO_3$ in liter volume

●★
Station at which values were obtained by direct weighing of suspended sediment on half of a millipore filter paper

●+
Stations for which one or more values were rejected when study of reserve half of filter paper showed Foraminifera, pellets, or aggregates. Others showed only aragonite needles, and organic matter which was eliminated by burning or acidifying

---- *3 fathoms* ----
Generalized bathymetric contour, based on fathograms and spot soundings along lines of traverse, May 1955

●*B6*—●*B5*
Line of traverse, showing location of May 1955 sample stations; traverse is in direction of increasing numbers. Check stations *A1′, A4′, B3′, G4′,* and *It′* occupied June 1956

FIGURE 8.—Distribution of suspended aragonite needles in 13 water samples west of Andros Island, May 1955.

4 km long by 0.8 km wide, with boundaries that seemed abrupt from a distance but actually graded to relatively clear water through a kilometer or so of less murky water on all sides. The vessel was first anchored at the center of the murkiest part, but was shortly moved to the clearer water at the whiting margin for bottom studies requiring better visibility. From first anchorage at 12:30 p. m., on June 11, until and after departure from the area 45 hours later at 9:00 a. m., June 13, we were within or in sight of this whiting, as it drifted back and forth with shifting tide. During about 6 hours under water within and at the edges of this whiting, no fish were observed other than the usual scattering of small *Halichoeres*, tiny *Eques* in and about the sponges, and, in the last 14 hours, five white sharks. No new whiting was observed to form in the neighborhood, as by the activities of a school of bottom-feeding fish that had been frightened off by the motors of the approaching boat.

Presumably accurate analyses of large samples from station *It′* revealed striking differences between the whiting water and that immediately and more distantly marginal to it. These are summarized from other parts of the text in table 6. The whiting water itself, after filtration of particles larger than 0.45 micron, analyzed significantly higher in calcium and phosphate and lower in alkalinity than that at its margins. Computations from other properties indicated relatively low partial pressure of CO_2 (P_{CO_2}) and high CO_2 evasion (ΔCO_2) in the whiting water. The pH of the whiting water also read higher, and oxygen evolved in Winkler bottles at the extraordinary rate of 1.5 milliliters per liter per hour, indicating a high rate of photosynthesis. Such high photosynthesis, probably resulting from the high phosphate content, would explain the high ΔCO_2 and low P_{CO_2} and alkalinity of the whiting water. As the large samples that showed these analytical differences were collected just before departure from the area, it is evident that chemically anomalous masses of water such as characterize the whiting at station *It′* can persist in such an environment for at least 45 hours without being eliminated by diffusion or mixing from without.

TABLE 6.—*Comparison of selected analytical and computed properties of water in and marginal to whiting at station* It′, *June 13, 1956*

	Whiting water	Marginal to whiting
Ca mg/l	490	477
Alkalinity mg/l	[1] 123	[1] 149
PO_4-P μg=atom/l	0.30	0.10
$P_{CO_2}\times 10^3$	0.35	0.51
ΔCO_2 mmole/l	0.31	0.16
pH	[1] 8.10	[1] 8.04
Salinity ‰	41.82	41.76

[1] Neither pH nor alkalinity was read in the field because of unsatisfactory operating conditions, and the water also stood for several days before filtration and analysis. Confidence cannot therefore be placed in the absolute values given, but they should be subject to comparable error.

Common characteristics of all whitings observed were their elongate form (pl. 2*B*) and tendency to drift with wind (pl. 2*C*) and tidal current. In one series of observations at *It′*, the whiting was seen to drift eastward against a light wind, and presumably with a 1-knot tidal current. The whiting of plate 2*C* streaks out westward from the main body in a strong easterly wind. The general elongation may reflect the opposing forces of tidal and wind-induced water movement. The whitings observed revealed no schooling fish, did not drift away from a fixed point or move erratically, and were not the sites of unusual continuing meteorologic or other disturbance. Rather they moved with the water mass as if a property of the water itself, and it seems that they may maintain their physical and chemical identity for days.

Two principal interpretations of these characteristics seem possible. The more likely calls on local and temporary bottom agitation resulting from such agencies as actively browsing animals, abrupt gas evasion, or highly localized meteorologic effects to stir up the saltier interstitial water and slightly phosphatic sediment [1] and mix it into the overlying water. Vigorous disturbances of this sort could account for the features observed, and these features might persist for a long time after their initial cause had been removed. In such case, some of the suspended aragonite would be stirred into suspension, and some precipitated as a result of the effect on the carbonate equilibria of CO_2 evasion due to acceleration of photosynthesis upon the introduction of sedimentary phosphate (and excess calcium ion). It seems unlikely that there would be sufficient local variation in phosphate content of the sediments to account for whitings as circumscribed areas of continuing precipitation that persist after general bottom disturbance following big storms.

Alternatively, such whiting waters might represent local masses of independently high phosphate and calcium content that have eddied upward from zones of turbulence along the steep bank margins or between opposing currents. To test this possibility, evidence should be sought of escape from depth of masses or streams of such water. The high salinity of the whiting water at station *It′*, however, minimizes the likelihood that such a mechanism could apply generally.

The possibility that the whitings might simply be local aragonite showers arising within a homogeneous water body is seriously weakened or eliminated by the higher calcium content of the whiting water as compared to surrounding water at station *It′*.

---

[1] Analyses of calcium carbonate mud from Middle Bight show 0.123 percent P_2O_5 and 0.054 percent N (Shattuck and others, 1905, p. 16, 171).

Any likely mechanism calls upon accelerated photosynthesis to play an important part in initiating and continuing a high rate of precipitation, a factor recalling a suggestion by Revelle and Fairbridge (1957, p. 258) that temporary morning clouding of still waters in the lagoon of Houtman's Abrolhos (southwestern Australia) might be due to photosynthetic reduction of CO_2 pressure. Such local sites of accelerated photosynthetic CO_2 uptake might well serve as triggering devices to induce more widespread $CaCO_3$ precipitation in the surrounding water mass.

BANK SEDIMENTS

GENERAL FEATURES

The mineralogy and mechanical properties of the sediments are the subject of exhaustive analysis in a following section by Blackmon; and previous investigations, together with much then new data for the surficial sediments, are summarized by Newell and Rigby (1957, p. 51–61, figs. 18–19). The present discussion is concerned with generalities only, as summarized in figures 9, 10, and 11. Questions to which answers were sought included the thickness of the unconsolidated sediments, proportion of aragonite and areal extent of aragonite muds, nature and distribution of the sedimentary components, chemistry of the interstitial waters, and resemblances to and differences from possibly comparable sediments of other areas.

Penetration of unconsolidated sediments by core barrel and probe at various places west of Andros Island establishes that they constitute a thin blanket of essentially pure calcium carbonate muds and sands, of which 88 to 94 percent is aragonite. Beneath is a slightly concave floor of porous limestone, now recrystallized to calcite, that is physiographically a very shallow rock basin between the outcrops of Andros Island and the line of limestone keys at the western bank edge. To judge from present data, the sediments are rarely more than 3 meters thick (fig. 9), unless it be where they fill deep local sinks in the old limestone surface—the ocean holes or blue holes of local parlance where unfilled. Continuous fathometer tracings along all cruising lines show that the sedimentary surface slopes almost evenly seaward at an average of 2 meters per 9 to 12 nautical miles to depths nowhere exceeding 10 meters and mainly less than 6 meters.

Aragonite mud may be conveniently defined as including those mainly aragonitic sediments which on mechanical analysis, have median diameter less than 0.09 mm and more than 20 percent by weight particles smaller than 2μ. This includes sediment classified in the field as limemuds and sandy or pelletal limemuds, and excludes those classified as muddy pellet sands and limesands. Mechanical analyses generally confirm the field classification of these sediments and allow them readily to be fitted into empirical categories as shown in table 7.

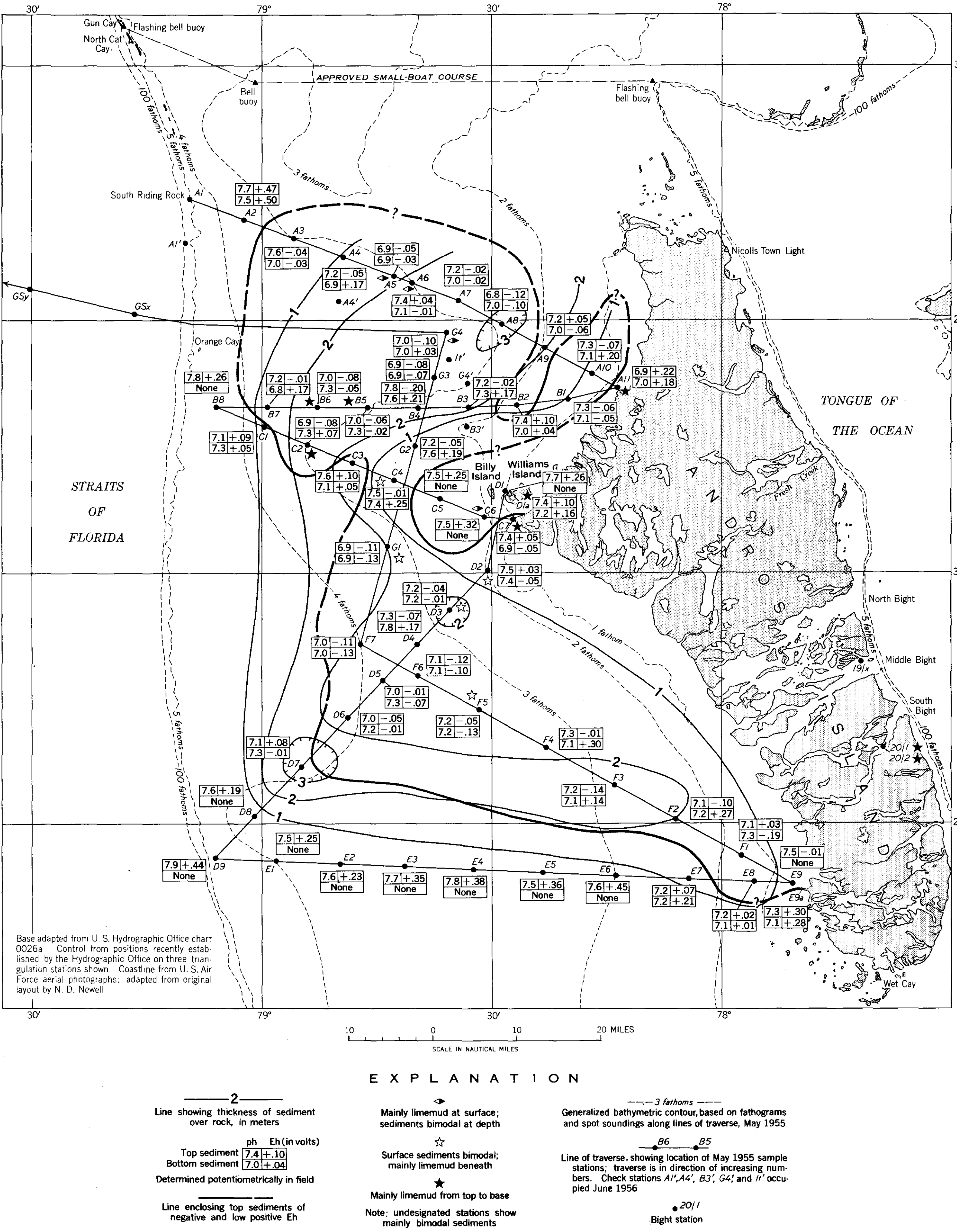
TABLE 7.—*Principal objective sediment types and their abundance*

Classification	Median diameter	Percent weight as particles $<2\mu$	Number of samples	Percent of samples
Limemud (aragonite mud)	<0.015	40–70	15	29
Slightly pelletal limemud	0.02–.04	25–40	3	6
Pelletal limemud	.04–.09	20–40	17	33
Muddy pellet sand	.09–.15	20–40	9	18
Slightly muddy pellet sand	.15–.2	13–15	2	4
Limesand	.2–.3	<13	5	10

This analysis brings out that two-thirds of all top sediments in the area studied are aragonite muds or pelletal limemuds, and nearly half of these include more than 40 percent by weight particles of smaller than 2 microns. The area occupied by such limemuds and pelletal limemuds is shown in figure 9 to differ somewhat from the limemud area outlined by Drew (1914). A striking correlation exists, however, between the present limemud boundary and a line enclosing sediments of negative and low positive Eh (<0.05 volt).

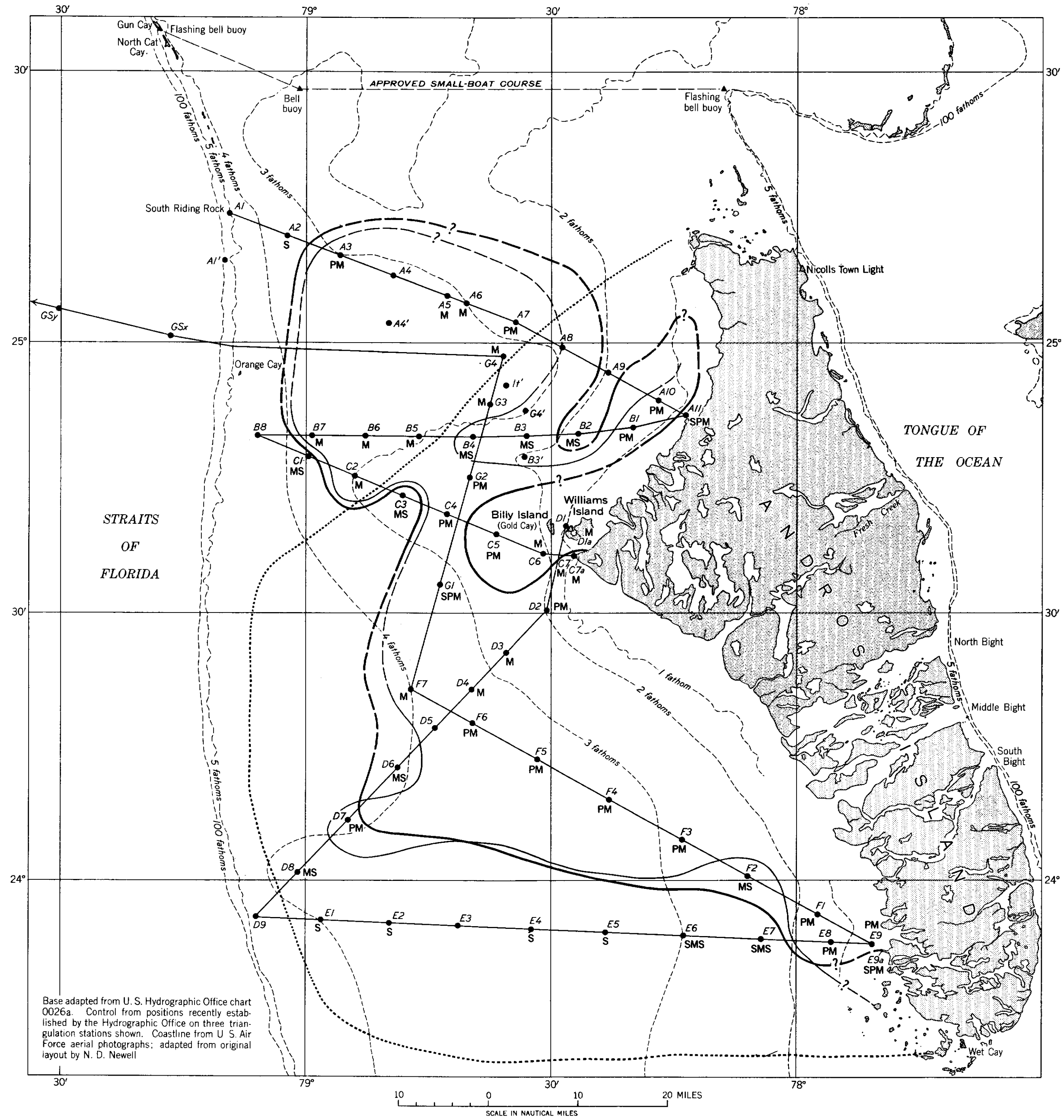
Within the limemud area, therefore, the sediments are prevailingly anaerobic to very low in oxygen. The pH of freshly collected sediments is generally below 7.8, ranging to slightly acid at 6.9. The data (fig. 9) do not show the systematic and reciprocal variation with depth between pH and Eh that might be predicted from the work of others on different sediment types (Emery and Rittenberg, 1952, p. 774–775; ZoBell, 1946a, p. 503). Possibly this is because the Bahaman samples are mostly from so near the surface that equilibrium is approximated, for in theory a low oxygen content should mean correspondingly low Eh and pH. The longest cores (*A8* and *D7*) do hint that below 3 meters pH may rise and Eh fall with depth, as ZoBell and Emery and Rittenberg have found.

High magnification reveals that the clay- and silt-sized fractions of these sediments abound in needles of aragonite 1 to 7 microns long and a fraction of a micron across; many are only 2μ or 3μ long; and some are as much as 15μ by 1μ. Electron micrographs and X-ray diffraction patterns show about 6 to 12 percent calcite, rare clay minerals, and ubiquitous traces of quartz. Most of the calcite contains some magnesium. Low-magnesian calcite (0–5 mole percent), logically interpreted by Blackmon as of complex detrital, organic, and possibly in part purely chemical origin is more abundant toward Andros Island and low in offshore cores; high-magnesian calcite (11–16 mole percent) is



Base adapted from U. S. Hydrographic Office chart 0026a. Control from positions recently established by the Hydrographic Office on three triangulation stations shown. Coastline from U. S. Air Force aerial photographs; adapted from original layout by N. D. Newell

FIGURE 9.—Thickness, pH, Eh, and changes with depth of sediment west of Andros Island, May 1955.



EXPLANATION

— — — — —
Line enclosing aragonitic sediments having median diameter <0.09 mm and more than 20 percent by weight of particles smaller than 2μ

——————
Line enclosing sediments of negative and low positive Eh

···············
Line drawn by Drew (1914) to enclose limemuds

Essentially all particles are calcium carbonate

M	Limemud (median diameter <0.015 mm; 40–70 percent of particles <2μ)
SPM	Slightly pelletal limemud (median diameter 0.02–0.04 mm; 25–40 percent of particles <2μ)
PM	Pelletal limemud (median diameter 0.04–0.09 mm; 20–40 percent of particles <2μ)
MS	Muddy pellet sand (median diameter 0.09–0.2 mm; 20–40 percent of particles <2μ)
SMS	Slightly muddy pellet sand (median diameter 0.15–0.2 mm; 13–15 percent of particles <2μ)
S	Limesand (median diameter 0.2–0.3 mm; < 13 percent of particles <2μ)

– – – – *3 fathoms* – – – – –
Generalized bathymetric contour, based on fathograms and spot soundings along lines of traverse, May 1955

B5 ● —— ● *B4*
Line of traverse, showing location of May 1955 sample stations; traverse is in direction of increasing numbers. Check stations *A1′, A4′, B3′, G4′,* and *It′* occupied June 1956

FIGURE 10.—Distribution of aragonite mud in top sediment west of Andros Island.

thought to be mostly of organic origin. No dolomite was found in any sample, although special watch was kept for it.

Mingled with the aragonite needles are small ovoid pellets and irregular bits of amalgamated finer grained material. These are believed to be mainly the fecal pellets or fragmentary fecal debris of various mud-ingesting organisms, and, in lesser amount, fragments of $CaCO_3$ that sheathed or impregnated algae. Through variations in proportion of mud and sand-sized grains, the sediment changes from sandy or pelletal limemud to muddy pellet sand. The rarity of intermediate sizes between pellets and needles produces strikingly bimodal grain-size distributions in mixed sediments. The proportion of sand-sized particles increases seaward, accompanied by rising pH as pore space and circulation of oxygen-bearing water increases, and also paralleled by an increasing but still fractional amount of skeletal debris. At the bank edge the sediments are well-oxygenated limesands having numerous skeletal fragments. Figure 11 diagrams the main steps in this progressive change and analyzes the distribution of important sedimentary components in selected individual samples.

COMPARISON WITH OTHER AREAS

Figure 11 shows that the sediments west of Andros Island differ greatly from Thorp's "average" sediment for the Bahama Banks, as well as from Straits of Florida samples. In contrast to the limemuds and bimodal mud and pellet mixtures that characterize the bank west of Andros Island, the straits samples are pelagic oozes having a high fraction of presumably authigenic montmorillonite filling foraminiferal tests, and Thorp's bank-composite shows a dominant skeletal fraction of shoal-water origin with a secondary clay-silt peak. Of the sediments west of Andros Island, only those of the western bank edge present a pattern even remotely resembling that of Thorp's samples, and his composite pattern would not show a clay-silt peak at all if the samples from the western side of South Bight were excluded from it (Thorp, 1936, figs. 6–7).

Ginsburg (1956, p. 2415–2418) compares the sediments west and east of Andros Island with those from Florida Bay and the Floridian reef tract, and in fact the reef-tract sediments from the two areas are very similar. The Florida Bay sediments differ from the true bank sediments west of Andros Island, however, in several apparently significant respects. They contain a very much higher proportion of molluscan and other skeletal debris, they are reported to contain only a small fraction of aragonite needles, and the fecal pellets in them seem to break down more readily than those west of Andros Island and may be of different origin. Certainly the nereidlike Floridian pelleting annelids figured by Ginsburg (1957, fig. 1) represent a different group of polychaetes from those believed to be most active in creating the commoner type of ovoid pellet west of Andros (pl. 6 *F–G*). In any case, the prevailing salinities of Florida Bay waters (Ginsburg, 1956, fig. 6) are so low that the mechanics of $CaCO_3$ origin there, whatever they are, necessarily operate in a very different milieu from that of the hypersaline environment west of Andros Island.

The fine-grained sediments at the center of the Persian Gulf (Houbolt, 1957, p. 56–59, 90–94) resemble the deposits west of Andros Island in their large percentage (40 to 43 percent) smaller than 2 microns. However, the Persian Gulf material is apparently mostly calcite, its insoluble residue content is very high, and it seems to be largely or wholly detrital. No deposits truly similar to the Bahaman aragonite muds are known from the Pacific or Indian Oceans either, although scattered aragonite needles have proved to be common enough in lagoonal sediments analyzed (for example, Lowenstam and Epstein, 1957, p. 364; Revelle and Fairbridge, 1958, p. 258), and McKee records a preponderance of aragonite, and "some aragonite needles," in richly foraminiferal plastic greenish limemuds that cover perhaps a square kilometer at depths below 60 meters in tiny (66 square kilometers) Kapingamarangi lagoon (McKee, 1958, p. 253, 271–272; 1956, p. 31–32; U.S. Hydrographic Office Chart 6042).

To conclude, although many shoal marine areas remain to be explored with care, a review of current knowledge indicates that the sediments west of Andros Island are unique among described modern marine deposits. Once comparable sedimentary provinces, however, may well be represented by some or many of the volumetrically important ancient aphanitic and pelletal limestones (Cloud and Barnes, 1948, p. 89).

INDIVIDUAL COMPONENTS

CLAY AND SILT FRACTIONS

Aragonite needles are the principal component of the sediment. Essentially all the clay fraction and a large part of the silt fraction is composed of them or their weakly bonded aggregates, representing well over half of the total sediment in the area (fig. 11). Similar aragonite needles are known to be formed both by purely physicochemical processes (pl. 4) and internally by codiacean and dasycladacean algae (pl. 5). Secondary biochemical effects such as photosynthetic withdrawal of CO_2 are certainly also important in their origin. The extent to which these and other factors may contribute to the sediment is discussed in a later section on "Origin of the sediments."

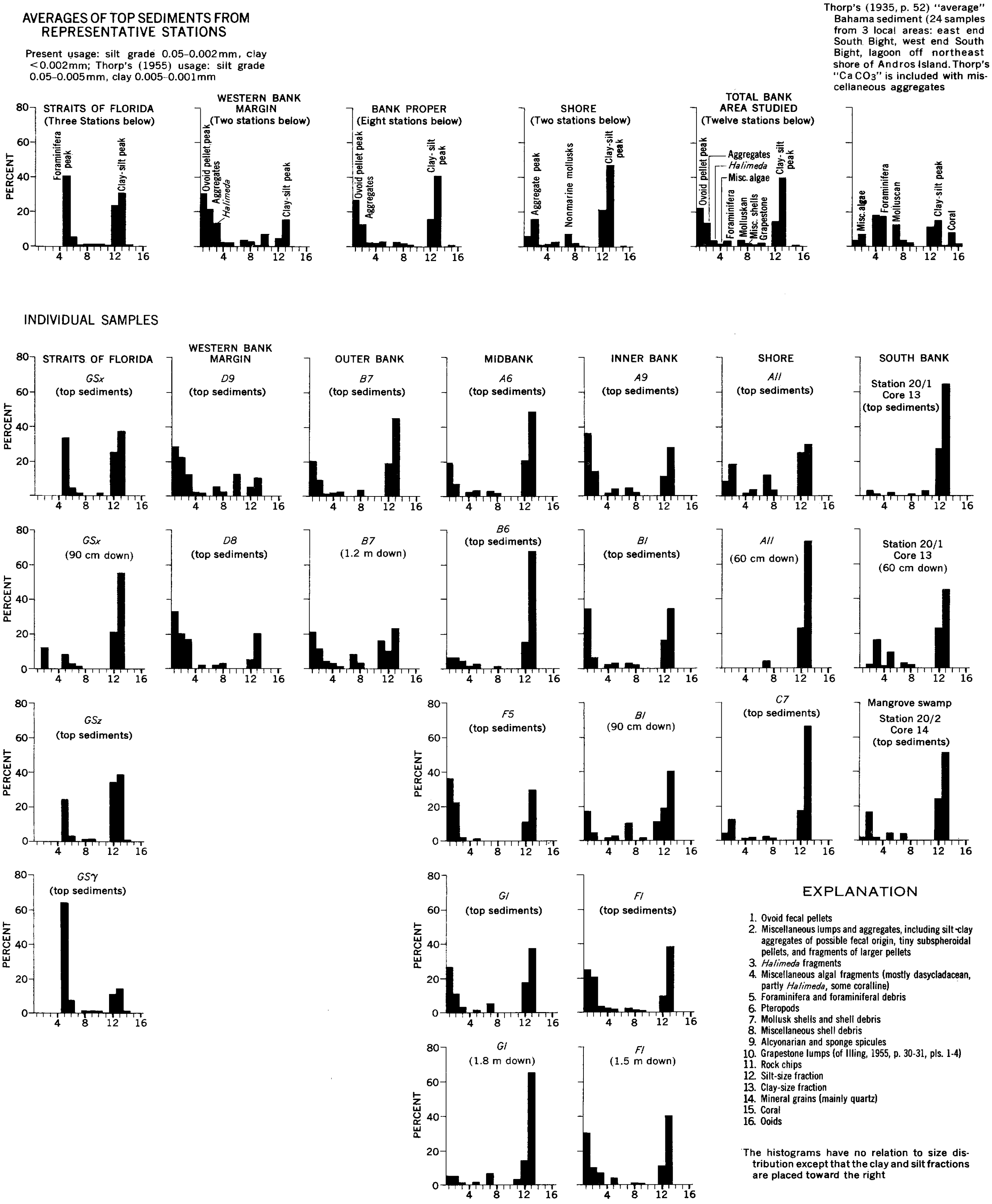


FIGURE 11.—Composition of representative sediments from west of Andros Island compared with deposits of adjacent areas.

Even in the samples from the bottom of the Straits of Florida, the large clay fraction is mostly, and the silt fraction partly, comprised of aragonite needles and their aggregates. It is not known whether, or to what extent, these aragonite needles come from the banks to the east or west or are perhaps precipitated directly from Straits of Florida surface water. Although none of the individual ovoid fecal pellets were seen in the straits samples, rare grapestone lumps (Illing, 1954, p. 30–31, pls. 1–2) at *GSx*, *GSy*, and *GSγ* indicate derivation in some way of some fraction of these sediments from banks at one side or the other. Didemnid tunicate spicules in the silt fraction and miliolid Foraminifera in the sand are other possibly shallow-water elements. Shoal sediment could, of course, be transported to depths by slides or turbidity currents from accumulations on the steep bank margins, but supporting evidence for such a mechanism was not found in the deep sediment. The needles might also have been winnowed in or settled from above, and the grapestone lumps could easily be carried to deep water on the original holdfasts of later floating sargassum. A high concentration of pelagic micro-organisms is characteristic of the sediments penetrated in this area.

Although the clay-sized fractions of bank and straits are generally similar to one another, the silt fractions are as distinctive as the contrasting pelletal and foraminiferal sands of the two environments. Silt-sized material in the straits includes coccoliths, discoasters, and rhabdoliths in equal total abundance with aragonite needles (pl. 9*D*), whereas not a single one of these pelagic forms (and rarely a pelagic foraminifer) was found in any of the many bank samples studied at high magnifications! Considering the broad interconnection between these two bodies of water and available data on nutrient distribution (table 2), such a pattern might logically be attributed to crowding toward the base of the photic zone by phytoplankton populations in the straits, in competition for mineral nutrients, and followed by the organisms that feed on them. A long-range plankton survey of the region, however, indicates that this is not what happens (Bsharah, 1957, p. 221, 224). Bsharah's data seem to require, instead, that live, test-secreting forms somehow avoid the banks, while the dead ones settle out of the weak bank-setting currents before they can be moved far beyond the straits edge. It is not known to what degree the nannoplankton of the straits and banks resemble one another, other than in their apparent general abundance.

Besides aragonite needles, the silt fraction of the bank (pls. 9*B*, 10) contains tiny lumps and clusters of uncertain origin, tiny ovoid fecal pellets (pl. 10*A*) and the minute burrlike spicules of didemnid tunicates, the "Calcarea" spicules of Illing (1954, p. 22–23, pl. 4, 9; Van Name, 1930, p. 428–444; Pobeguin, 1954, fig. 36; Deflandre and Deflandre-Rigaud, 1956; Cuvillier and Sacal, 1951, pl. 3) (pl. 7*K–L*, 10*A*). Many of the tiny lumps and clusters in the silt fraction are probably whole or fragmentary fecal pellets. Others may be physical aggregates of aragonite needles, for these show a marked tendency to cluster in tangential orientation about bubbles or larger objects on a wet slide.

Although diatom fragments occasionally showed up in electron-microscope scanning of sediment preparations, none were seen at ordinary high-magnification inspection of either straits or bank samples. Check samples from stations *GSx*, *C3*, *B3*, and *G3* were prepared and studied for diatoms by Kenneth Lohman, but none were found.

PELLETS

Ovoid pellets dominate the sand fraction, and altogether make up about 22 percent of the total sedimentary mass as free, coherent grains. Another 1.5 percent are clustered as grapestone lumps (pls. 7*C–D*, 8*C*). Some doubtless disintegrate to become a part of the silt or clay fraction on mechanical analysis. These pellets are of interest, among other reasons, because of their striking resemblance to similar bodies in ancient pelletal and aphanitic limestones.

The Bahaman pellets average near 0.2 by 0.5 mm, and range from very small to 0.5 by 1.1 mm. A selection of different-sized ovoids from the top sediment is illustrated on plate 6*H*, and ovoids in sediment samples may be seen on plate 8 and plate 9*E–F*. Tiny ovoids in the silt fraction are shown on plate 10*A*, and the large fecal pellets of *Chiton tuberculatus* Linné are shown on plate 6*I*, for comparison. Thin sections of the pellets (pl. 7*A–E*) show them to have an ultramicrogranular internal structure. Some are strongly consolidated and split sharply under firm pressure of a hard edge; others fall to pieces at the touch of a needle. Both coherent and soft pellets occur at all depths and in all parts of the bank studied, but there is a preponderance of shiny-surfaced strongly consolidated pellets around the western and southern margins of the low Eh area shown in figure 9 and a paucity of large and firm pellets in the nearshore and bight samples.

Moore (1933, p. 25) suggested that ovoid pellets found in marine sediments were probably those of either polychaete annelids or mollusks, and Cloud and Barnes (1948, p. 18) accepted this as likely. It was readily confirmed that mollusks form ovoid pellets (pl. 6*I*), but the only really abundant mollusk over the area studied, is the gastropod *Cerithium algicola* Adams, which feeds on seaweed, and in whose intestines no sediment was found. *Batillaria* (*Lampanella*) *minima*

Gmelin produces round-ended subcylindrical pellets (Kornicker and Purdy, 1957) somewhat resembling those of *Chiton tuberculatus* Linné, but it is limited, or nearly limited, to the mangrove swamps. These *Batillaria* pellets are more elongate than the typical ovoid pellet of the banks, are to be expected only near shore, and apparently do not hold together very well. Worms, on the other hand, had only rarely been noticed in the sediments in 1955, although they are well-known makers of ovoid pellets. To find the pellet maker was, therefore, one of the objectives of the 1956 trip.

Sieving of the mud at station *It'* soon revealed a tiny brown elverlike annelid that lay still when exposed and thus resembled a small piece of dead turtlegrass. Specimens obtained were 1 to 3 cm long and 1 to 2 mm across; they were identified by Dr. Marion Pettibone as *Armandia maculata* (Webster), a polychaete of the Family Opheliidae. Twenty-two were collected from 160 liters of the upper 10 to 15 centimeters of mud during daylight and 12 from 40 liters of surficial mud collected at night. A second nighttime sample of only 4 liters yielded 6 of the little worms. In all samples, many could have been bypassed as bits of debris or could have squirmed through the sieve. Previous night diving had showed the surface mud to be full of wriggling phosphorescent objects of about this size, and "eye spots" along the sides of the Armandias suggest that they are bioluminescent (Parker and Haswell, 1949, p. 354). Unfortunately none of the wriggling objects were collected, new night diving was not feasible, and captive Armandias refused to glow in darkness. Individuals kept alive for 24 hours, however, passed all the limemud in their guts, some of it as relatively coherent pellets of the same size and shape as the typical ovoid pellets of the bank sediment. In addition, later accidental shrinkage of a preserved individual under photographic lights produced (or emphasized) internal pellets within the gut (pl. 6*F–G*).

There remains no reasonable doubt that the Armandias contribute importantly to the formation of the ovoid pellets although associated burrowing terebellids and polyopthalmids, and perhaps some of the numerous sponge-dwelling polychaetes, also contribute to the total bulk. Possibly the Armandias, and perhaps other primarily mud-ingesting forms, burrow downward in the daytime and come to the top of the sediment at night, thereby creating the surface phosphorescence observed and inducing the burrow-living shrimp to their nightly repast. The oxygen requirements of these burrowing annelids are evidently low.

The suggestion by Newell and Rigby (1957, p. 53) that crustaceans "may produce the most abundant fecal pellets" cannot be applied to the ovoid pellets. The excrement of the common crustaceans in the area, as of crustaceans in general, is in poorly bonded strings or rods which do not normally preserve a well-defined structure in the sediments.

Besides the distinctive ovoid pellets, the sediments contain occasional rodlike fecal structures probably formed by crustaceans, as well as numerous subovoidal to supspherical blebs that may be fragments of the larger pellets, or from different organisms. No aggregate of any sort not demonstrably of other origin is above suspicion of being fecal. Shrimp, portunid crabs, and sediment-ingesting labrid fish are all common in the area; and on the mounds that surround the numerous crustacean burrows are abundant weakly bonded stringlike to cylindrical pellets in process of disintegration. The gut of the conspicuous colonial tunicate *Ecteinascidia turbinata* Herdman is usually filled with glomular lime mud which gives rise to small and mostly incoherent pellets and aggregates on evacuation. The snail *Batillaria* (*Lampanella*) *minima*, which browses on algal mats in mangrove swamps, provides abundant pellets along the coast, but apparently most of these also break up under subsequent sedimentary and diagenetic processes.

A realistic estimate of the volume of sediment represented by fecal aggregates, therefore, would add a large fraction of the 13 percent miscellaneous aggregates that make up column 2 of figure 11 to the 22 percent ovoid pellets of column 1. In addition, many of the separate aragonite needles of the clay and silt fractions have probably been repeatedly recycled as the constituents of incoherent pellets. The important point, however, is that, taken together, aragonite needles and fecal aggregates are estimated to represent about 75 or 80 percent of the total sediment.

The shore-zone muds, those of the bights, and even some midbank muds, however, are poor in pellets of the ovoid type (marked stations on fig. 9). Many rounded bodies and clusters in these sediments probably are of fecal origin but come from such organisms as the mangrove-swamp snails, crustaceans, ascidians, and perhaps polychaetes other than the Armandias. The rarity of ovoid pellets in the bight areas might be attributed to the strong currents that race through here with each change of tide. In addition to transporting fine sediments into the bights from the banks, such currents should also tend to pick up and sweep away small nonswimming organisms such as *Armandia* whenever they appear above the sediment water interface. Such an explanation, however, cannot account for the rarity of the typical ovoid pellets in the nearshore sediments at the west of Andros Island. The pellet makers apparently do not do well here—either because of occasional fresh-water influx from flood rains, or because the sediments are too thin or too highly oxidizing or lack appropriate nutrients or favor a strong enemy or competitor, or for some other now equally uncertain reason. The rarity of pellets at some midbank stations may indicate simply that pellets formed there were not sufficiently coherent to survive. This problem is discussed in more detail by Blackmon in the section on "Mechanical characteristics and mineralogy of the sediments."

Hard pellets with a shiny superficial coating are found mainly in the outer bank sediment. Those from the inner-bank sediments, even where firm, mostly have dull roughish surfaces. Occurrences of hard pellets coincide with sites of maximum calcareous infiltration of the pore spaces of *Halimeda* and other algal fragments and with sites of deposition of surface coatings around sand-sized skeletal particles of all sorts. Also at such places interstitial cementation may occur, and eventual solid coating of groups of pellets to form the grapestone lumps already mentioned (pl. 7*B*). Sediments of this nature have much higher pH and Eh than the limemuds.

OOIDS

Ooids were unexpectedly rare in the sediments studied, although Thurber and others (1958) report oolitic sediment within an area that apparently fell between stations of the present survey. Thin sections of suspected oolitic sands showed only smooth-surfaced, well-indurated pellets except at station *B4* (pl. *7G*) where a few thin-skinned ooids were found. In contrast, emerged rock at Fresh Creek is highly oolitic (pl. *7H–K*), and Illing (1954, p. 35–44, pl. 4) describes and illustrates superficial ooids comparable to those from station *E4* from the southeastern banks. Thin sections from a random sample of supposed oolite at the southwest corner of North Bimini Island showed only Foraminifera and detrital grains, of which a small proportion had superficial ooidal coatings. It is evident that thin sections are required for sure distinction of oolitic deposits from pelletal rocks and sediments—all that glisters is not ooid!

Illing's excellent discussion of ooid origin leaves little unsaid. It should be supplemented, however, by the suggestion (previously made by Thorp (1936, p. 69, and others and supported by present studies) that ooids without obvious nuclei may have started from tangential clustering of aragonite needles around gas bubbles that later collapsed. The structure of some Bahaman ooids, and their at least locally high content of organic matter, also suggests possible buildup by tangential aggregation of aragonite needles around successive mucilaginous layers of bacteria that cling to the surfaces of nuclear particles, such as pellets.

SKELETAL FRACTION

Setting aside 75 to 80 percent of the total sediment mass as aragonite needles or fecal aggregates (including a few grapestone lumps) leaves 20 to 25 percent to be accounted for. Study of 13 selected cores indicates that slightly less than half of this remainder (about 11 percent of total) consists of recognizable skeletal material larger than silt size, leaving a final 9 to 14 percent of the total still unassigned; but, as will be seen, perhaps also mainly of skeletal origin. Illustrations of some of the skeletal types are given on plate 6, and approximate percentages of surface sediment are given in table 8.

TABLE 8.—*Approximate composition of the recognizable skeletal fraction in percent of total sediment*

	Percent
Algae:	
Halimeda	3+
Mainly dasycladacean (probably includes some *Halimeda* and *Penicillus*)	1−
Coralline	trace?
Foraminifera	3
Others:	
Mollusk fragments and whole small shells	3
Miscellaneous (*Spirorbis* and other annelid tubes, ostracods, alcyonarian and tunicate sclerites, sponge spicules, rare coral, rarer bryozoans)	1

The only species of stony coral found in the sediment was an occasional whole small *Manicina areolata* (Linné), which attaches to stems of algae and so survives in the limemud areas. Alcyonarian sclerites are not uncommon but are of small bulk, being dispersed from minor areas of hard bottom. The dermal sclerites of didemnid tunicates (pl. *10A*) occur in most samples that have significant silt fractions, especially near shore; they are of trivial total volume but significant as facies indicators. Other skeletal debris is of types which are briefly described in the section on "Organic community."

INTERSTITIAL WATER

Analyses of the interstitial waters are difficult to interpret, especially because of inconsistencies that probably reflect the small sample size and unsatisfactory sampling and storage procedures as much as they do true differences in the waters found in place. These samples were obtained on the spot by centrifuging the sediment and passing the water through a millipore filter under semivacuum. Thereafter they were stored in partly filled polyethylene bottles.

If the sediment values for pH and Eh (fig. 9) are accepted as approximating those of the interstitial waters, then the readings on the waters themselves are consistently and considerably too high. Partial pressure of CO_2 and O_2 was probably so far out of equilibrium with the atmosphere to begin with that first centrifuging and then filtration brought drastic changes in O_2 and CO_2 equilibria. Such changes are reflected also in the erratic alkalinity values, and poor comparison between field and laboratory alkalinities taken from parallel samples. However, although probably not quantitatively accurate, alkalinity shows a general tendency to run high in the interstitial waters, and this value would be more likely to lose than gain through atmospheric exchange.

In addition, the values for the principal salts are believed to be fair approximations allowing for the relatively small samples available (generally only 20 to 40 ml for all analyses). Therefore, the absence of systematic departure of chloride values from those of the overlying water is probably real, and it is concluded that no perceptible general concentration has taken place in the upper 15 cm of sediment.

In spite of such lack of concentration, however, both calcium and alkalinity are generally somewhat higher in the interstitial water than in the open water above. Their high values make the relatively low pH and Eh of the sediments look reasonable as that of the interstitial waters, and such is considered to be the case without further discussion.

Ratios of calcium to magnesium and strontium were computed and graphed for interstitial, surface, and bottom waters, but the graphs showed no consistent variation and are not given here. A general impression was derived that there might be some loss of magnesium and gain of strontium in the interstitial waters, which, as far as magnesium is concerned, is consistent with the findings of de Sitter (1947) and others for oil-field brines. These variations need to be further investigated, however.

The volume of interstitial water in four 200-milliliter samples of fresh 1956 sediment from station *It′* was estimated by oven drying at 140°C for a week, followed by a second week at 220°C with only slight additional loss. End results shown in table 9 indicate an average of 64 percent interstitial water. The apparent bulk specific gravity of the remaining dry sediment—2.78 without allowing for dry intragranular pore space and minor retained water—is clearly that of an aragonitic sediment (calcite 2.72, aragonite 2.95).

TABLE 9.—*Water content and specific gravity of sediment at station* It′

Depth in core (in cm)	Percent weight loss	Percent volume loss	Specific gravity of dry sediment	Specific gravity of whole wet sediment
0–15	43.3	67.5	2.79	1.60
15–30	42.6	66.9	2.80	1.62
30–45	36.2	60.5	2.79	1.72
45–60	37.6	61.6	2.75	1.69
Average	39.9	64.1	2.78	1.66

Samples of sediment sealed in plastic containers for a year at room temperature, and split samples wrapped in cellophane and refrigerated for the same length of time were also dried for water volume. Two whole warm core samples from 60–75 centimeters down showed 45 percent (sta. *F6*) and 36.4 percent (sta. *G3*) loss of water by volume after 24 days of oven drying. Water losses by volume from the refrigerated samples after rapid drying of small samples were found to be 55 percent at 22–24 cm down in core *G3*, 40 percent at 24–26 cm down in core *B3*, 40 percent at 30–32 cm down in core *C3*, and 39 percent at 29–31 cm down in Straits of Florida core *GSx*.

A sediment with so large a volume of hypersaline interstitial water as that of the bank samples would seem in an excellent position to undergo diagenetic changes—such as cementation and mineralogic alteration. However, only minor interstitial cementation and no mineralogic alteration was observed.

The prospects of magnesium enrichment were, nevertheless, reviewed. Analyses of 42 samples of interstitial water showed an average magnesium content of 1,757 mg/l. Reducing by 4 percent to allow for the systematic titration error mentioned elsewhere, and rounding off, leaves 1.7 g/l. Now 64 percent of the upper 30 cm of sediment is water, so if all the water could be expelled leaving all the magnesium behind, at the decreased solid volume there would be roughly 4.7 g/l Mg, or the equivalent of 16.2 g/l of $MgCO_3$. Were this combined with an equivalent weight of $CaCO_3$, in the ratio 84.3:100, a weight of 35.5 g/l $CaMg(CO_3)_2$ would be represented. At a bulk dry specific gravity of 2.78, a liter of sediment would weight 2,780 grams. Thus if all the magnesium could be withdrawn from the interstitial waters and combined with calcium and carbonate (by cation exchange and precipitation, de Sitter, 1947), about 1.2 percent of the total rock formed from the primary sediment could be converted to dolomite. If all of the magnesium in the calcite fraction of the primary sediments could be added to this, the total fraction of the resulting rock that could be made into dolomite without addition of magnesium from external sources would be only about 2 percent.

ECOLOGIC COMMUNITIES

The main intent of the studies here reported was to advance understanding of the processes involved in calcium carbonate sedimentation and diagenesis and of the broad relations between these processes and the organic community—not a detailed analysis of entire biotas and ecosystems. It will be obvious, therefore, that the following discussion of the communities to be found in different habitats is limited by the uneven distribution and restricted nature of the observations and samples on which it is based. Nevertheless, analysis of the limemud community, in which principal interest resides, suffers less from these shortcomings than does that of the communities of impinging habitats. Fortunately, also, an overlapping ecologic study by Newell and others (1959), which appeared while this work was in the hands of the editors, supplies helpful supplemental detail on these impinging areas, together with general ecologic and substrate maps of the region.

MUDS AND MUDDY SANDS

The biotas of the limemuds and muddy limesands are distinctive for the area studied (pl. 2*E–H*), varying only slightly in composition with changes in the bottom from beach toward bank edge, but changing markedly with approach to the outer cays. (See also Newell and others, 1959, p. 222–224, figs. 8, 9, 16.)

Both plants and animals of this habitat are of restricted variety as compared with a reef or wharf biota, for instance, and first view of the area gives the impression of poverty in numbers as well. On study however, it is soon realized that the commonest organisms except sponges and many seaweeds either blend into the background so well as to make little impression, live within the sediments or sponges, or belong to the nannoplankton. The blenders are white with brown streaks that simulate floating blades of dead turtlegrass (portunid crabs and labrid fish, pl. 2*E*), just brown streaks (*Armandia*, pl. 6*E–G*), translucently white (shrimp), or whitish gray (didemnid tunicates). Night diving reveals a myriad of dancing copepods and other zooplankton, darting translucent shrimp, swimming portunid crabs, and tiny blue-streaked fish rarely seen in daylight. Probing into the bottom sediment or dismembering sponges uncovers additional polychaetes and fishes. Oxygen generation in Winkler bottles indicates a teeming population of minute phytoplankton. And culture of mud samples shows a teeming bacterial microflora (pl. 9*C*), described by F. D. Sisler in a following section. The most distinctive organic features of the sediments themselves include (a) their impoverishment in macroscopic organic remains other than algal fragments and the plant browsing gastropod *Cerithium*, (b) the presence of fairly abundant valvulinid and miliolid Foraminifera, and (c) the almost ubiquitous occurrence of the foraminiferal genus *Archaias* (pl. 6*D*) in the sand fraction and didemnid tunicate spicules (pl. 10*A*) in the silt fraction.

The first forms of life to arrest the eye, however, are the seaweeds and sponges. The so-called turtlegrass, *Thalassia testudinum* Koenig and Sims, not a grass at all but a marine phanerogam, is the most abundant plant and the dominant element at the base of the nutrient pyramid. It spreads over most of the area as a scraggly mat of wispy grasslike blades 15 to 25 centimeters or so high with thick, hardy roots that reach down into the sediment an equal or greater depth. The algae are sparsely to moderately well represented by tuftose to pagoda-shaped and fan-shaped forms of the codiaceans *Halimeda, Penicillus, Rhipocephalus, Avrainvillea,* and *Udotea*; the creeping fernlike *Caulerpa*; the dasycladacean *Batophora,* commonly attached to the creeping rhizomes of *Caulerpa*; the tumbleweedlike brown *Laurencia*; *Microdictyon*; and a variety of minor green algae and microscopic forms. Coralline algae, on the other hand, are rare or absent. *Thalassia* and the algae are certainly among the primary nutrient concentrators of the area, and their detritus is one of the principal foods for other organisms. Dry-weight analyses (by Mrs. Elizabeth Murphy, U.S. Dept. Agr.) show 1.162 percent nitrogen and 0.014 percent phosphorus in a composite algal sample and 0.850 percent nitrogen, 0.025 percent phosphorus in *Thalassia*, both from station *It′*, collected June 1956.

Scattered within this sparse and muddy marine meadow are also a variety of branching to loaf-shaped or irregular sponges. The commonest is a soot-black to brown *Hircinia* that has adapted itself to the muddy substrate by growing bosslike about the base of a sturdy species of *Avrainvillea* with a distinctive slashed flabellum (pl. 2*G*; *Avrainvillea* cf. *A. nigricans* Decaisne). Species of yellow *Verongia* (pl. 2*F*), and blue to black *Haliclona* and *Iotrochota* appear to be the principal branching sponges, followed in abundance by an unidentified but distinctive brownish-black organ pipe type (pl. 2*H*). *Halichondria* is represented by an encrusting species. The commercial *Spongia* (pl. 2*F*) was rarely seen, and the great loggerheads (*Spheciospongia,* de Laubenfels, 1936, p. 140–141) were not observed at all away from their preferred rocky substrate along and beyond the Cays.

A small fish, identified as *Eques acuminatus* (Blochand and Schneider) by Leonard Schultz, takes shelter in the hollow organpipe sponges, and the soft *Hircinia* masses are inhabited by a variety of polychaete annelids, crustaceans, and even an anemone. Most conspicuous among the sponge-dwelling polychaetes is the predaceous 10- to 25-centimeter-long *Eunice filamentosa* Grube whose burrow is surrounded by a parchmentlike tube of its own making that both follows and cuts the natural body canals of the sponge. A partial composite list of animals found in and on five small sponges collected at station *C3* is given in table 10.

TABLE 10.—*Animals from five small sponges at station* C3

Kind	*Number of specimens*
Anemone (identified by Charles E. Cuttress, U.S. Natl. Mus.): *Bartholomea annulata* (Lesueur)	2 young
Polychaetes (identified by Marion H. Pettibone, U.S. Natl. Mus.):	
Ceratonereis	1
Eunice filamentosa Grube	5
spp	4
Syllis (*Haplosyllis*) *spongicola* Grube	1
(*Typosyllis*) sp	5
Trypanosyllis sp	1
Spirorbis sp	1
Vermiliopsis sp	1
Crustaceans:	
Ostracod (identified by W. L. Tressler, U.S. Hydrographic Office):	
Xesteloberis depressa (Sars)	1
Copepods (identified by T. E. Bowman, U.S. Natl. Mus.):	
Asetrocheres sp	160
Harpacticoida gen. and sp. indeterminable	1
Malacostracans:	
Mysidacean (identified by T. E. Bowman, U.S. Natl. Mus.):	
Heteromysis aff. *H. formosa* Smith	2
Tanaids (identified by Karl Lang, Naturhistoriska Riksmuseet, Stockholm)	
Apseudes propinquus Richardson	2
Kalliapseudes viridis Menzies	1
Leptochelia dubia (Kröyer)	16
Isopods (identified by T. E. Bowman, U.S. Natl. Mus.):	
Exosphaeroma sp	12
Janiridae gen. and sp. indeterminable	4
Stenetrium antillense Hansen	1
Amphipods (identified by C. R. Shoemaker, U.S. Natl. Mus.):	
Carinobatea cuspidata Shoemaker	5
Ceradocus chiltoni Sheard	13
Elasmopus sp.?	2
Ericthonius brasiliensis (Dana)	3
Lembos concavus Stout	18
Leucothoe spinicarpa (Abildgaard)	16
Maera inaequipes (Costa)	14
Decapods (identified by Fenner A. Chace, Jr., U.S. Natl. Mus.):	
Dardanus venosus (H. Milne-Edwards)	1
Lobopilumnus agassizii (Stimpson)	1
Synalpheus brooksi Coutière	3
townsendi Coutière	1
Thor floridanus Kingsley	2
Sponges (identified by Willard D. Hartman, Peabody Mus., Yale Univ.)	
Halichondria sp	1
Hircinia fasciculata (Pallas)	1
strobilina (Lamarck) [2]	3
Spongia obliqua Duchassaing and Michelloti	1
Verongia longissima (Carter)	3

Table 11 lists the fauna from a single random bucketful of mud and water dredged at nighttime at station *It′*.

TABLE 11.—*Fauna from a bucketful of mud and interface water at station* It′

Kind	*Number of specimens*
Polychaetes (identified by Marion H. Pettibone, U.S. Natl. Mus.):	
Armandia maculata (Webster)	6
Polyopthalmus pictus (Dujardin)	1
Sthenelais sp	1
Terebellides stroemi Sars	1
Crustaceans:	
Decapods (identified by Fenner A. Chace, Jr., U.S. Natl. Mus.):	
Mithrax (*Mithrax*) *spinosissimus* (Lamarck)	1
Neopanope packardii Kingsley	2
Amphipods (identified by C. R. Shoemaker, U.S. Natl. Mus.):	
Ceradocus chiltoni Sheard	2
Leucothoe spinicarpa (Abildgaard)	2
Maera inaequipes (Costa)	4
Miscellaneous (identified by T. E. Bowman, U.S. Natl. Mus.):	
Copepod:	
Asterocheres sp	1
Isopods:	
Janiridae gen. and sp. indeterminable	2
Sphaeromidae gen. and sp. indeterminable	1
Leptostracan:	
Paranebalia longipes (Willemoes-Suhm)	1
Insect (identified by Grace Glance, U.S. Natl. Mus.):	
Thysanura, immature sp.?	1

The coiled, adnate, calcareous tubes of the tiny polychaete *Spirorbis* are commonly abundant on surfaces of algae and turtle "grass." Foraminifera, a few ostracods, and the snail *Cerithium algicola* (Adams) also live and apparently feed on the seaweed surfaces.

At every locality visited, several of the small brown-striped, white labrid fish *Halichoeres bivittatus* (Bloch) would dash up and begin feeding indiscriminately on mud, broken sponge surfaces, or algae the moment the bottom or anything on it was disturbed. The 10-cm-broad white swimming crab *Portunus* (*Achelous*) *spinimanus* Latreille, with its crosswise orange-brown streaks and red claw ends, and its smaller (2.5–5 cm) all-white congener *P.* (*Achelous*) *bahamensis* Rathbun were also seen at many stations, although they spend most of the day in the mud. Occasionally one of these crabs would take refuge in the 3-cm-wide vertical holes at the centers of the numerous mounds and depressions on the bottom. More commonly, however, they simply slipped sideways into the mud when pursued. White shrimp of about the same diameter as the holes are probably their normal inhabitants, but the shrimp were seen only at night and were not observed to enter or leave the holes.

To judge from the occurrence of their shells in the sediment (table 3; pl. 6*C*), a number of mollusks live or recently lived in the area. Except for *Cerithium* these were not seen alive. Perhaps they inhabit the occasional areas of rocky bottom and get washed out from there, or perhaps search would reveal them in special niches within the area of the muddy bottom.

A specimen or two of the small flowerlike stony coral *Manicina areolata* (Linné) could be found at most places, attached to the stem of an alga, or, rarely, lying in the mud. In the sediments these were never found as fragments, but only as rare whole small skeletons several centimeters across. The only other cnidarians observed in the mud areas were a transient swarm of tiny (1 cm± diameter) purple medusae seen in the surface water at one midbank station.

Few starfish were observed within the area of limemuds and these were all red to tan echinasters 7 to 12 centimeters across, probably *Echinaster sentus* (Say).

A bright orange colonial ascidiid tunicate (*Ecteinascidia turbinata* Herdman) was collected at station *C7*, near shore, and the grayish-white *Didemnum candidum* Savigny thinly encrusts sponges and other organisms in all parts of the area. The tiny burrlike dermal sclerites of the latter or a similar didemnid tunicate are a distinctive if trivial element of the silt fraction of sediment samples from the limemud environment.

Except for the *Halichoeres*, *Eques*, occasional seahorses clinging to some branched object with their tails, and the small blue-striped nocturnal fish mentioned earlier, fishes are uncommon in the limemud area. The usual pelagic forms are conspicuously rare. Individual ½-meter-long brownish belonids were occasionally observed wiggling aimlessly at the surface, but no barracuda and few sharks were seen. A small brown sand shark was flushed near the bights in 1955, and in 1956 five medium-sized dark-tipped dusky-white to light-tan sharks apparently followed drifting garbage to the prolonged anchorage at station *It′*; they were probably *Eulamia limbata* Muller and Henle (J. L. B. Smith, 1949, p. 40–41) or *Carcharhinus maculipinnus* (Poey) (Phillips and Brady, 1953, p. 11, 15).

ROCK SURFACES SURROUNDED BY MUDS

Although the limemuds nearshore are thin over rock, exposed rock surfaces within the areas of mud are unusual. Such surfaces were seen, however, between stations *D1* and *C7* and at and northward from *B3′*. They are characterized by an abundance of whiplike plexaurid and other gorgonacean corals not seen in the areas of loose sediment, and by absence of the grasslike *Thalassia*. A variety of sponges and scattered codiacean and dasycladacean algae grow here also, attaching directly to the rock surface beneath a thin layer of sediment. Excellent photographs of somewhat similar communities near Bimini were published by Squires (1958, pl. 28, fig. 1; pl. 30, fig. 1).

MARGINAL SANDS AND THE BANK EDGE

Seaward from the area of limemuds delimited in figure 9, the biotas, like the sediments, change markedly. Floating *Sargassum* is seen more commonly to the west of this area, as also are a few porpoises and pelagic fish. The bottom sediment itself becomes sandy, loose, and well oxygenated and supports burrowing mollusks, such as the handsome *Macrocallista maculata* (Linné), and the keyhole dollar *Mellita sexiesperforata* (Leske). Newell and others (1959, p. 220–222, figs. 8, 9, 15) describe this as their stable-sand habitat, occupied by their *Strombus costatus* community. The identifiable skeletal fraction of the sediment is much larger than among the muds and muddy sands, and is characterized by the foraminifer *Asterigerina carinata* d'Orbigny and several buliminids. The reedlike manatee "grass," *Cymodocia manatorum* Aschers, appears more commonly among the *Thalassia* "meadows" toward the west side of the bank, and as the bottom becomes quite sandy, seaweed shows less of a tendency to grow in a continuous sparse blanket and more penchant to form rich concentrations, separated by bare sands.

Approach toward the outer edge of the bank is heralded by increasing clarity of the water. In calm water and bright light, one can easily see the great conch *Strombus gigas* (Linné), flagged with streamers of *Sargassum*, peacefully ingesting the bottom sediment 9 to 13 meters below. Where the bottom has a fairly thick sand cover, the strombids and burrowing mollusks are likely to have it to themselves (unstable sand habitat and *Strombus samba* community of Newell and others, 1959, p. 217–218). Where it is bare or thinly covered, loggerhead sponges, gorgonaceans, and algae take over (rock pavement habitat and plexaurid community of Newell and others, 1959, p. 214–215). Reef-building types of corals, but no reefs, are also found here, and many kinds of fishes. This is a favored barracuda habitat. Illustrations of the stony corals and good descriptions of their habitats in the Bimini area are given by Squires (1958).

TIDAL LAKE

The only tidal lake visited was that at the northwest corner of Williams Island, and that for only a short while late in the day. On the upstream trip the clear, narrow tidal channel suddenly ramified into an extremely shallow, very salty muddy-bottomed lake, with a dense mat of the dasycladacean alga *Batophora*. Here was found the only living specimen collected of the tulip-shell snail *Fasciolaria tulipa* (Linné)—the only other shell of this species found was being worn by a hermit crab far out on the bank (sta. *C1*).

MANGROVE SWAMP

Mangrove swamps (pl. 1*F*) are a subject in themselves, touched here only because they abut the bank environment along much or all of western Andros Island. (See also Newell and others, 1959, p. 224–225.) The stiltlike aerial roots and the distinctive tracery of the mangrove leaves shelter a horde of biting flies. Down at the surface of the sediments is a thin rubbery mat of gelatinous blue-green algae that holds the sediments in place and binds new sediment that is washed in. Browsing on this mat are countless tiny high-spired gastropods, *Batillaria* (*Lampanella*) *minima* Gmelin. And burrowing into the mud beneath it are a host of tiny, big-clawed, soldier crabs of the genus *Uca*. Less abundant are little green shore crabs, grapsids of some sort, that follow the tide up the mangrove stilts. The distinctive small gastropod *Cerithidea costata* (da Costa), sought as a delicacy by flamingos, flourishes locally. As the swamp gives way to dry or rocky areas, *Cerion*, *Polygyra*, and other pulmonate mollusks appear, and these get into the beach and swamp deposits. Such a biota hardly resembles that of the banks at all. In older deposits it would be considered strongly suggestive of a fossil mangrove swamp, especially if accompanied by downward-spreading root casts.

PLANKTON

Plankton tows were made at two localities along the edge of the Tongue of the Ocean and over the western banks, just east of Orange Cay. A standard No. 20 silk bolting cloth net about 3 meters long and 0.5 meter in diameter at the mouth was towed for one hour at each locality, during full daylight, at a speed of 2.5 knots. The sites marked May 18, 1955, May 19, 1955, May 30, 1955, on figure 3 show the approximate location and direction of tow. Samples were preserved by freezing, a poor method, as cellular deterioration of frozen samples increases difficulty of identification.

These samples were thawed out and inspected by David L. O'Berry, Jr., of the University of Miami Marine Laboratory, who reports that "virtually all of the animals found in these samples were typical inshore forms and mostly minute." Excluding small fish, they are as follows:

Sample May 18, 1955, from Tongue of The Ocean, consisting of a drained volume of 7.5 ml, contained about 6,000 copepods, nearly all calanoids; and 4,000 pteropods, mostly *Limacina* or a related genus. Only 100 meters of line was out on this tow; so the sample was from near the surface.

Sample May 19, 1955, from the same area and of about the same volume as May 18, 1955, included about 6,500 copepods; 1,500 pteropods, mostly *Limacina* or a related genus; and numerous algal fragments. This sample was from about 30 meters depth, with 300 meters of line out.

Western bank sample May 30, 1955, produced fewer than 100 copepods, mostly *Cyclopoida*; no pteropods; 1 chaetognath; a few polychaete and mollusk larvae; and rare diatoms.

No fish larvae were seen in any of the plankton samples.

The contrast between observed high biologic oxygen demand and low normal-sized plankton counts in the bank waters west of Andros Island indicates that the planktonic biota consists mainly of individuals too small to be retained in the net used. These would be nannoplankton, such as characterize the surface waters of the Straits of Florida (Bsharah, 1957, p. 213–215, 246).

FORAMINIFERAL ASSEMBLAGE

Because the Foraminifera are as much a part of the sediment as of the biota, it seems desirable to review separately some apparent highlights of their distribution. Study of this group is being undertaken by Ruth Todd and Doris Low for separate publication, and table 12 merely presents selected data from their preliminary inspection of samples for principal trends. Here listed are 54 species in 13 families, but a number of species are also omitted. The latter are mostly miliolids, a group which represents perhaps 10 to 25 percent of the total population by specimens.

TABLE 12.—*Distribution of selected species of Foraminifera in selected sediment samples from banks west of Andros Island*

[Identified by Doris Low and Ruth Todd; A, indicates abundant; C, indicates common; R, indicates rare]

	Outer bank station—		Midbank station—			Near shore station—	
	A2	*D8*	*G3*	*C3*	*F7*	*A11*	*E9a*
Valvulinidae:							
Valvulina oviedoiana d'Orbigny	C	C	C	C	C	------	R
Clavulina tricarinata d'Orbigny	------	C	C	C	C	R	------
Miliolidae:							
Quinqueloculina lamarckiana d'Orbigny	R	C	C	A	C	R	R
poeyana d'Orbigny	R	C	C	R	R	R	R
reticulata d'Orbigny	C	R	R	C	C	------	R
torrei Acosta	R	------	R	------	R	R	------
Triloculina linneiana d'Orbigny	C	C	R	A	R	------	R
oblonga (Montagu)	------	C	A	A	A	R	C
quadrilatera d'Orbigny	------	C	C	------	C	R	R
sidebottomi (Martinotti)	------	------	------	R	------	------	------
tricarinata d'Orbigny	------	------	------	------	R	------	------
trigonula (Lamarck)	------	R	------	C	R	------	------
Dentostomina bermudiana Carman	R	R	------	R	R	------	------
Pyrgo carinata (d'Orbigny)	------	R	------	------	------	------	------
denticulata (Brady)	R	------	------	------	------	------	------
subsphaerica (d'Orbigny)	R	R	------	C	R	------	R
Miliolinella circularis (Bornemann)	------	------	R	R	------	------	------
fichteliana (d'Orbigny)	------	R	R	R	------	------	------
labiosa (d'Orbigny)	R	------	R	------	R	------	R
Biloculinella eburnea (d'Orbigny)	------	R	R	------	R	A	R
Articulina mexicana Cushman	R	C	------	------	------	------	------
mucronata (d'Orbigny)	C	R	C	R	R	------	------
sagra d'Orbigny	------	------	------	------	R	------	------
Ophthalmidiidae:							
Cornuspira planorbis Schultze	------	------	R	------	R	R	------

TABLE 12.—*Distribution of selected species of Foraminifera in selected sediment samples from banks west of Andros Island*—Continued

[Identified by Doris Low and Ruth Todd; A, indicates abundant; C, indicates common; R, indicates rare]

	Outer bank station—		Midbank station—			Near shore station—	
	A2	*D8*	*G3*	*C3*	*F7*	*A11*	*E9a*
Nonionidae:							
Nonionella atlantica Cushman	------	R	------	------	------	------	R
Peneroplidae:							
Peneroplis proteus d'Orbigny	C	C	C	C	R	R	R
Spirolina arietina (Batsch)	R	------	------	------	------	------	------
Archaias angulatus (Fichtel and Moll)	A	A	A	A	A	C	R
Sorites marginalis (Lamarck)	------	------	R	R	------	------	------
Marginopora vertebralis Blainville	R	------	------	------	------	------	------
Buliminidae:							
Buliminella milletti Cushman	------	R	------	------	------	------	------
Bolivina pulchella d'Orbigny	------	C	------	------	------	------	------
rhomboidalis Millett	------	R	------	------	------	------	------
subexcavata Cushman and Wickenden?	R	R	------	------	------	------	R
Loxostomum limbatum (Brady) *costulatum* (Cushman)	------	------	------	------	------	------	R
Fissurina lucida (Williamson)	------	------	------	------	------	------	R
Discorbidae:							
Rosalina candeiana d'Orbigny	C	C	R	R	A	R	R
opima (Cushman)	------	R	------	------	------	------	C
rugosa d'Orbigny?	R	------	------	------	------	------	------
Discorbis? aguayoi Bermudez	------	------	------	------	------	------	R
Neoconorbina terquemi (Rzehak)	------	R	------	R	------	------	------
Rotorbinella? mira (Cushman)	------	------	------	------	------	C	C
Buccella? sp. A	------	------	------	------	------	R	A
Cymbaloporidae?:							
Cymbaloporetta? sp. juv	R	R	------	------	------	------	------
Amphisteginidae:							
Asterigerina carinata d'Orbigny	C	A	------	------	------	------	------
Elphidiidae:							
Elphidium advenum (Cushman)	R	R	R	------	R	------	------
discoidale (d'Orbigny)	C	C	C	C	C	C	C
cf. *E. gunteri* Cole	------	------	------	------	------	R	R
morenoi Bermudez	------	------	------	------	------	A	A
poeyanum (d'Orbigny)	R	R	R	C	R	R	A
sagra (d'Orbigny)	------	------	------	------	------	------	R
Anomalinidae:							
Cibicides lobatulus (Walker and Jacob)	------	R	------	------	------	------	------
Planorbulinidae:							
Acervulina inhaerens Schutze	------	R	------	------	------	------	------
Homotremidae:							
Homotrema rubrum (Lamarck)	------	------	------	R	------	------	------

From table 12 it appears that the outer bank is characterized by abundant to common *Asterigerina carinata*, and by several buliminids. *Bolivina pulchella* was found only at station *D8*, where it is common. Across the central part of the bank, valvulinids and miliolids seem to be more abundant and diversified than toward the outer part.

The nearshore assemblage is apparently characterized by common to abundant *Rotorbinella? mira*, *Buccella?* sp., and *Elphidium morenoi*, which were not found elsewhere. The nearshore belt is also marked by a scarcity of valvulinids and miliolids at the stations examined, although miliolids were common at station *C7*, along the shore.

Archaias (pl. 6*D*) is a conspicuous genus in most sediment samples examined, but was less common and generally more corroded at the shore stations.

ROCK FLOOR AND AGE OF THE DEPOSITS

Beneath the sediments, of whatever variety, at depths that range from a few centimeters to three meters (maximum penetration) or more is a floor of highly porous limestone from which samples were obtained at depths up to 2.4 meters below the sediment-water interface. This rock (pl. 7*F*) is a largely recrystallized pelletal and foraminiferal limestone that contains many shells of mollusks in which the original aragonite has been altered to calcite. On its surface is commonly an accumulation of unaltered aragonitic shells of the same biologic kinds—apparently all modern species. The rock matrix consists of clear calcite grains, mostly about 0.04 mm in diameter but ranging down to 0.01 or smaller. In some samples the now calcitic interior of former pellets is ringed by a discrete band (pl. 7*F*), also calcite, indicating different reaction to alteration of structureless interior and fibrous external sheath (cf. also pl. 7*H*).

Samples of the rock floor from stations *C2* and *F2* were submitted to Z. S. Altschuler for study of possible phosphate content. Analyses of splits from both samples by A. Sweeney gave less than 0.05 percent P_2O_5. X-ray patterns of the same samples by George Ashby indicated less than 10 percent aragonite and more than 90 percent calcite in the supposedly once mainly aragonitic sediment of the rock floor.

No such alteration was detected in either the overlying sediments or the local concentrations of loose mollusk shells directly on the rock floor; and no record has been found of alteration from aragonite to calcite in sediments continuously in contact with sea water. It is inferred, therefore, that the rock floor antedates the present sedimentary cycle by an interval long enough for it to have been emerged, altered subaerially to calcite, leached to a spongy texture, and resubmerged.

The most recent opportunities for such exposure to have taken place without local tectonism were during later Wisconsin glaciation, 12,000 to 18,000 years or more ago; or perhaps after the Two Creeks (Alleröd) phase of genial climate about 10,000 to 12,000 years ago but preceding final retreat of glacial ice beginning 9,000 years or less ago (Flint, 1957, p. 395; Zeuner, 1952, p. 33, 62, 345). Radiocarbon ages, therefore, were obtained and evaluated for their bearing on the age of the rock floor and the beginning and duration of the present sedimentary cycle (table 13 from Rubin and Alexander, 1958, p. 1476).

Taken at rounded face values, the apparent carbon-14 ages for eight widely scattered surface samples of the rock floor suggest an average of 17,000 years. The range of individual ages from 12,000 to 21,000 is reasonable for a single genetic cycle, considering the area covered and the fact that the bulk samples analyzed include varying proportions of matrix, shell, pellets, and ooids, the latter themselves of complex origin. Allowing a systematic positive error of 500 years to compensate for the apparent age of sea water

(Rubin and Alexander, 1958, p. 1476) does not significantly affect the order of magnitude. However, the probability of CO_2 exchange during recrystallization and cementation implies that the carbon-14 age is really a value intermediate between date of sedimentation and time of alteration to calcite. This seems to be confirmed by the fact that the age range indicated coincides with a well-defined glacial maximum and thus, presumably, emergence (barring crustal instability of unexpected degree for the region in question).

TABLE 13.—*Apparent carbon-14 ages for rock floor and sediment west of Andros Island (from Rubin and Alexander, 1958, p. 1476)*

Station	Distance from shore	Description (See fig. 9 for general depth of water and sediment. All samples obtained May 1955)	Date of report in 1956	Apparent age in carbon-14 years (wood=$CaCO_3$)
		Rock floor		
A11	100 yd	Hand sample from porous calcitic rock beneath a few centimeters sediment.	July 17	15,600±80
D1	½ mile	Core sample from surface of porous calcitic rock beneath a few centimeters sediment.	Jan. 5	16,960±400
E9	½ mile	Hand sample from porous calcitic rock beneath about 30 cm sediment.	July 17	15,440±800
C6	4 miles	Core sample from surface of porous calcitic rock beneath about 60 cm sediment.	July 17	16,730±850
B1	5 miles	Core sample from surface of porous calcitic rock beneath 1 m sediment.	Apr. 9	21,300±1,000
F2	12 miles	Core sample from surface of porous calcitic rock beneath 1.8 m sediment.	July 17	12,400±600
D5	26 miles	Core sample from surface of porous calcitic rock beneath 1.2 m sediment.	Apr. 9	19,300±1,000
C2	30 miles	Core sample from surface of porous calcitic rock beneath 2.1 m sediment.	July 17	17,000±800
		Emerged mud		
C7a	0	Surface 10 cm of punky compact aragonite mud in low beach "cliff" (pl. 1*G*)	July 17	1,020±400
C7a	0	Somewhat indurated, irregular "nodules" from layer 30—70 cm below surface of muds in low beach "cliff".	Jan. 5	1,670±200
		Bank sediment		
G3	20 miles	Pelletal aragonite mud 15–30 cm below sediment-water interface.	July 17	450±200
G3	20 miles	Pelletal aragonite mud 2–2.1 m below sediment-water interface.	July 17	2,490±400

The sediments that now form the surface of the rock floor thus probably were deposited during a (late?) Wisconsin interstadial, emerged and altered during later Wisconsin glaciation, and resubmerged as a cacitic rock with post-Wisconsin rise of sea level. Conditions of deposition were apparently more favorable to the shelly biota and less favorable to limemud formation than now; probably more normal marine water circulated more freely across the present area of restricted flow.

A sample of aragonite mud from two meters below the sediment-water interface at station *G3* gave an apparent radiocarbon age of about 2,500 years; and a sample from the lower part of the 15- to 30-cm interval in the same core gave 450 years. As both determinations were on aragonite, presumably formed in equilibrium with sea water, they would seem to indicate the approximate dates of sedimentation, and the date of the upper sample implies equilibrium between water and atmosphere and no need to correct for age of sea water. Whether or not a correction is made, the difference in age of roughly 2,040 years from lower to upper sample should approximate the actual time represented. This implies a rate of about 0.8 mm per year for accumulation of the wet sediment, and the maximum permissible range from carbon-14 data is 0.6 to 1.2 mm per year. The implied rate of 0.8 mm per year reconciles unexpectedly well with the figure of 1.1 mm per year independently estimated as an approximate rate of sedimentation from computed rates of $CaCO_3$ precipitation and water exchange—especially when allowance is made for probable loss seaward of some of the finer bank sediments after precipitation.

On the basis of an accumulation rate of 0.8 mm annually, sediments at the deepest penetration of three meters would be about 3,800 years old. The present sedimentary cycle thus, presumably, began somewhere between this age of 3,800 years and the end of the last major ice advance and sea-level depression 9,000 to 10,000 years ago, and probably closer to the lower figure—a conclusion anticipated by Newell and others (1959, p. 193) from the same and concordant data. Warming of the sea during the postglacial thermal maximum and possible changes in wind and water circulation could have helped to start the present cycle of aragonite precipitation over the banks.

A break in the sequence is indicated by the marine sediments in the 70-cm-high beach "cliff" at station *C7a*. Surface sediments here give an apparent radiocarbon age of 1,000 years, and irregularly indurated sediment from 30 to 70 cm beneath is dated at 1,700 years. This cliff, therefore, is considered to be recently emerged, either in connection with temperature decrease and polar ice formation during the recently ended so-called little ice age, or as a result of local crustal warping. This conclusion seems to be at variance with that of Newell and others (1959, p. 195), based on the same and similar data, that the mangrove swamps are actively expanding westward. However, data available are not yet sufficient to warrant a general conclusion—it seems likely that the mangrove swamps may be expanding in some places, while retreating or remaining essentially stable at others.

MECHANICAL CHARACTERISTICS AND MINERALOGY OF THE SEDIMENTS

By Paul D. Blackmon

MECHANICAL CHARACTERISTICS

ANALYTICAL PROCEDURES AND TERMS

The sediments under discussion are essentially pure calcium carbonate, and the terms "clay," "silt," "sand," and "gravel" are here used in a mechanical sense only, to refer to grain size.

The 50 cores of bottom-sediment taken west of Andros Island were sealed on collection in the plastic liners in which taken and were thereafter stored under refrigeration in order to inhibit drying, hardening, or chemical change until ready for study. Samples of approximately 40 grams each were taken from top, bottom, and roughly 30-cm intervals along the length of each core. Each sample was then prepared for study and analyzed mechanically by Mr. Harry Starkey, in the manner described below.

Soluble salts were removed by washing with distilled water utilizing a Pasteur filter (0.6-micron maximum pore diameter) to remove the solute. Where excessive organic material was present, it was removed by treatment with hydrogen peroxide. In most samples where hydrogen peroxide was used, the treatment consisted of one to three hours of digestion of the sediments in diluted peroxide at a temperature of 80° to 90°C. Only *A6* top, *A11*, *C1* top, *C2* top, *C7a*, *D1a*, *E9A*, and *F6* top were treated for more than three hours, and many samples required no peroxide treatment. More distilled water was then added, with a small quantity of sodium tetraphosphate to act as a dispersing agent. The resulting slurry was then stirred for 10 minutes with a mechanical stirrer, after which sand-sized particles were removed by wet sieving through a 270-mesh U.S. Standard sieve. The sand-sized particles were dried in an oven and classified in the U.S. Department of Agriculture grain-size scale (table 14) by passing through a nest of six U.S. Standard sieves.

The silt and clay suspensions were shaken for 4 hours in 1-liter cylinders on an end-over-end shaker. The percentages of silt and clay were then determined by standard pipet analysis utilizing Stokes settling law. Particles of less than 2 microns median diameter were designated as clay.

After the mechanical analyses were completed, the clay was separated from the silt by centrifuging. The clay and silt fractions were oven dried in preparation for mineralogical analysis by X-ray diffraction.

Table 14.—*Dimensional classification of sediments according to U.S. Department of Agriculture scale*

Fraction	Median diameter of particles (in mm)	U.S. Standard Sieve Series No.
Gravel	>2.0	10
Very coarse sand	1.0 -2.0	18
Coarse sand	.5 -1.0	35
Medium sand	.25 - .5	60
Fine sand	.1 - .25	140
Very fine sand	.05 - .1	270
Silt	.002- .05	Pipet
Clay	<.002	

The weights of the fractions obtained in the mechanical analyses were plotted in cumulative form to obtain the median diameter and first (fine) and third (coarse) quartile diameters. Trask sorting coefficient ($So=\sqrt{Q_3/Q_1}$) and skewness were calculated from this data where it was sufficient. Sorting coefficient and skewness could not be computed for some samples, however, because facilities were not available for subdivision of the size fraction smaller than 2μ, and therefore, it was not possible to determine the first quartile diameter for many sediments, or even the median diameter for some. Although, in theory, the use of the Pasteur filter might be considered to place a lower size limit of 0.6μ on particle size of the clay fraction retained, and therefore permit estimation of the missing data; in practice the tendency of the filter to cake up on application of a vacuum, plus the fact that many of the initial pore spaces are smaller than 0.6μ, results in retention of practically all of the solid fraction, as indicated by the clarity of the filtrate.

POSSIBLE BIAS RESULTING FROM PREPARATION PROCEDURES

Before considering the interpretation of the mechanical analyses, the degrees of bias introduced by the procedures described above need to be evaluated, particularly in view of the drastic loss of fecal pellets noted by Ginsburg (1956, p. 2416–2417, 2423) during disaggregation of Florida Bay muds in hydrogen peroxide.

To begin with, Ginsburg (1956, p. 2423) digested his samples in a strong solution of hydrogen peroxide for as long as "a day or two." In contrast, the samples here described were treated with dilute hydrogen peroxide, most for only one to three hours and none for more than eight hours. Ginsburg (1956, p. 2417) also observed that the pellets in the Bahaman sediments are much more resistant to mechanical breakdown than those of Florida Bay.

Selected samples from the area west of Andros Island were checked to ascertain the extent to which peroxide treatment might be a source of error in the mechanical analyses. Three of the cores for which first-run analyses indicated high clay and silt content and low 0.1- to 0.5-mm sand content (*B5*, *C7*, and *D1a*), as well as two displaying a bimodal pattern (*B3* and *D6*), were analyzed with and without peroxide treatment. In each analysis there was little shift from the sand to the silt and clay fractions after treatment. In addition, untreated sediments from parts of other cores (from stations *A5*, *A6*, *A11*, *B6*, *C2*, *C7a*, *D3*, *E9a*, and *G4*) with a high silt and clay content and mainly nonbimodal pattern were examined microscopically to estimate the prevalence of pellets before peroxide treatment. Pellets in the 0.05- to 0.1-mm fraction were common in all the cores. The large (0.1- to 0.5-mm fraction) ovoid pellets were common only in the total length of the cores from *A5* and *A6* and in those parts of the other cores which displayed a bimodal pattern. Few or no large pellets were found in the untreated parts of high silt and clay content, although small pellets and weakly bonded aggregates were noted. This indicates that the nonbimodal, high silt and clay patterns for those samples are not markedly favored by breakdown to silt- or clay-sized particles of large pellets, either by hydrogen peroxide treatment, stirring, or sieving. It looks as if some disaggregation of the small pellets and aggregates may take place where these are not well indurated, but the procedures adopted at least provide an objective way of looking at the general pattern of size distribution and probably do not distort it very much.

To check the possibility that mechanical analyses alone might disaggregate the pellets, samples were tested from eight different stations (*D8*, *D9*, *E1*, *E2*, *E4*, *E5*, *E6*, and *G3*). These particular cores were selected by Cloud after microscopic examination in order to compare the behavior of samples that contained large quantities of both soft and hard or firm pellets with others that contained hard pellets almost exclusively. Lengthwise splits of each core were analyzed for grain size without mechanical stirring, whereas the other half was put through the described procedure for mechanical analysis. In the sediments containing only hard pellets, the use or lack of stirring made little or no difference in the weight percentages of the fractions. Where soft pellets were present, the stirred part of the split showed a 5- to 10-percent increase in the clay and silt fraction with a corresponding decrease in the sand fractions.

A different test was made on fresh samples from between the top of the core and the 30-cm depth at stations *B5* and *B6*. Each was washed and sieved wet, with no stirring action, to remove clay- and silt-sized particles. Microscopic examination showed the presence of some pellets, both hard and soft, in the 0.1- to 0.5-mm range and many rounded aggregates of aragonite in the 0.05- to 0.1-mm range. The samples were then stirred vigorously in identical manner and for the same duration as in the mechanical analyses. Clay- and silt-sized particles were again removed by wet sieving, and the sediments examined microscopically. The well-formed pellets in the 0.1- to 0.5-mm range were not greatly affected by the action. Some loss was noted in the 0.05- to 0.1-mm range. The main effect of the stirring, however, seemed to be a disaggregation or cleaning off of masses of needles which had no specific form or were merely clinging to the pellets and aggregates. It looks, therefore, as though mechanical breaking up of soft pellets did not contribute importantly to the high clay and silt, nonbimodal pattern in these cores; certainly not enough to warrant introduction of the known bias in the opposite direction that would have resulted from failure to disperse the sediments before analysis.

Thus it is believed that in most of the mechanical analyses no important bias was introduced by the procedures followed. Nevertheless, wherever microscopic examination of a particular sample suggested the possibility of bias, this is noted in the descriptive section that follows.

DESCRIPTION OF SAMPLES

The results of the mechanical analyses are given in figures 12–20. The strikingly bimodal nature of many of the size-distribution patterns is the most conspicuous mechanical feature of these sediments.

From left (west) to right (east) on each figure, the histograms represent the stations of the individual traverses in a direction approaching Andros Island, except those that parallel its western shore or do not approach it. These have the west or north end to the left. The depths of the samples along the cores from each station increase toward the bottom of the figures as indicated.

Traverse A.—This traverse runs east-southeast from the Straits of Florida to the western shore of Andros Island. At station *A2*, near the outer bank, is a very well-sorted ($So=1.31$) sediment containing mainly medium- to fine-grained sand with little change of composition with depth. Microscopic examination of the individual fractions shows a high percentage of ellipsoidal pellets or ovoids composed of well-cemented cryptocrystalline aragonite in the medium- to fine-sand fractions. These aggregates are about 0.3- to 0.7-mm long and 0.1- to 0.5-mm in median diameter.

Skeletal fragments make up most of the larger grain sizes, and aggregates of fine aragonite make up the finest fractions.

Shoreward, the size distribution of the sediments becomes bimodal as the amount of clay and silt increases and pelletal sand sizes decrease. Where the

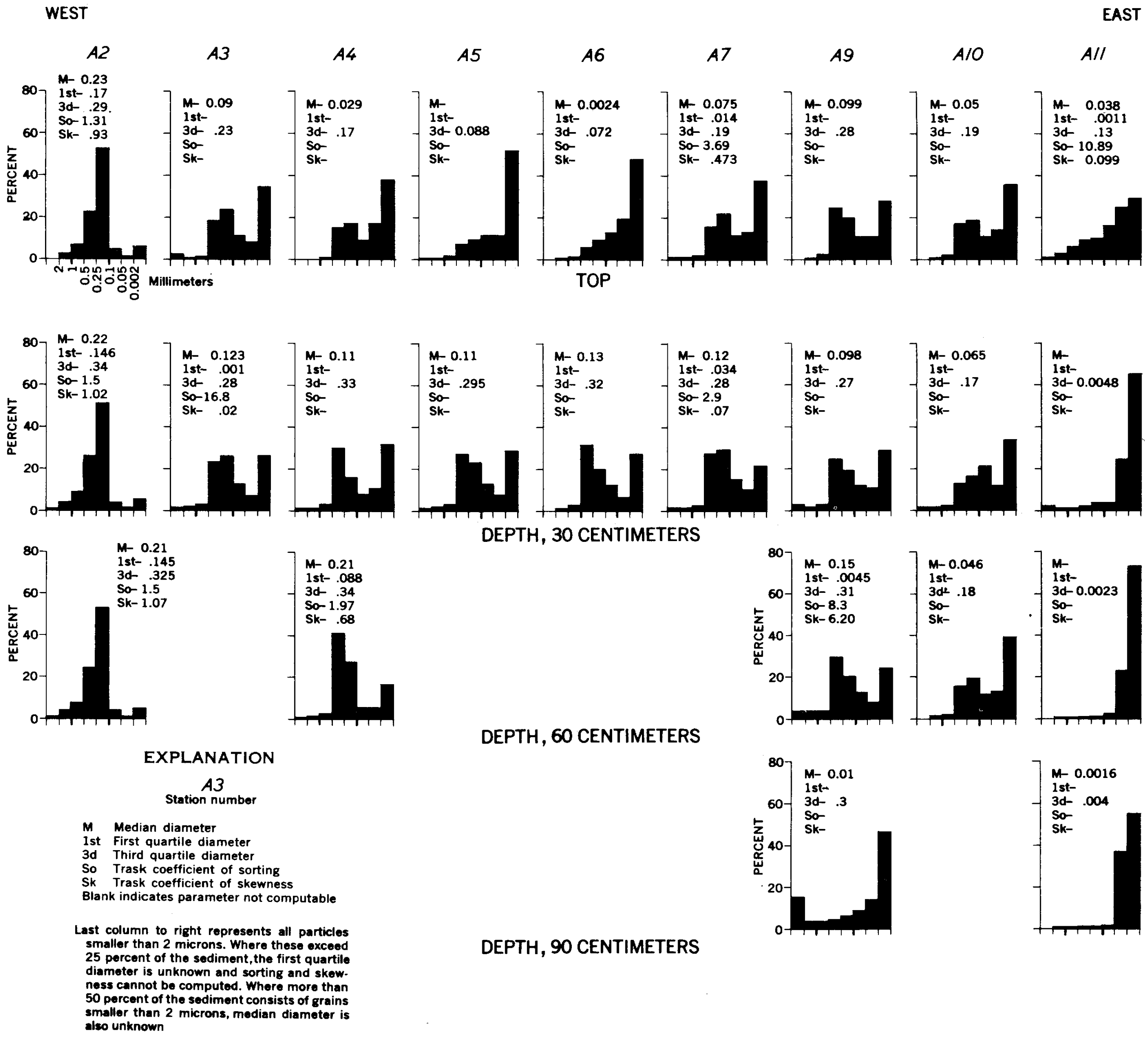


FIGURE 12.—Mechanical analyses of sediments along traverse *A*.

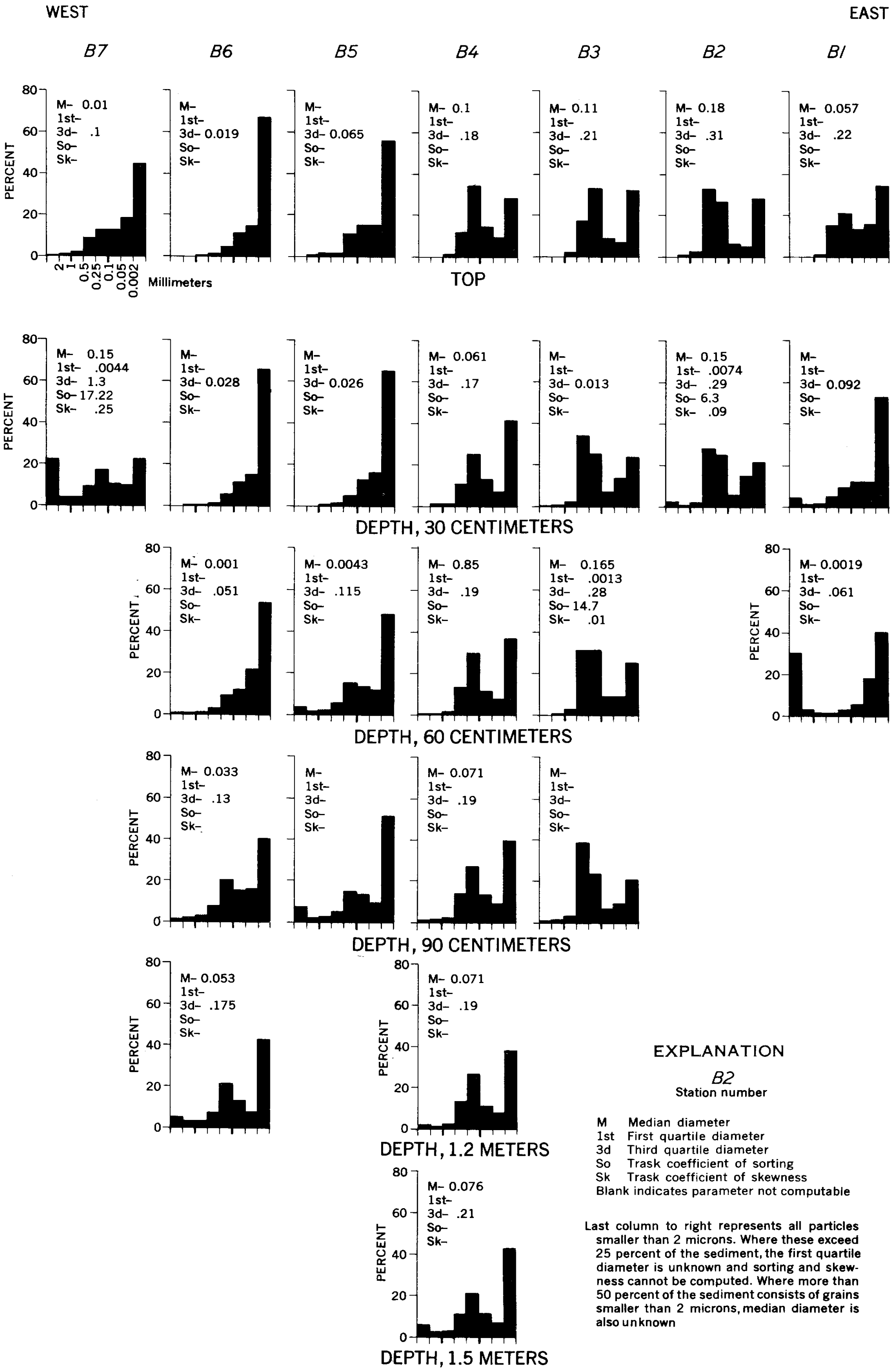
bimodal characteristic prevails, the median diameter of the ovoid pellets is generally between 0.1 and 0.5 mm. Many of the cores maintain a fairly consistent mechanical composition with depth.

The top samples from stations *A5* and *A6* are not bimodal and show a much larger percentage of clay- and silt-sized particles than adjacent stations to the west and east. However, at a depth of 30 cm they again assume the bimodal form. Similar occurrences of high clay and silt content have been noted in cores taken from other parts of the Bahama Banks.

The sample from a depth of 90 cm at station *A9* is a sediment with few pellets but with an unusually high content of gravel-sized particles. This pattern appears at several stations where bedrock was cored below the unconsolidated sediments. Microscopic examination of the gravel and sand sizes shows fragments of dark-gray calcite-cemented limestone.

Core *A11* shows a high clay and silt content throughout. The larger sand fraction at the top of the core is mainly of shell fragments with a few identifiable ovoid pellets. The 0.05- to 0.1-mm-sand fraction of the same sample includes mainly subspherical to cylindrical pellets.

Traverse B.—This traverse extends directly west from the shore of Andros Island to the edge of the Straits of Florida. At station *B1*, which is only 6 miles west of Andros Island, appreciable quantities of the ovoid



Last column to right represents all particles smaller than 2 microns. Where these exceed 25 percent of the sediment, the first quartile diameter is unknown and sorting and skewness cannot be computed. Where more than 50 percent of the sediment consists of grains smaller than 2 microns, median diameter is also unknown

FIGURE 13.—Mechanical analyses of sediments along traverse *B*.
]

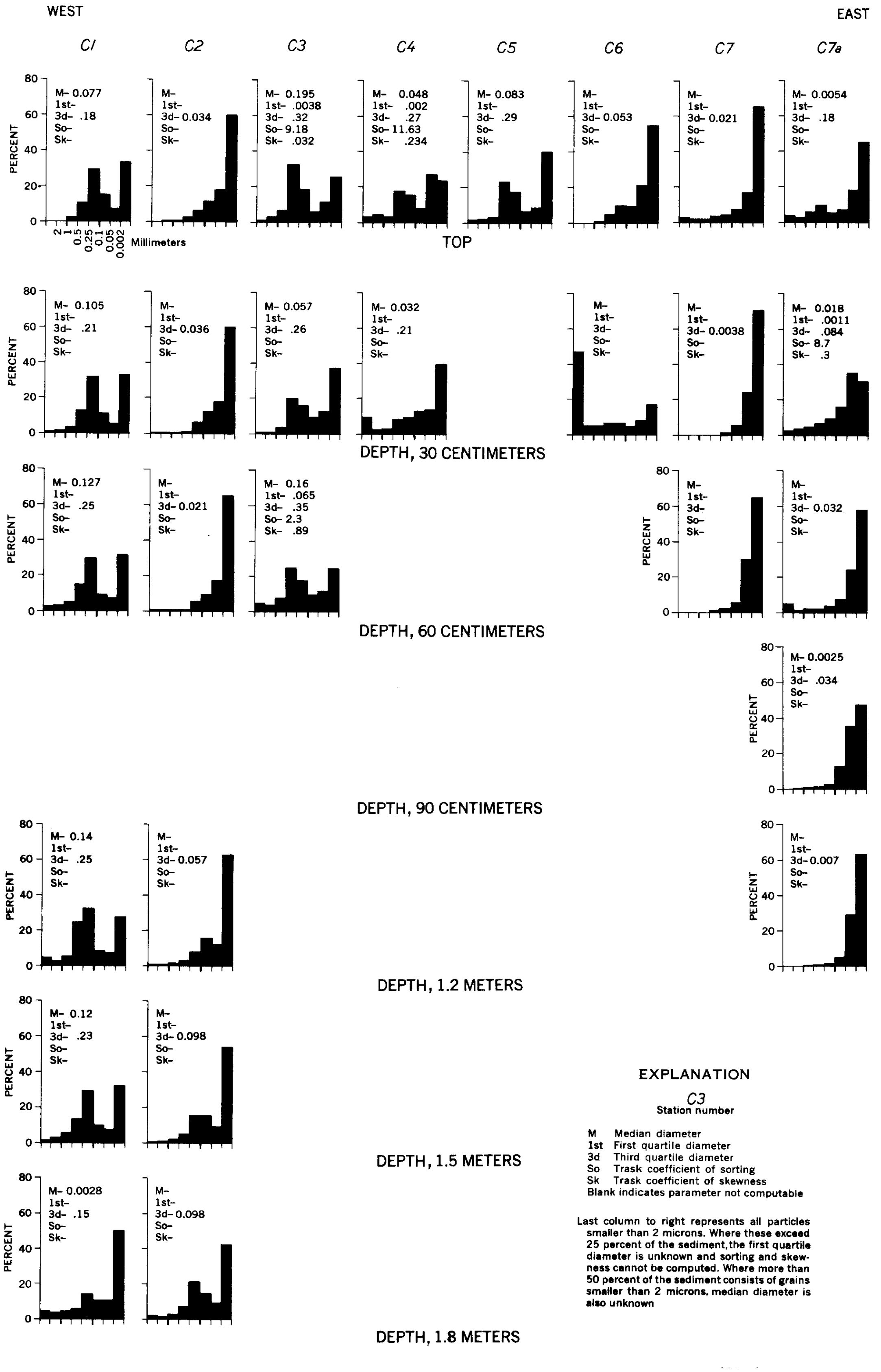
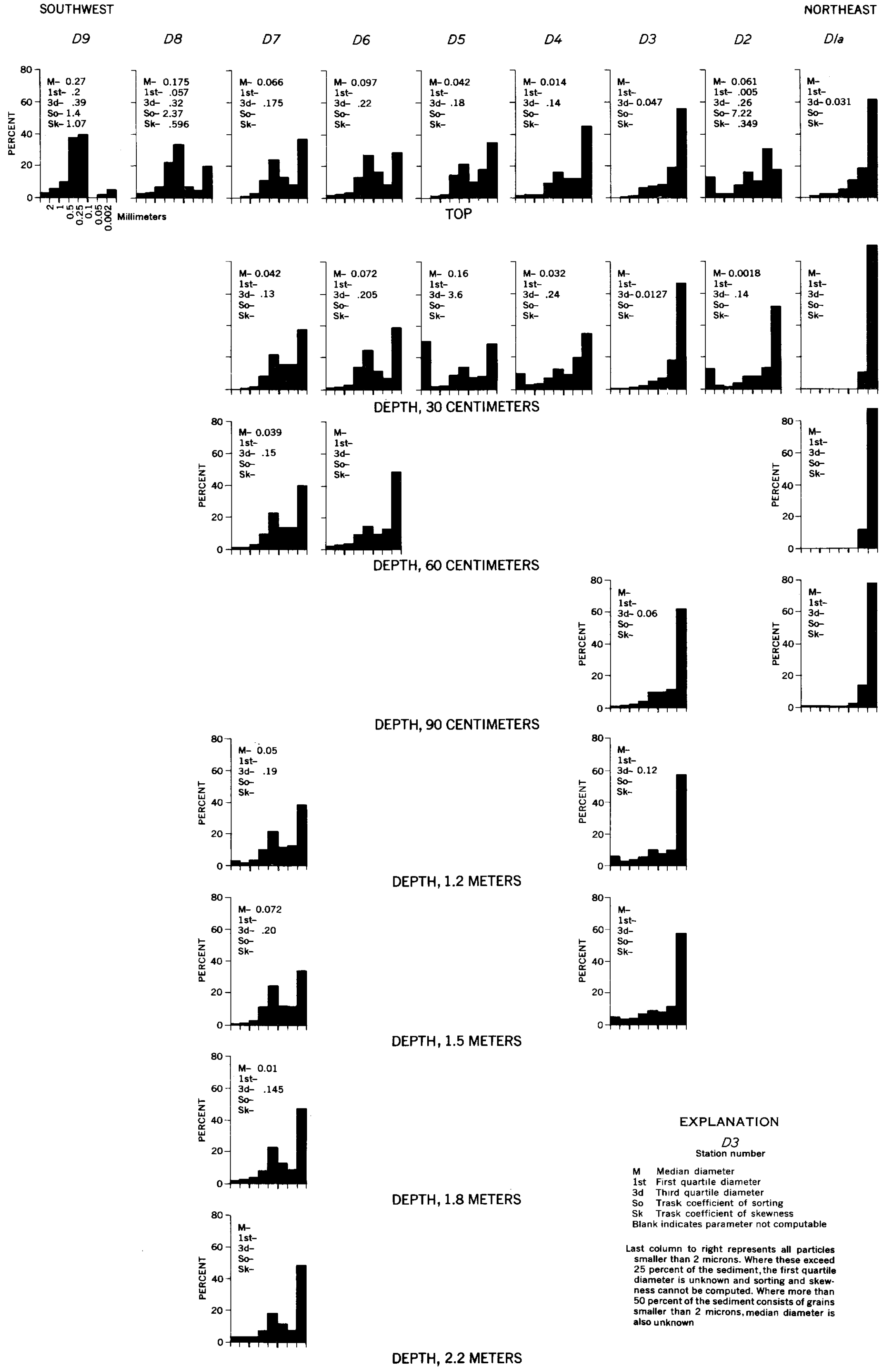


FIGURE 14.—Mechancal analyses of sediments along traverse *C*.



EXPLANATION

D3
Station number

M Median diameter
1st First quartile diameter
3d Third quartile diameter
So Trask coefficient of sorting
Sk Trask coefficient of skewness
Blank indicates parameter not computable

Last column to right represents all particles smaller than 2 microns. Where these exceed 25 percent of the sediment, the first quartile diameter is unknown and sorting and skewness cannot be computed. Where more than 50 percent of the sediment consists of grains smaller than 2 microns, median diameter is also unknown

FIGURE 15.—Mechanical analyses of sediments along traverse *D*.

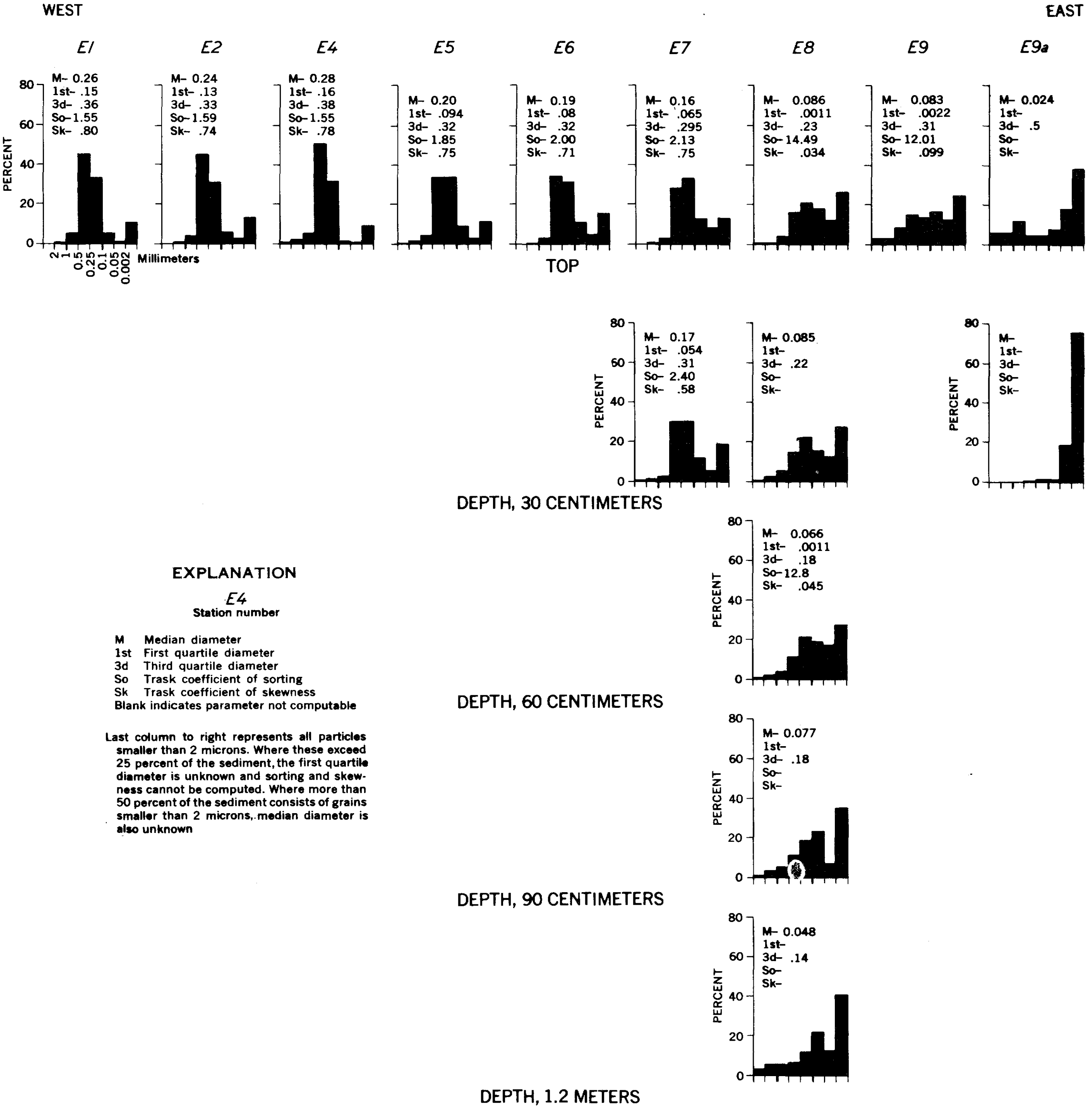


FIGURE 16.—Mechanical analyses of sediments along traverse *E*.

pellets are found at the top of the core. At the 30-cm depth, although many pellets are present, the sand fraction is insufficient to give a bimodal histogram. Bedrock was reached at 90 cm, accounting for many pieces of gravel-sized gray limestone at the base of the core. Here, as at the bottom of the core from station *A9*, there are very few hard pellets in the medium- to fine-grained sand sizes.

Sediment samples from stations *B2*, *B3*, and *B4* show pronounced bimodal size-distribution patterns and include a predominance of the ellipsoidal pellets in the 0.1- to 0.5-mm-sand sizes. The core from station *B4* extends to a depth of 1.5 m, where there is a small decrease in the pelletal content and a corresponding increase in the clay-sized aragonite needles.

At the midbank stations *B5* and *B6*, samples of the sediments from the top and from 30-cm depth and the sample from a depth of 60 cm at *B6* contain large amounts of clay-sized material but have insufficient pelletal material to give a bimodal pattern.

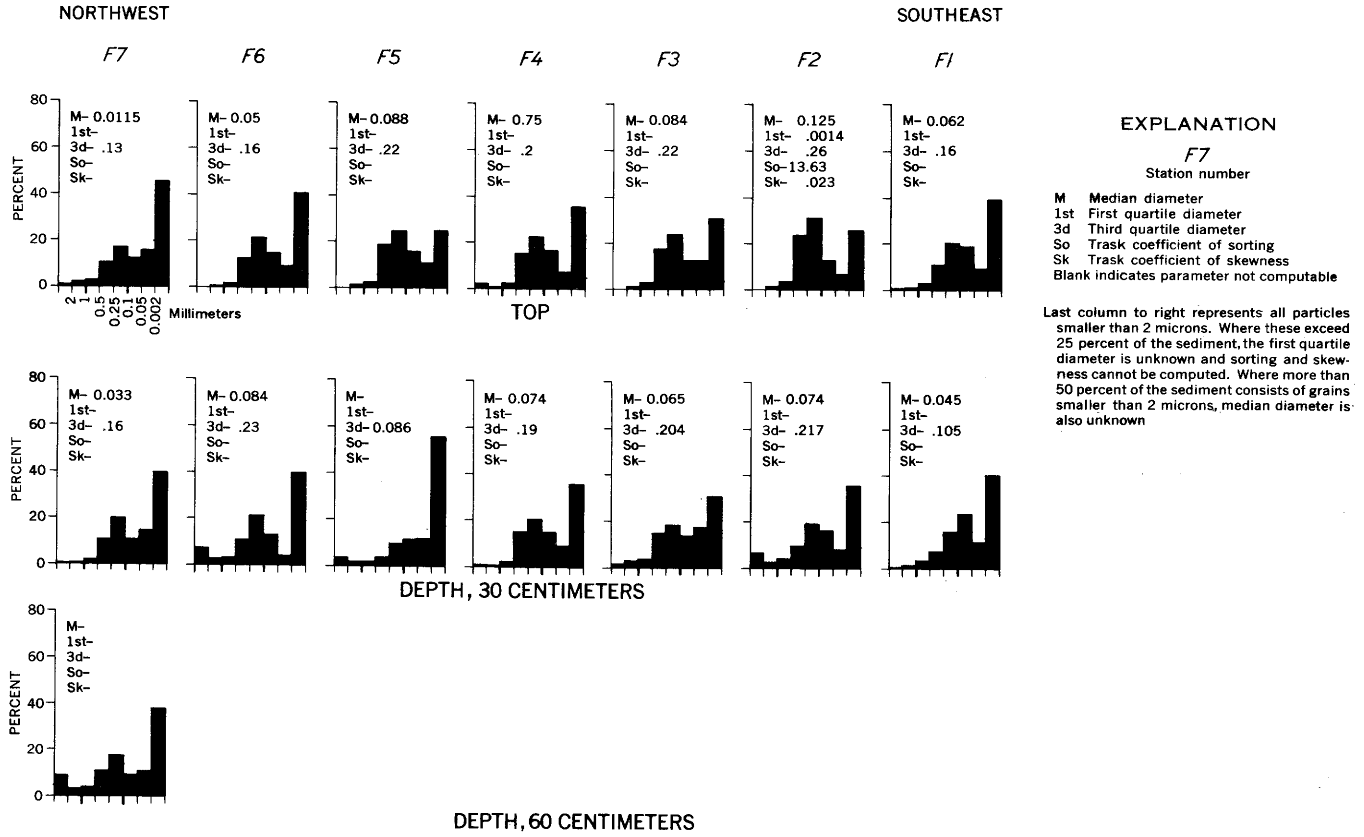


FIGURE 17.—Mechanical analyses of sediments along traverse *F*.

These are similar in composition to the top samples at midbank stations *A5* and *A6*. The cores samples of traverse *B* become bimodal at lower depths, as did *A5* and *A6*.

The core bottom from *B7* contains gray limestone fragments of gravel size; it is another core that reached bedrock. The top sediment at *B7* is similar to that at *B5* and *B6*.

Traverse C.—This traverse extends east-southeast from the outer banks to the western apex of Andros Island. Samples from stations *C1*, *C3*, *C4*, and *C5* are similar to the bimodal type of traverses *A* and *B*. Midbank station *C2* agrees well with midbank stations of traverses *A* and *B* in that it displays a high content of clay and silt and a nonbimodal pattern in the upper 60 cm of sediments and becomes bimodal in the lower 90 cm.

The high gravel content at the bottom of the core from *C4* is attributed to shell material from a shelly layer at a 30-cm depth. No bedrock fragments appeared in this sample. The bottom of the core from *C6* contains much bedrock and displays the typical near-bedrock pattern of samples from stations in other traverses such as *A9*, *B1*, and *B7*. Few pellets occur at the top of the core from *C6* and throughout *C7*. The core from *C6* was taken in a whiting area where abundant aragonite needles are suspended in the waters, and the core from *C7* was from very close to shore.

The sediments in the core from *C7a*, taken at the shore edge of a mangrove swamp, are nonbimodal. Small spheroidal and varishaped pellets and pellet fragments appear in this core, however.

Traverse D.—This traverse extends southwestward from Williams Island, off the west coast of Andros Island, to the bank edge west of the southern tip of Andros Island. The core from *D1a* was taken in a hypersaline lake at the head of a tidal inlet at the northwest corner of Williams Island. No pellets were found in the 0.1- to 0.5-mm-sand fractions. The top of the core contains mainly tests of Foraminifera and shell fragments in the gravel to fine-sand fractions. In addition to the shell fragments, the very fine sand, silt, and clay sizes contain a large percentage of rounded aragonite aggregates or small pellets. The extreme paucity of sand-sized material in samples below the surface is unique among the sediments studied.

Thick-walled shell fragments, which form a thin layer on the bedrock at the base of most cores penetrating to it, account for the gravel-sized particles in the core from *D2*. Although the bimodal form is not conspicuous in this core, some of the ellipsoidal

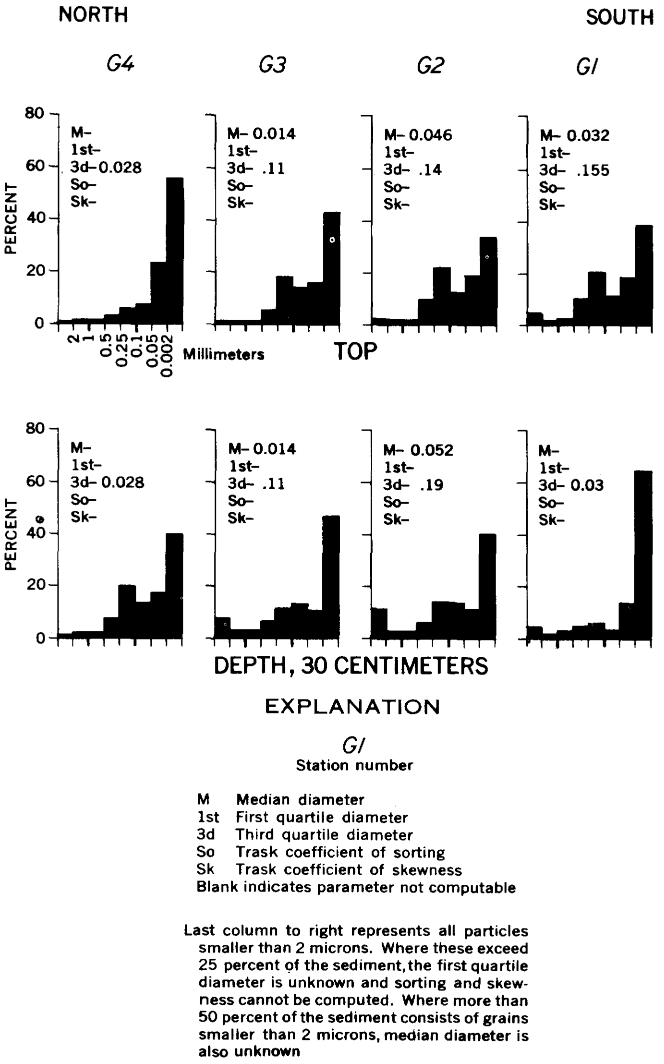


FIGURE 18.—Mechanical analyses of sediments along traverse *G*.

pellets are found in the 0.1- to 0.5-mm range. The core from *D3*, in the midbank area, displays a content of clay-sized particles and a nonbimodal sequence similar to that of the midbank cores of traverses *A*, *B*, and *C*. Sediments at station *D4* have characteristics intermediate between those af *D3* and the conspicuously bimodal sediments of the seaward half of traverse *D*. At the base of the core from *D4* are the distinctive limestone and shell fragments of a bedrock sample. The high gravel content of *D5* is due to a shelly layer in the sediments.

Traverse E.—This traverse extends directly east from the outer bank to the southern part of Andros Island, just south of the principal limemud area. The samples from *E1*, *E2*, *E4*, *E5*, *E6*, *E7*, *E8*, and *E9* contain large quantities of pelletal material. Although only small amounts of silt- and clay-sized material are found in the cores from *E1* through *E7*, the cores from *E1* to *E9* also contain enough clay-sized material to give bimodal histograms. The sorting coefficients for samples *E1* through *E7* are less than 2.15. This is the only traverse in which the sediments are consistently well sorted. Shoreward the smaller pellets become more numerous, and the larger pellets fewer. The pellets have a better indurated, more polished surface than most of those from traverses to the north. Few or no soft pellets were found in the 0.1- to 0.5-mm range.

At *E8* and *E9*, too, the finer sizes increase shoreward, and the pellets are small (0.05 to 0.1 mm). The

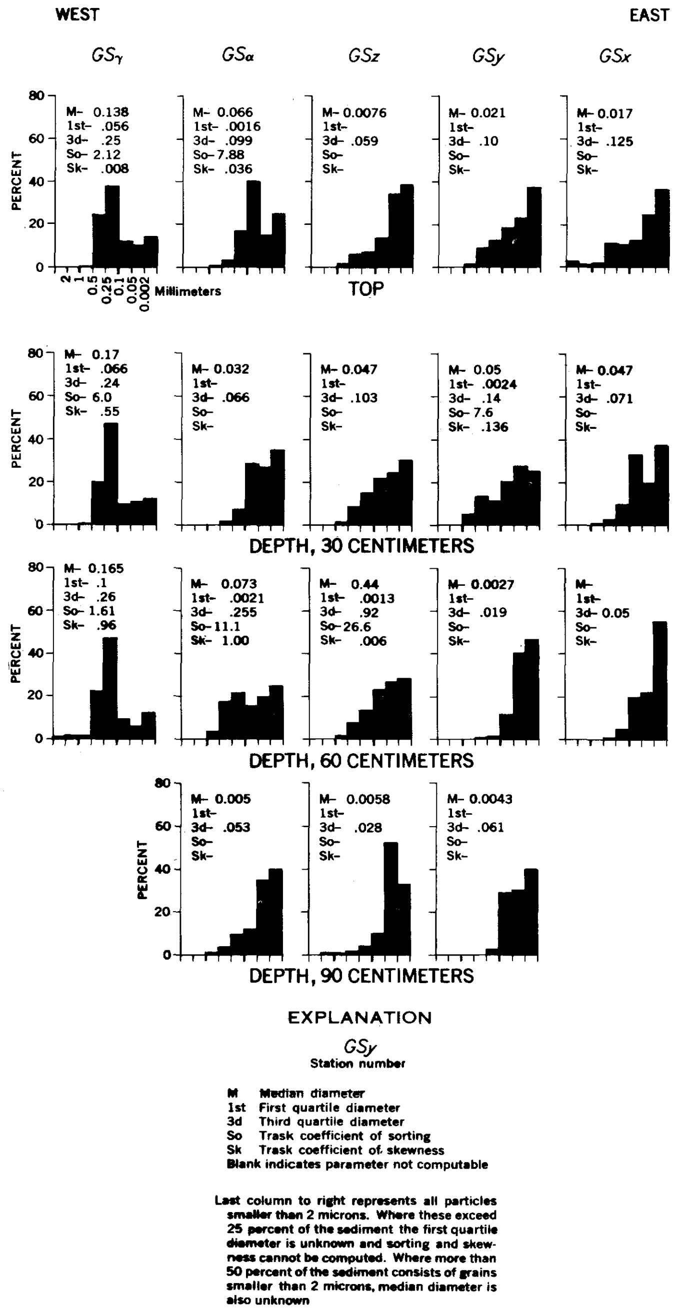


FIGURE 19.—Mechanical analyses of sediments across Straits of Florida (traverse *GS*).

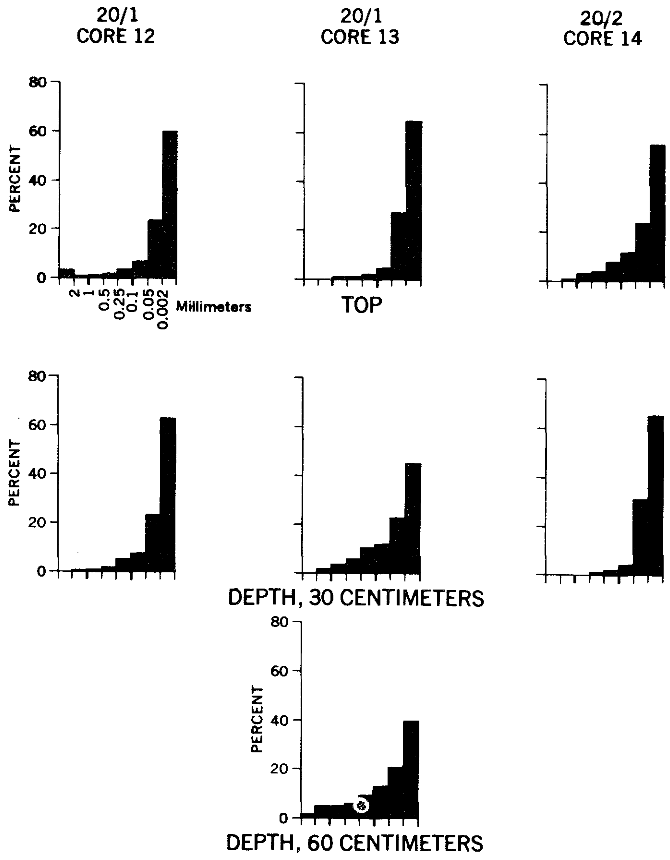


FIGURE 20.—Mechanical analyses of sediments from South Bight.

core from *E9a* taken at the edge of a mangrove swamp shows characteristics resembling those of the core from *C7a*, a similar location. Large quantities of shell material but very few pellets in the 0.1- to 0.5-mm range were found at *E9a*. Part of the high clay and silt content at *E9a* at the 30-cm depth may be due to breakup of the soft, very small (0.05 to 0.1 mm) pellets during mechanical analyses.

Traverse F.—This traverse roughly parallels the shore and extends from near shore at the southern end of Andros Island west-northwest to the midbank area west of the center of the island. The samples from station *F1* are very similar to those from *E8* in their sediment content. More pellets occur in the smaller sizes from *F1* than in the >0.25-mm range. The median diameters of pellets from the stations of *F* traverse, except for *F7*, range between 0.05 and 0.125 mm. Even though this general tendency toward predominance of the small pellets seems to prevail throughout the *F* traverse, the bimodal pattern is still conspicuous in all samples except at the bottom of the core from *F5*. Small pieces of gray limestone, shell fragments and a nonbimodal pattern similar to the bottom of the samples from *A9* and *B1* confirm that the core from station *F5* bottomed in bedrock. The smaller pellet sizes of this traverse are consistent with its rough parallelism to the shoreline in the inner-bank area. Microscopic examination of sediments from other traverses shows tendency toward higher percentages of small pellets near shore, whereas larger pellets predominate in the offshore area.

Traverse G.—This traverse runs roughly northward up to the center of the banks west of Andros Island. The surface samples of *G1*, *G2*, and *G3* are similar to those of traverse *F*. Their histograms are prominently bimodal, and more pellets come in the smaller sand sizes than in the >0.25-mm-sand sizes. Cores *G1* and *G3* each penetrated to bedrock and include shells and fragments of gray limestone in the gravel size of their bottom fractions. A shelly layer in the sediments accounts for the >2-mm material in the bottom cut of the core from *G2*. No bedrock fragments were found here. The sample is very similar to the bottom fraction from core *C4*, which is south of *G2*. Both have a shelly layer at the same depth. The sediments of the core from *G4* resemble those at midbank station *A6* in their high clay and silt content and nonbimodality, but they show more small pellets at a depth of 30 cm.

South Bight.—Three cores were taken in the South Bight of Andros Island, toward its east side. These cores contain abundant aragonite needles in the predominantly very finely particulate sediments, but ellipsoidal pellets are lacking. Shells and small aragonite aggregates constitute the sand-sized particles in these samples.

Straits of Florida.—Another series of samples was taken in a traverse across the Straits of Florida, west of the northern end of Andros Island. Microscopic analyses of the sediments show aragonite needles to be common, especially in the clay fraction. These aragonite needles might suggest spilling over of the sediments from Great Bahama Bank into the strait waters, but none of the ovoid pellets were found in the sand sizes. The bimodal patterns of the sediments seen at some of the strait stations are due to abundant sand-sized Foraminifera and pteropods. The sediments contain much fine material near the bank edge at station *GSx* and have a general trend toward increased medium- and fine-grained sand sizes with decreased clay and silt sizes outward into the straits toward Florida. The sorting coefficient of *GSγ* at the end of the traverse is 2.12. Bankward from *GSγ* the sorting is very poor—as it is nearly everywhere on the banks except at stations *A2*, *E1* through *E7*, *D8*, and *D9*, all of which are probably affected by stronger currents than prevail generally over the more easterly and northerly parts of the banks west of Andros Island.

INTERPRETATION

The combination of mechanical analyses and microscopic examination of these Bahaman bank sediments brings out certain general trends. Many of the offshore sediments are characterized by bimodal histograms resulting from large weight fractions in the 0.1- to 0.5-mm range and the clay and silt range. The 0.1- to 0.5-mm range is dominated by ovoid fecal pellets which field observations indicate to be primarily those of mud-ingesting marine annelids. The pellets observed are in large part firm to well indurated, but fresh ones are only weakly bonded.

Petrographic study by Cloud and electron micrographs taken by John Hathaway show the clay-sized particles to be almost exclusively small, needle-shaped crystals of aragonite. The silt and very fine sand sizes include many aggregates of these needles. Many of the aggregates of the 0.05- to 0.1-mm range are thought by Cloud to be fecal pellets of invertebrates other than the polychaete annelids which deposit the usual larger ovoid pellets. These smaller sized pellets become more common toward shore, whereas the larger, ellipsoidal pellets are more abundant offshore. Samples from traverses *F* and *G* illustrate this tendency.

Prevalence of the bimodal pattern may indicate areas having large and persistent annelid populations, or sites of slow or intermittent sedimentation. Samples showing high clay and silt content and no bimodal pattern possibly represent areas ecologically unsuitable to the makers of the large ovoid pellets, sites of rapid and essentially continuous deposition of aragonite needles, or in some samples, possibly an artifact of mechanical analysis or chemical disaggregation procedures.

In areas where histograms of the top sediments are prominently bimodal, little variation in particle size occurs with depth unless the core has reached bedrock. Pellets are likely to be scarce in sediments directly over bedrock. Being dependent on soft sediments for nourishment and shelter, the worms presumably do not thrive, if present, until a reasonable thickness of sediment blanket has accumulated.

On the other hand, the upper sediments of an area about midway between Andros Island and the Straits of Florida, and including stations *A5*, *A6*, *B5*, *B6*, *C2*, *D3*, and *G4*, show very high percentages of clay-sized particles and few pellets. Here it seems possible that a high rate of accumulation of fine-grained sediments and a high bacterial concentration may keep the oxygen content so low that an impoverished annelid population cannot produce pellets fast enough to make bimodal sediments. A trend toward bimodality at depths of 90 to 120 cm indicates a reversal of conditions.

The sediments again become bimodal toward shore. Although many ovoid pellets occur here, there is also an increase of smaller pellets in the 0.05- to 0.1-mm range. Presumably these are produced either by smaller or different pellet makers.

At the shoreline (*A11*, *C7*, *C7a*, *B1a*, and *E9a*) a still different condition is observed. Again aragonite needles are abundant and ovoid pellets rare. No bimodal pattern appears at depth as it does in the midbank sediments. Shells, shell fragments, Foraminifera, and small rounded pellets in the 0.05- to 0.1-mm range constitute the relatively small sand fractions. If these sediments accumulated in or adjacent to a marginal mangrove swamp environment such as prevails where now found, the ovoid pellet makers may have been excluded by ecologic factors.

Sediments taken in the southern part of the bank west of Andros Island show a bimodal pattern, but the pellets in the 0.1- to 0.5-mm range are much harder and shinier than those in the northern material. Here, too, in keeping with the more vigorous current action over this part of the bank, sorting of the sediments is consistently good, whereas it is poor over the rest of the bank west of Andros Island.

Finally, cores from the eastern side of South Bight and from the Straits of Florida are characterized by a large clay-size fraction and few or no ellipsoidal pellets. Cloud suggests that the fast tidal currents through South Bight might sweep away pellet-making worms that settled there whenever they come to the surface, thereby keeping the population down; or that occasional fresh-water influx here and near shore elsewhere might be a factor in keeping down the populations of the ovoid pellet makers. Of course, the Straits of Florida is a totally different habitat from that of the shoal-water pellet makers, and its sand-sized fraction is almost exclusively foraminiferal.

MINERALOGY

EQUIPMENT USED

The mineralogy of the cores, and of sediments filtered from the interstitial water, was investigated by means of a North American Phillips wide-range goniometer-diffractometer with strip-chart recorder. The minute quantities of sediment filtered from suspension in surface and bottom water were analyzed with a 114.6-mm-diameter Debye-Scherrer diffraction camera. A nickel-filtered copper-radiation source was employed in both methods.

The ratios of calcite to aragonite and the mole percentages of magnesium in the calcite can be more accurately determined with the goniometer-diffractometer than with the Debye-Scherrer diffraction camera. With regard to the suspended sediment, however, the small quantities available for analysis precluded the use of the goniometer-diffractometer and required instead the diffraction camera.

STANDARDS

As a preliminary step to mineralogical analysis, a set of standard mixtures of calcite and aragonite was prepared in order to evaluate properly the ratio of calcite to aragonite in the sediments. Pure, crystalline calcite and aragonite, crushed to pass a 400-mesh sieve, were mechanically mixed in an alcohol suspension to prevent solubility loss. Varying ratios of calcite to aragonite were used. The mixtures ranged from 2.5 percent calcite and 97.5 percent aragonite by weight to 90 percent calcite and 10 percent aragonite by weight. After drying, each mixture was sieved directly into a standard diffractometer sample holder for unoriented mounts. This tended to minimize the effect of preferred orientation of the minerals. Patterns were run on the diffractometer under standardized conditions, and the relative heights of the principal peaks compared: $d=3.035$ Å, $2\theta=29.40°$ for calcite and $d=3.396$ Å, $2\theta=26.22°$ for aragonite. The relative heights of two secondary peaks, $d=1.913$ Å, $2\theta=47.48°$ for calcite and $d=1.977$ Å, $2\theta=45.86°$ for aragonite, were also compared as a check. A curve was plotted (fig. 21) with the percentage of calcite in the known standard as the abscissa and the calculated percentage of calcite, taken from the line intensities of the diffractometer pattern, as the ordinate. Calculations from secondary peaks as well as principal peaks are shown in the figure. The results agree well enough to warrent the use of the X-ray diffractometer in determining the ratios of calcite to aragonite in the sediments. When analyzing the core samples, if the indicated ratios from both principal and secondary peaks did not agree exactly, an average of the two was used. The method is accurate within about 5 percent and will measure a minimum of about 1 percent calcite.

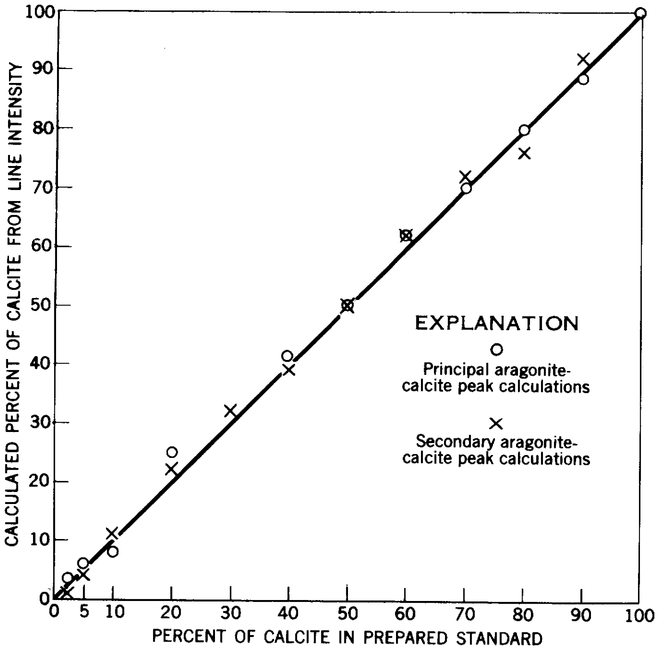


FIGURE 21.—Correlation of diffractometer peaks for standard mixtures of calcite and aragonite.

Using the same mechanical mixtures of calcite and aragonite, a second set of standard patterns was made with the Debye-Scherrer diffraction camera. In order to achieve consistent results, each spindle was rolled to the same diameter, and each contained approximately the same amount of material. The length of exposure to the X-ray beam was also the same for every spindle. These standard patterns were used in analyzing the suspended sediment removed from the surface and bottom waters on the millipore filters.

LABORATORY PROCEDURE

Because of the nature of the millipore filters and the very small amounts of sediment adhering to them after filtration of the surface and bottom waters, a special technique was employed in the analyses of the sedimentary residue. Each filter was put in a centrifuge tube, and the tube filled with acetone. The millipore filters are soluble in acetone; therefore, the insoluble carbonates and siliceous materials, if any, could be readily centrifuged to the bottom, and the dissolved filter paper removed by decantation. Several washings with alcohol removed any remaining acetone or dissolved filter paper. The remaining insolubles were washed onto a watch glass, dried, and used in preparation of a spindle. Quantities of material, thickness of spindle, and length of exposure to the X-ray beam were similar to those used in the standard spindles. A correction for film shrinkage of patterns taken with the diffraction camera was made by making use of the Wilson-type mount. This was done to facilitate accurate measurements of the 3.035 Å calcite line in order to determine the magnesium content of the calcite.

Recent works by Chave (1952, 1954a, 1954b) and by Goldsmith, Graf, and Joensuu (1955) have shown that a direct relationship exists between the position of the main peak (interplanar spacing 3.035 Å) in the calcite X-ray diffraction pattern and the mole percentage of magnesium substituted for calcium in the calcite structure. The amount of displacement of the peak from its normal position in the pattern increases with an increase in percentage of magnesium in solid solution. The interplanar spacing represented by the peak ranges between 2.975 Å and the normal 3.035 Å.

This change in spacing occurs because of the smaller unit cell which results upon substitution of Mg for Ca in the calcite structure. The observed variation of 0.06 Å represents approximately 21 mole percent $MgCO_3$ (Goldsmith and others, 1955). This means a change of approximately 0.0029 Å per mole percent of $MgCO_3$. This method was used to determine the magnesium content of the calcite on the filter papers and the content of the calcite in the sediments of the core samples described previously.

Many of the core samples included normal calcite with little or no magnesium, as well as some which contained fairly high percentages of magnesium. This situation produced two distinct peaks in the range between 2.975 and 3.035 Å - one for normal calcite and one slightly removed from the normal position as previously described. By measuring the relative heights of these two peaks, the distribution of magnesium in the calcite of the sediments could be determined. If the two peaks were too close together to differentiate between them, a range of magnesium content was given instead of a single mole percentage.

Where larger quantities of sediments were filtered from the interstitial waters a simpler technique was employed for analysis. The untreated filter was mounted on a glass slide with water-soluble gum arabic. An X-ray diffractometer pattern was made with the slide inserted in the diffractometer like a standard mount. When the pattern was completed, the filter was dampened with water, removed from the slide intact and sent to the rapid-chemical-analysis laboratory for further analyses.

The laboratory procedure for determining the composition of the core samples was as follows. The oven-dried clay and silt fractions saved from the mechanical analyses were hand ground by mortar and pestle. An oriented aggregate of the clay fraction from each sample was prepared by allowing 4 cc of a suspension to dry on a glass slide 25 by 45 mm. Randomly oriented mounts were prepared by sieving the clay or silt directly into the diffractometer sample holder as done with the standards. A diffraction pattern was made for each of the following of each sample:

1. Oriented aggregate of clay size to determine if appreciable quantities of clay minerals were present.
2. Randomly oriented mount of clay size and of silt size at a goniometer scanning speed of 2° 2θ per minute to determine overall mineral content.
3. Randomly oriented mount of clay size and of silt size at a goniometer scanning speed of ½° 2θ per minute over the range of 26° 2θ to 33° 2θ to look for quartz, calcite, dolomite, and magnesite. This procedure is capable of revealing very small percentages of these minerals which would be missed at the more rapid scanning speed.

In addition, microscopic examinations were made of the individual sand fractions of many of the samples. Mineral analyses were made by X-ray diffraction of the individual sand fractions of samples from *A2* top, *A5* top and bottom, *A11* top, *B3* top and bottom, *B7* top and bottom, *C2* top and bottom, *D1a* top, *D2* bottom, *D7* at a 30-cm depth, *E5*, and *E8* top and bottom. These samples included the main environments found in the area west of Andros Island.

Clay and silt fractions were taken from some samples of each traverse and treated with 4-percent formic acid to remove the carbonates. Oriented mounts of the insoluble residues were prepared, and an X-ray diffractometer pattern was run. Mineralogical results are shown in table 16.

DESCRIPTION OF SAMPLES

In the following descriptions of the samples, all ratios given will be in terms of calcite to aragonite.

SEDIMENT FILTERED FROM WATERS

Analyses of material filtered from the surface and bottom waters showed no definite trends in their ratios of calcite to aragonite. The ratios ranged from 1:2 to 1:50 in both surface and bottom waters. The only consistent feature appeared to be that calcite was invariably subordinate to aragonite. Some gypsum was noted, but since none has been found in any of the cores, this can be attributed to evaporation of the sea water on the filters.

The sediments filtered from the interstitial waters as would be expected, show trends in general agreement with those of the clay fraction of the cores taken in the same areas. The ratio of calcite to aragonite at *A2* in the outer banks is 1:9. The aragonite increases shoreward along traverse *A*, reaches its maximum of 1:19 at *A7* in the midbank area, and again decreases to 1:10 at the shore station *A11*. There is a slight decrease of aragonite at station *A6*.

B traverse is fairly constant at 1:19 from *B1* to *B4*, decreases slightly in aragonite at *B5* and then increases to a maximum of 1:32 at *B7*. Station *B8* at the outer bank drops to 1:10. *C* traverse shows an aragonite increase from the outer bank at 1:19 to a maximum of 1:28 at *C5* and then drops to 1:10 at the *C7* shore station. *D*-traverse samples increase in aragonite from 1:7 at *D1a* to 1:15 at *D2*. *D3* and *D4* have a decrease to 1:10 followed by an increase through *D5* to a maximum 1:24 at *D6*. Aragonite decreases through *D7* to 1:6 at *D8* near the outer bank. At *D9* the ratio is 1:19. All of traverse *E* is constant in the vicinity of 1:6 with a low of 1:4 at shore station

E9. Traverses *F* and *G* are consistent with the other traverses.

In summary, the sediments from the interstitial waters indicate that aragonite percentages are lower, and calcite concurrently higher at the bank edges and along the shore. The aragonite increases toward the midbank area, where the highest percentages are found. One anomalous situation was found. At the midbank stations *A6*, *B5*, and *D3*, where high deposition of clay- and silt-sized particles is indicated by the mechanical analyses, a slight decrease of aragonite occurs relative to the surrounding sediments. Possibly calcitic Foraminifera in these samples could account for it.

The patterns of the interstitial sediments indicated that both high- and low-magnesium-bearing calcite was present. Calcite containing from 11 to 15 percent magnesium was greatly dominant, and in some samples excluded the low-magnesium calcite completely.

CORES

RATIOS OF CALCITE TO ARAGONITE

The X-ray diffraction patterns of the clay and silt fractions from core samples in all traverses were compared with the standards described. Ratios of calcite to aragonite were calculated from the relative peak heights. Using these ratios, diagrams illustrating the mineral content of the clay and silt fractions were prepared as shown in figures 22–30. Because the percentage of minerals other than calcite and aragonite are essentially nil in the sediments, percentage figures rather than ratios of calcite to aragonite will be used in the mineralogical descriptions to follow. The diagrams from left to right on each figure represent the silt and clay fractions of the stations along each traverse in the same order as shown on the histograms of mechanical analyses. The depths of the samples along the cores at each station increase toward the bottom of the figure as indicated. Distribution of magnesium in the calcite is indicated by shading.

The overwhelming dominance of aragonite over calcite in the silt and clay sizes for most of the offshore sediments is immediately seen. However, none of the samples taken in the bank area showed a complete lack of calcite. With a few exceptions in each traverse, the percentages of calcite in the clay and silt fractions of the sediments were consistent within a narrow range, both laterally over the bank and with depth. In the silt fraction the percentage of calcite ranged from 10–20 percent, and most samples fell within the 12- to 18-percent range. Concurrently, the clay fractions contained less than 5 percent of calcite. The notable exceptions were the lower parts of cores which reached the calcitic bedrock and those taken at or near the shoreline of Andros Island. The following description of the sediments refers only to their clay and silt fractions.

In traverse *A*, core *A9* penetrated to bedrock, thereby causing a jump in percentage of calcite at a depth of 90 cm. Substantial quantities of the grayish limestone bedrock are readily recognized in the sediments. Core *A11*, taken near shore, yields large quantities of

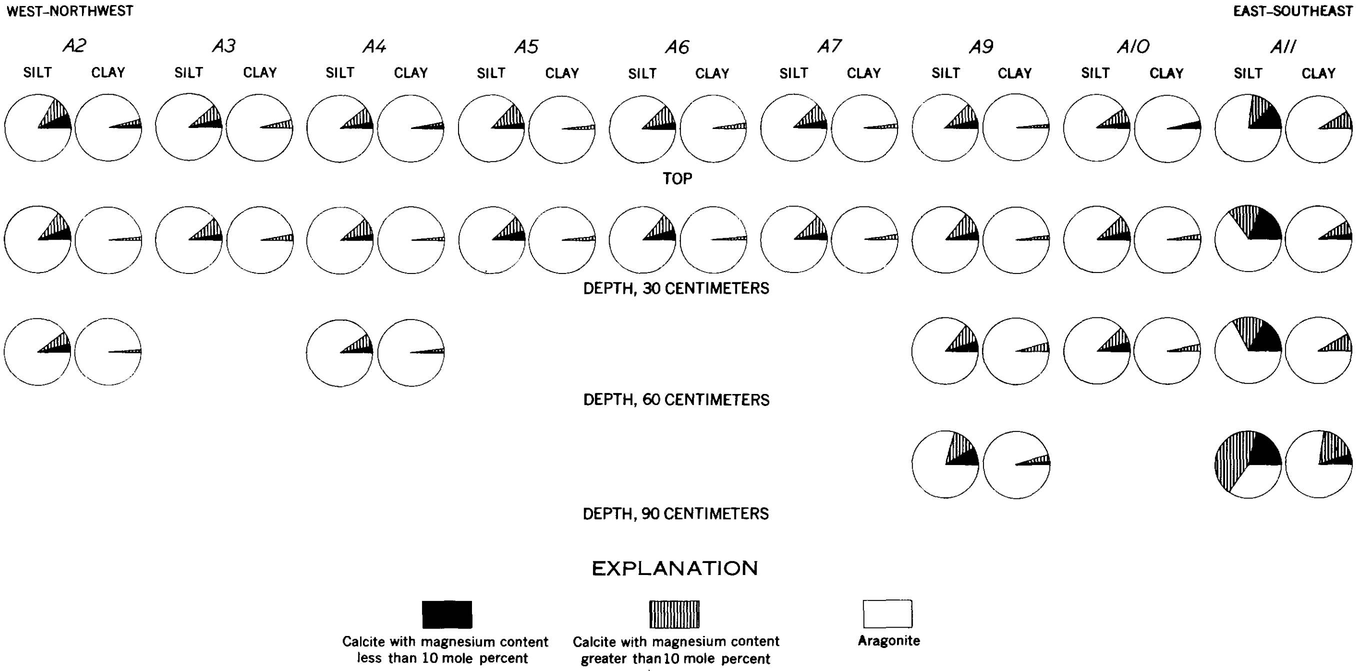


FIGURE 22.—Mineral content of clay and silt fractions along traverse *A*.

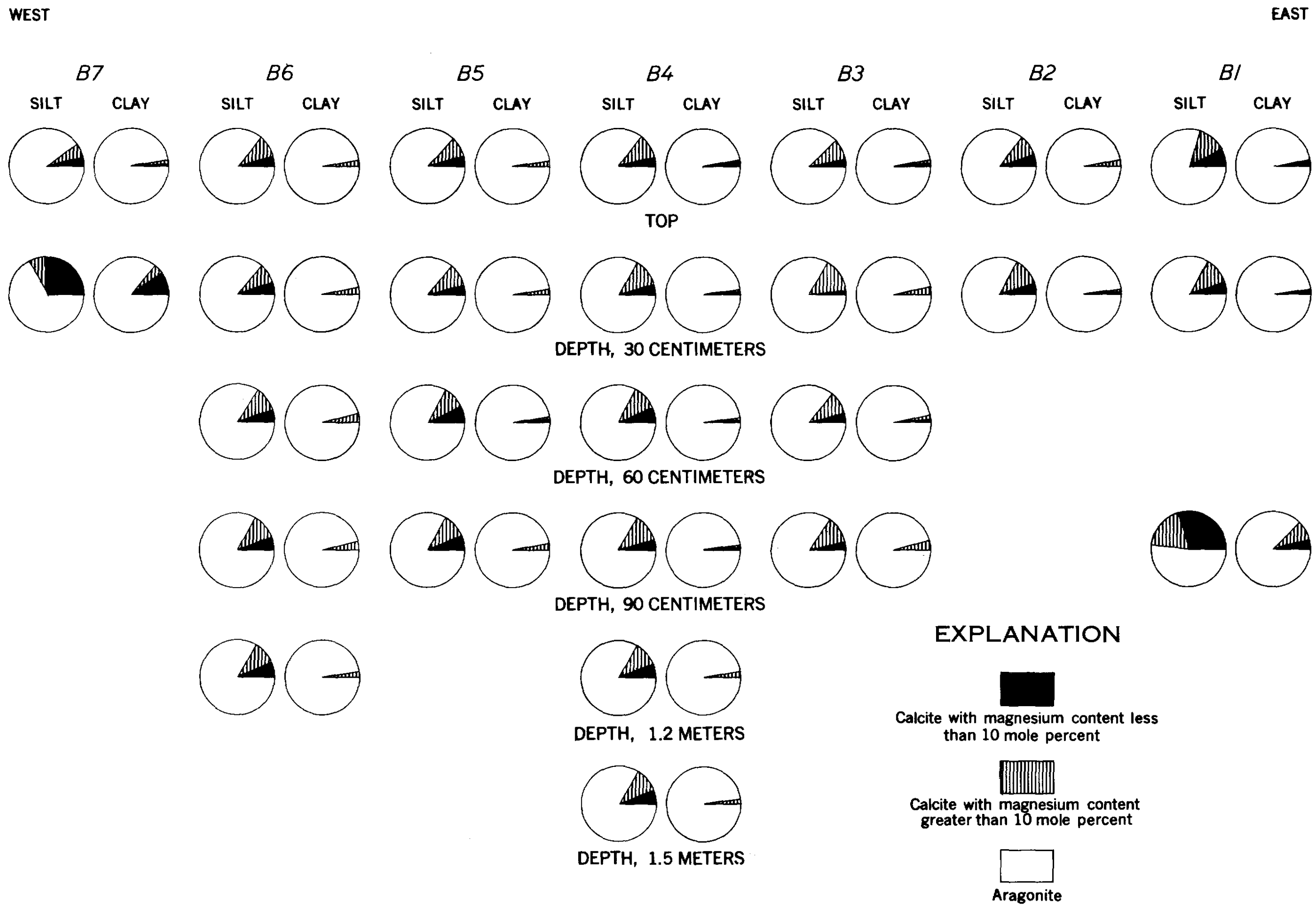


FIGURE 23.—Mineral content of clay and silt fractions along traverse *B*.

calcite; increasing from 22 percent in the silt fraction and 8 percent in the clay fraction of the surface sample to 65 percent in the silt and 22 percent in the clay fraction at the bottom of the core. The rest of the samples from traverse *A* are about average in respect to calcite content.

Cores *B1*, *B7*, *C6*, and *G1* are all comparable to core *A9* in that they penetrate to bedrock and so show unusual increases of calcite in the bottom samples. The top of core *B1*, taken 6 miles from shore, contains slightly more calcite than the average of the rest of the traverse. Cores *B2* through *B6* are consistent in calcite content both laterally and with depth.

Shell concentrations account for a fair increase of calcite in the bottom sediments of cores *C1* and *D6*. Cores *C7* and *C7a*, both taken near shore, contain above average amounts of calcite in both silt and clay fractions. An unusually large amount of powdery calcite is seen in *C7a* at a depth of 30 cm. The remainder of the silts and clays of *C* traverse are about average.

A situation similar to *C7a* is seen with core *D1a*, which was taken in a then hypersaline lake at the head of a tidal inlet in Williams Island. Substantial amounts of fine calcite grains are found at the 30-cm and 50-cm levels, whereas sediments at the top and bottom contain average amounts. The rest of the cores of traverse *D*, except *D9*, conform in calcite content to those of traverses *A*, *B*, and *C*, both laterally and with depth. *D9* is unusually low in calcite, but this lack is attributed to abundance of the aragonitic alga *Halimeda* in this core.

The core sediments taken at stations *E1* through *E7* are similar to the average sediments described above in that calcite ranges from 15–20 percent in the silt to less than 5 percent in the clay. Calcite increases to a maximum of 30 percent in the silt fractions of *E8*, *E9*, and *E9a*, and the calcite content of the clay fraction increases correspondingly up to 8 percent.

Samples from traverses *F* and *G* are about average in the calcite content of the silt, but calcite in the clay fraction decreases an average of 2 percent. In traverse *F* the cores with highest calcite content are *F1* and *F2* surface, which are adjacent to high-calcite cores *E8* and *E9*, and which contain 20 percent calcite in the

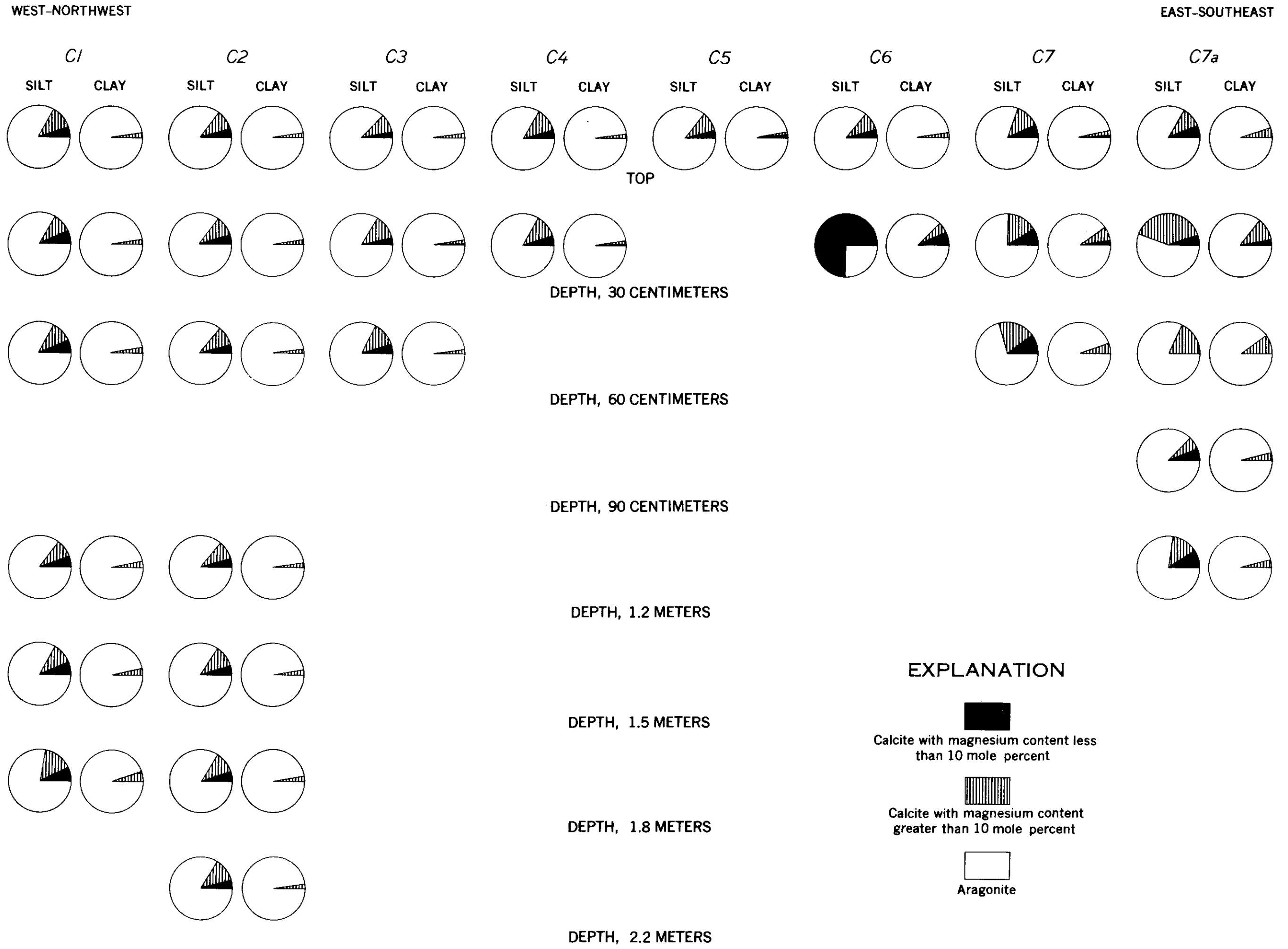


FIGURE 24.—Mineral content of clay and silt fractions along traverse *C*.

silt fraction. The bottom of core *G1* penetrated to bedrock, which increased the calcite content of the silt fraction to 28 percent.

Samples taken in the Florida Straits indicate random layering with depth, calcite ranging from 8 to 50 percent in both silt and clay fractions. No mineralogical trends with depth were observed, but calcite increases progressively toward Florida. Cores taken at *GSγ*, the farthest station from the banks, contain 30 to 50 percent calcite in the silt fraction and 25 to 30 percent in the clay fraction. Cores from *GSx* and *GSy*, near the bank edge, contain approximately the same percentages of calcite in the silt as the sediments on the banks (10 to 20 percent), but calcite in their clay fractions is substantially greater than that of the bank sediments.

The core samples taken in the South Bight of Andros Island are a little higher in calcite content than those over most of the bank area. They are similar to the sediments from *E8* and *E9*, having up to 30 percent calcite in the silt and 4 to 12 percent in the clay fraction.

MAGNESIUM CONTENT

The magnesium content of the calcite in the clay and silt fractions is roughly indicated by shading in figures 22–30. The ratios of <10 mole percent magnesium to >10 mole percent were determined by measuring the relative heights of the main calcite peaks produced on the X-ray diffraction pattern.

The average percentages of total magnesium in the calcite are variable throughout the banks, only slight trends being detectable in certain relations. At various depths along the cores, the average percent of magnesium rises or falls in small increments or may remain practically the same for several tens of centimeters. Although the changes are small the overall trend with depth in the silt fraction is toward a decrease in average percentage of magnesium in the total calcite. Core *D7* exemplifies this. The trend does not hold true in every core, but it is general over the bank area studied. Very large changes in magnesium content, generally toward the low side, are found in samples taken at or near shore or those which penetrate to bedrock. Examples are the basal fraction of cores *B1*, *B7*, *C6*, and *G1*, all of which penetrate to or near bedrock, and *D1a* and *E9a*, which are very near shore. Core *A11*, however, also near shore, shows a relatively large increase of high-magnesian calcite in the silt fraction of its lower part.

The X-ray analyses of the cores indicate an areal trend toward a higher percentage of magnesium in the calcite of the silts west of the southern part of Andros Island than that west of its middle and northern parts. Comparison of traverses *E* and *F* with *A*, *B*, *C*, and *D* will illustrate this. As previously indicated, the nearshore samples generally have a lower percentage of magnesium in the calcite of the silt fraction than do the offshore sediments. In traverses *A*, *B*, and *C* a slight decrease of magnesium is also noted in the silt-sized calcite of offshore samples taken closest to the bank edge. Cores *E1*, *E2*, and *D9* also show this trend, but core *D8* reverses it.

The calcite of the clay fractions exhibits a prevailingly high average magnesium content throughout the area west of Andros Island. Whereas the calcite of most of the silt fractions contains less than 16 mole percent magnesium, many of the clay fractions contain calcite with up to 19 mole percent of magnesuim. Low-magnesian calcite was commonly lacking entirely in the clay fraction or was present in amounts less than the minimum sensitivity of the method would measure. Conversely, some of the silt fractions contained only low-magnesian calcite, and none lacked it entirely. Examples of silt containing only low-magnesian calcite were samples from *C6* bottom, *D1a* middle, and *E9a* bottom. Analyses of the clay fractions showed that calcite had a generally high magnesium content except for those samples taken near shore, such as *D1a* and the bottoms of cores penetrating to bedrock such as *B1* and *C6*. There are no trends laterally or with depth other than those noted above.

Cores from stations in the Straits of Florida show increasing percentages of magnesium away from the bank edge because of the increase of calcite. This

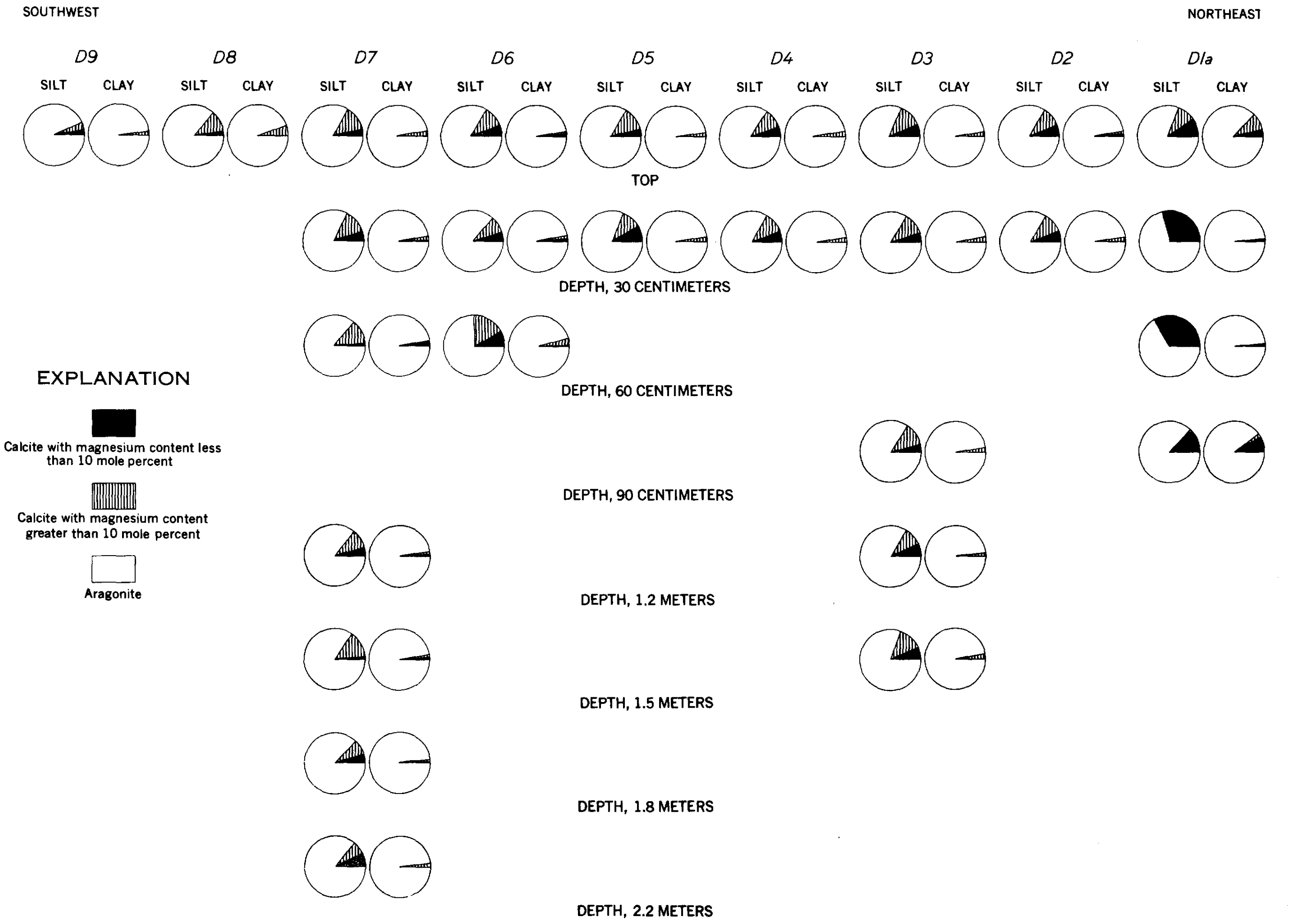


FIGURE 25.—Mineral content of clay and silt fractions along traverse *D*.

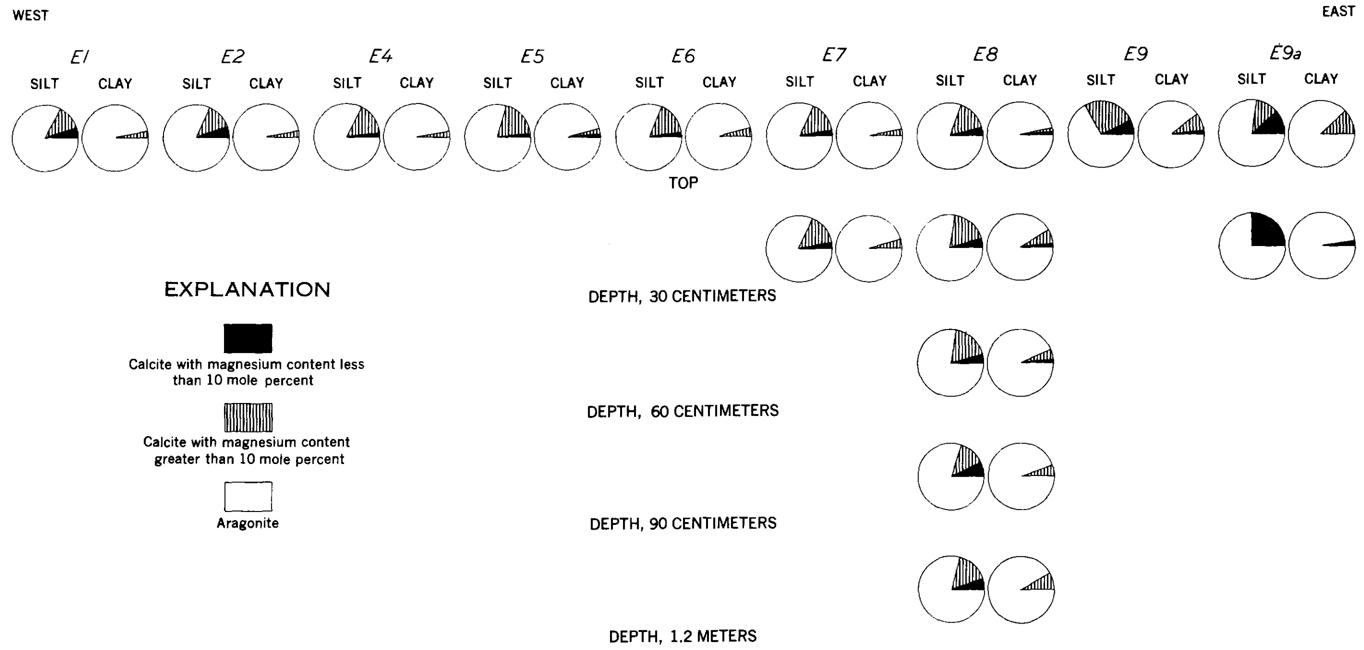


FIGURE 26.—Mineral content of clay and silt fractions along traverse *E*.

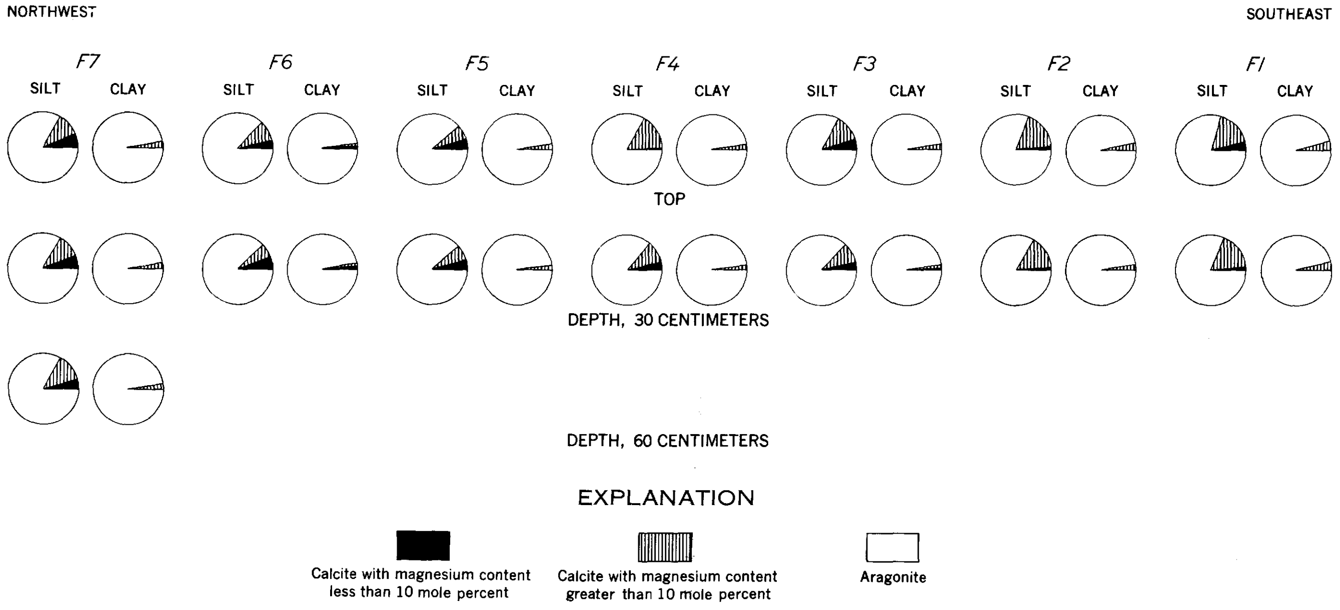


FIGURE 27.—Mineral content of clay and silt fractions along traverse *F*.

occurs in both the silt and the clay fractions. No definite trend laterally or with depth is noted for average percentages of magnesium in the calcite.

DETAILED ANALYSIS OF SELECTED SAMPLES

Sixteen samples were selected, on the basis of their mechanical analyses, as supposedly representative of the various sediment types found on the Great Bahama Bank west of Andros Island. Each individual sand, silt, and clay fraction was examined microscopically and by X-ray diffraction as described above. The mineralogical results of the examination are illustrated in figures 31 and 32.

The histograms constituting the left-hand graph of each block in figures 31 and 32 shows both the percentage distribution by weight of standard grain-size classes and the proportion of calcite and aragonite in each class, plotted to the same scale.

The graph at the right-hand side of each block shows distribution of magnesium in the calcite of each fraction.

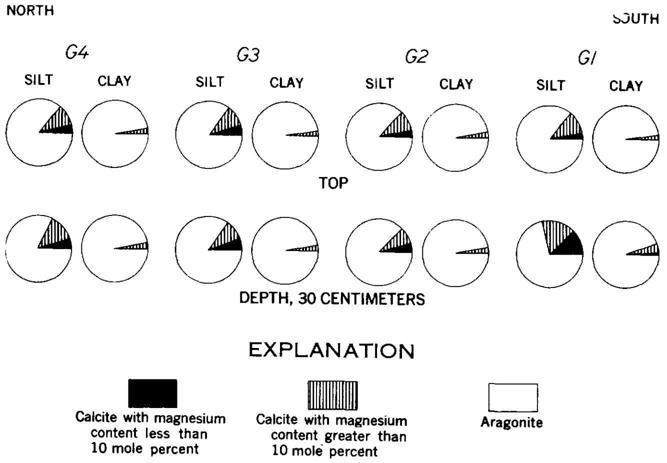


FIGURE 28.—Mineral content of clay and silt fractions along traverse *G*.

Here the percentage of calcite in each size fraction is replotted with reference to the scale at the left of this graph, and the different mole percentages of magnesium are plotted proportionally. The number at the top of each bar gives the percentage of the calcite in the fraction which contains less than 10 mole percent of magnesium in solid solution with the calcium.

Table 15 shows the total percentage of calcite in the whole sample, the total percentage of low-magnesian calcite in the total calcite of the sample, and the percentage of low-magnesian calcite in the whole sample.

As may be observed on the left-hand sides of the various blocks in figures 31 and 32 the average range of calcite per fraction is about 1 to 3 percent of the total split, with a maximum of 8 percent in the finest fraction of the sample from shore station *D1a*. No single fraction consistently contains the greatest percentage of calcite of the total sample. In most fractions, however, as shown on the right-hand side of the diagrams, the percentage of calcite per fraction is higher in the larger sand sizes, especially in samples toward shore or reaching bedrock. The silt fraction almost invariably contains 10 to 20 percent calcite, and the clay fraction, less than 5 percent calcite.

Certain peculiarities are noted in the patterns formed by the proportions of calcite in different size

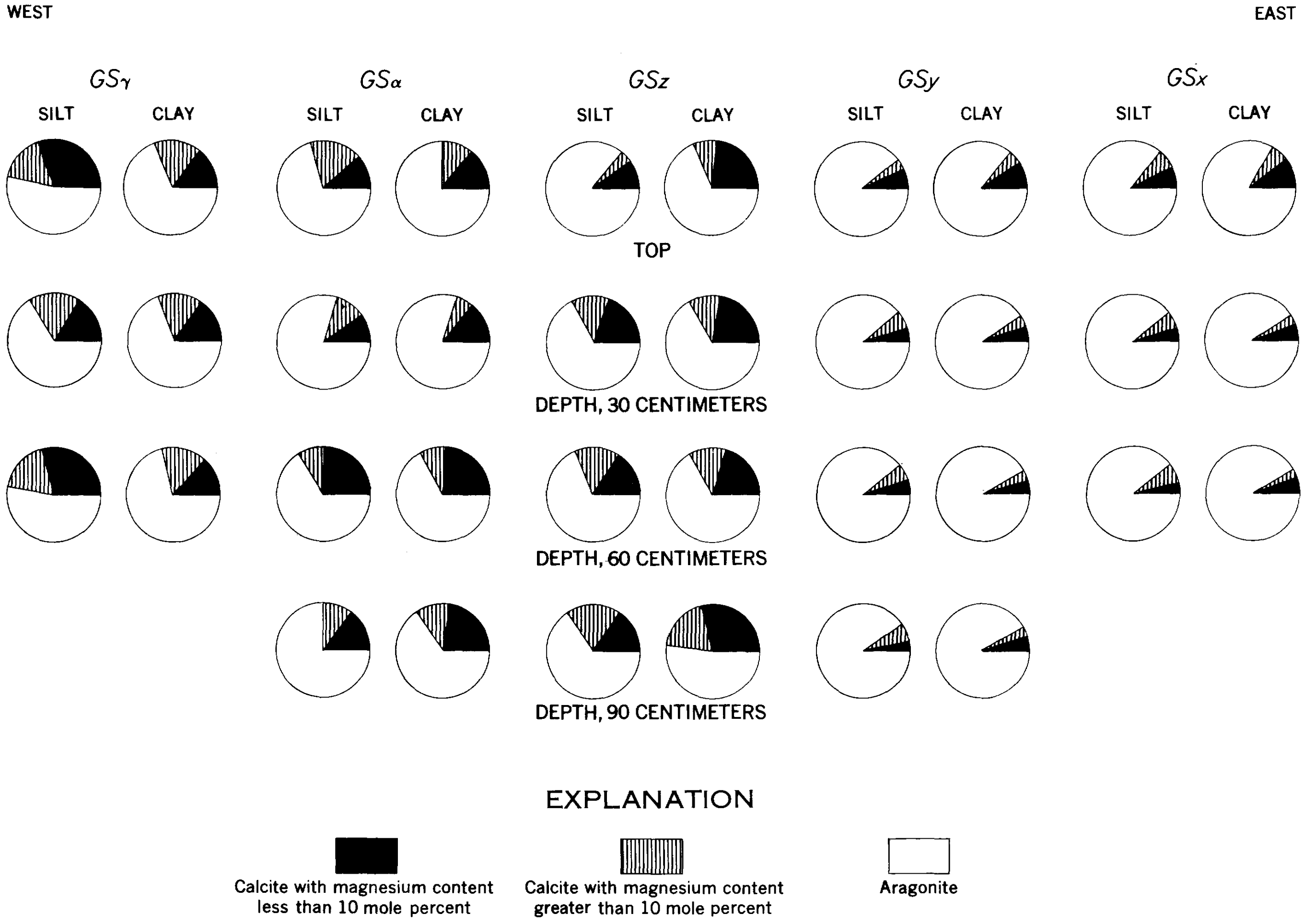


FIGURE 29.—Mineral content of clay and silt fractions across Straits of Florida (traverse *GS*).

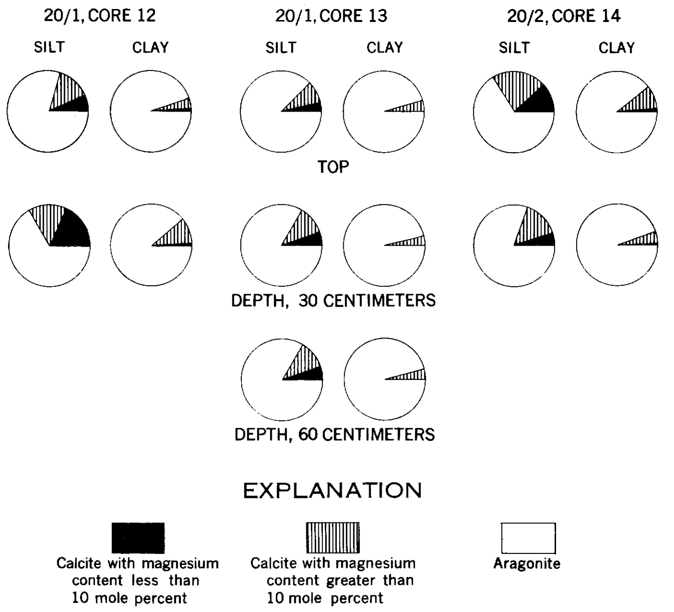


FIGURE 30.—Mineral content of clay and silt fractions from sediments of South Bight.

TABLE 15.—*Total calcite, low-magnesian calcite in total calcite, and total low-magnesian calcite in 16 sediment samples*

Sample	Percent of total calcite in whole sample	Percent of low-magnesian calcite in total calcite	Percent of low-magnesian calcite in whole sample
A2 top	8. 0	15. 0	1. 2
A5 top	8. 5	10. 5	. 9
A5 bottom	10. 0	15. 1	1. 5
A11 top	18. 0	65. 0	11. 7
B3 top	8. 0	13. 6	1. 05
B3 bottom	8. 0	13. 6	1. 05
B7 top	8. 0	16. 0	1. 3
B7 bottom	16. 0	84. 0	13. 4
C2 top	7. 0	18. 0	1. 3
C2 bottom	8. 0	26. 0	2. 1
D1a top	18. 0	16. 5	3. 0
D2 bottom	8. 0	20. 0	1. 6
D7 1-ft depth	11. 5	16. 0	1. 8
E5	6. 5	9. 0	. 6
E8 top	15. 0	8. 0	1. 2
E8 bottom	23. 0	10. 0	2. 3

classes. Thus, the larger calcite fractions of individual size classes tend to correspond strongly to the lower percentages of total calcite by weight, and the reverse is also true. Moreover, where the size distribution of the sediments is bimodal, the calcite content of the silt fraction shows a large proportional increase over the bordering very fine sand and clay fractions. With a nonbimodal pattern as in samples from *C2* top, *D1a* top, and *D2* bottom, the calcite content of the silt doesn't take this apparent jump. These peculiarities are evidently due to the fairly symmetrical or regularly skewed, low percentage distribution of the calcite in the total sample as shown in the histograms on the left. Where pelletal content or aragonite needle content in the sediments cause a high percentage of the sediments to fall into a particular grain-size class or classes, the percentage of calcite in that fraction correspondingly appears low, and the reverse.

The magnesium content of the calcite in these selected samples is characteristically either high (11 to 19 mole percent) or low (0 to 5 mole percent). Samples with magnesium in the range of 6 to 10 mole percent are rare. The high-magnesium calcite is greatly predominant through most of the samples, as was noted in the clay and silt fractions described earlier. The same exceptions for near-shore and bedrock samples apply to the total sample as for the clay and silt. Although there is seldom more than 15 mole percent magnesium in the calcite of the silt fractions, the highest percentage noted in the bank area, 21 mole percent magneisum, was found in the calcite of the silt in the core from *C7a* at a depth of 30 centimeters. The percentages of low-magnesium calcite in the calcite of the whole samples range between 8 and 26 percent with most of them falling in the range of 10 to 18 percent. This low percentage is consistent over the banks except for unusual samples such as those from *A11* top with 71 percent and *B7* bottom with 84 percent of total calcite as low-magnesium calcite. No consistent change in magnesium content is found with depth in the total calcite of the cores.

In the selected samples examined, the grain size of the various fractions doesn't seem to be significant in regard to total magnesium content. No one fraction or group of fractions was predominantly high or low in average magnesium content of the calcite although for the banks as a whole there is a broad tendency for high-magnesian calcite itself to favor the clay fraction over the sand and silt fractions. Some of the selected samples showed a progressive increase in average magnesium content as the grain size increased; some showed a progressive decrease in magnesium over the same range; and some just varied up and down at random through the sand, silt, and clay fractions.

INSPECTION FOR DOLOMITE

All the clay and silt fractions of samples taken on the bank area and many of the sand fractions were specifically examined for dolomite. X-ray diffraction and microscopic examination gave negative results. Residues from leaching of sediments in weak formic acid and acetic acid also yielded no dolomite. Leaching of other samples was tried in the same acids under refrigeration, to prevent any dolomite that might be present from going into solution. This attempt was also unsuccessful. Dolomite is either absent in the sediments or is in quantities too small to be detected by the methods employed.

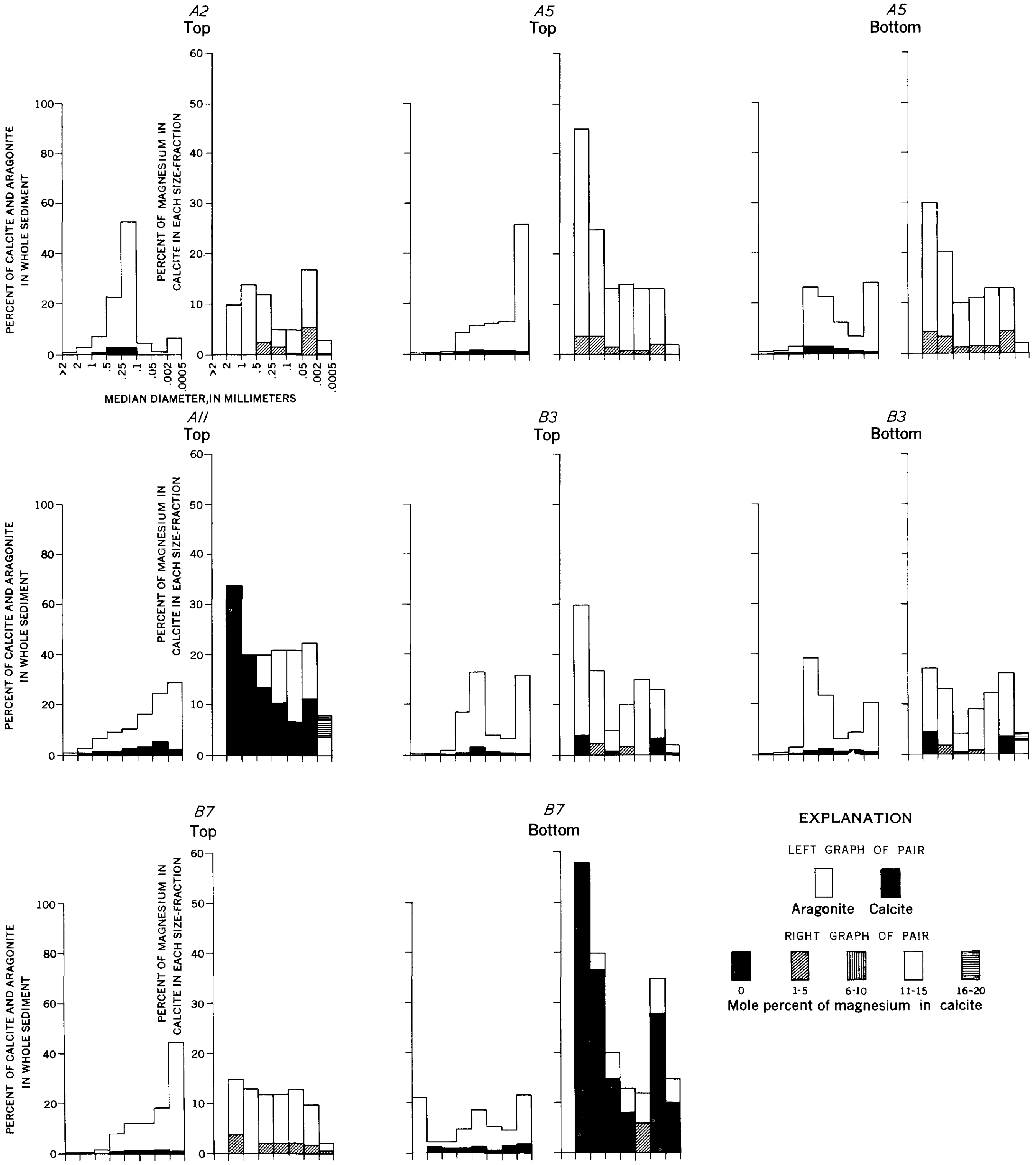


FIGURE 31.—Bar graphs of eight samples from traverses *A* and *B* showing distribution of calcite and aragonite in different size classes and of magnesium in the calcite of each size class.

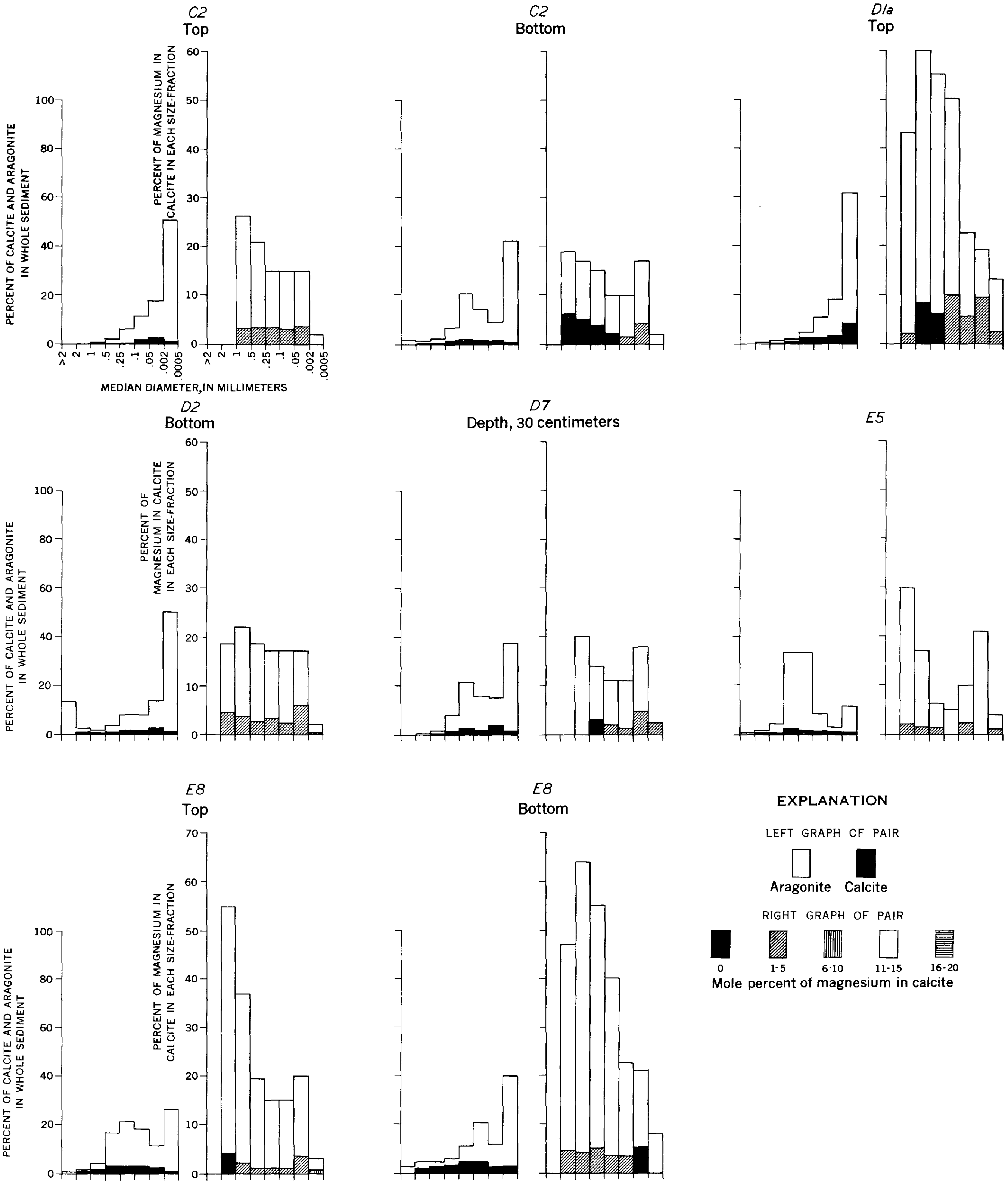


FIGURE 32.—Bar graphs of eight samples from traverses *C*, *D*, and *E* showing distribution of calcite and aragonite in different size classes and of magnesium in the calcite of each size class.

TRACE MINERALS

Small quantities of quartz have been found along every traverse west of Andros Island although in most samples it constituted less than 1 percent of the sediments. Only in the cores from *A1* through *A8* was there any consistent lack of the mineral. It is found at all depths but not necessarily along the total length of any one core. More quartz was found in cuts at or near the bottoms of the various cores than at the surface or middle except in samples from near the shore of Andros Island such as *D1a*, *E9a*, *A11*, *B1*, and *C7*: here it was found throughout the core. In nearly all samples the quartz seemed to be in a part of the core where larger than ordinary amounts of calcite were found. The greatest quantities of quartz were associated with samples *D1a* middle and *E9a* bottom where all the calcite was low-magnesium calcite. Other cores which penetrated to bedrock also contained more than traces of the mineral. Most of the quartz was concentrated in the silt fractions of the samples. Most of the clay fractions contained only traces of quartz or quantities too small to register on the X-ray diffraction pattern in the presence of the carbonates. In a few places where the core penetrated to bedrock, such as stations *B7* and *C6*, appreciable quantities of quartz were noted. Microscopic examination showed at least some of the quartz to be euhedral in nature.

Core samples from the Straits of Florida contain relatively large amounts of quartz in both clay and silt fractions. In the core from *GSx*, nearest the bank, the most calcite is at the top, and it decreases at 30 to 60 cm. The prevalence of quartz follows the same pattern. The core from *GSy* contains only traces of quartz but they are strongest where calcite is most abundant. Cores from *GSz*, *GSα*, and *GSγ* all contain much quartz that varies in quantity at different levels. Quartz is more abundant in these three more westerly straits samples than in the two to the east or any of the banks samples. Low-magnesium calcite is equal to or dominant over high-magnesium calcite in all straits samples.

A number of clay fractions and of silt fractions from various parts of the bank west of Andros Island and from the Straits of Florida were treated with formic acid to remove the soluble carbonates. The insoluble residues were examined by X-ray diffraction, and the results are shown on table 15. All the silt and most of the clay fractions contained quartz, which again shows the ubiquity of the mineral on the banks. Feldspar occurred in some middle and bottom sediments near Williams Island and in one bottom sample, from *A4*, in the northern midbank area. The bottoms of cores from *GSx*, *GSy*, and *GSz* in the Straits of Florida also contained feldspar.

Of the true clay minerals, hydrous mica and kaolinite were predominant in nearly every clay and silt fraction examined. Only the bottom samples of *A11*, *C6*, *D7*, *G1*, and the Straits of Florida core from *GSα* were devoid of hydrous mica. One silt fraction of a bank sample lacked kaolinite. With the above-mentioned minerals, the similarity between the clay minerals of the bank samples and those taken in the Straits of Florida ends.

Montmorillonite is conspicuous in every clay fraction from the straits area that was examined. No montmorillonite at all was found in the clays or silts of the bank area. Conversely chlorite or vermiculite or both occur in some fractions from each traverse on the bank area but not in the straits. Vermiculite is present in only a few of the clay fractions, but chlorite occurs in both clay and silt fractions in widely scattered localities over the bank.

Boehmite ($Al_2O_3 \cdot H_2O$) has been recognized in many clay and some silt fractions from banks cores. In all but one, the clay fraction from the top of core *E9a*, the mineral occurred deep in the sediments, ordinarily at the bottom of the core. Except in the silt fraction from the bottom of core *D1a*, the boehmite was associated with either chlorite or vermiculite and kaolinite. The iron mineral lepidocrocite is sometimes mistaken for boehmite; therefore, each fraction that contained the "boehmite" was treated with boiling, concentrated HCl for 1 hour. This treatment should remove the lepidocrocite in solution without affecting the boehmite. In each test, the mineral remained undisturbed and hence was assumed to be boehmite. The main lattice spacings according to the ASTM card file agreed perfectly with those indicated on the X-ray diffraction patterns obtained of the boehmite in the bank sediments.

The monohydrate calcium oxalate mineral whewellite was fairly common in the bottom silts from near shore sample *D1a*. Numerous small red-brown aggregates were picked from the *D1a* bottom sample. The *d* spacings of the mineral indicated by the peaks of the X-ray diffraction pattern agreed perfectly with those described by Pecora and Kerr (1954) for the mineral whewellite. A red brown coating of ferric oxalate accounts for the color of the whewellite crystals. Environmental conditions were similar to those proposed by Pecora and Kerr for the occurence of the mineral. The sediments were alkaline, and plenty of organic material was available from marine organisms and the nearby mangrove swamps. Calcite was abundant and gypsum was identified in the same core. These two minerals were associated with the whewellite in previously described occurrences. The gypsum laths were in the silt fraction at the middle of the core.

SUMMARY AND INTERPRETATION

PRINCIPAL MINERALOGICAL FEATURES OF THE SEDIMENTS

RELATIONS BETWEEN CALCITE AND ARAGONITE

The high preponderance of aragonite over calcite throughout the bank area is easily seen in figures 22–32. Electron micrographs show the clay-sized particles to be small lath- or needle-shaped aragonite crystals. Microscopic examination of the silt and sand fractions and X-ray diffraction analyses show them to have a high percentage of pellets and aggregates composed of clay-sized aragonite particles. Many species of Foraminifera, mainly calcitic, as well as both aragonitic and calcitic hard parts of other organisms are scattered through the sediments. Aragonitic algae are found in all parts of the bank area. The combination of all these sources of calcareous material has produced a sedimentary body which is strikingly consistent in its overall mineral composition.

Laterally across the banks, and with depth in the cores, the sediments were mainly aragonitic, averaging only 6 to 12 percent total calcite. Both total calcite and calcite percentage of the principal size fractions tend to increase with increasing grain size. However, no one fraction of the sediments was consistently highest in calcite content, and the selected samples of figures 31 and 32 do not show a consistent relation to total calcite.

Calcite in the silt fraction generally constitutes from 10 to 20 percent of the fraction or 1 to 3 percent of the total sediment, and is approximately 15 to 30 percent of the total calcite. In the clay fraction, calcite was generally less than 5 percent of the fraction, or about 1 percent of the total sediment, and approximately 8 to 16 percent of the total calcite. The remaining calcite, about 4 to 8 percent of the total sediment or 50 to 75 percent of the total calcite, was distributed fairly evenly through the several sand fractions. Exceptions, in which calcite content was much higher than average, were samples from the lower parts of cores which penetrated to bedrock (cores from *A9*, *B1*, *B7*, *C6*, and *G1*) or which were taken from near shore (cores *A11*, *C7*, *C7a*, *D1a*, and *E9a*). A small increase of calcite is also found in sediments in the southeastern part of the bank at stations *E8* and *E9*, and calcite generally tends to increase with depth in the core.

Samples from the Straits of Florida have larger calcite fractions than those of the bank area, with calcite from 8 to 50 percent in both clay and silt fractions. There is no particular trend with depth in the straits, but calcite increases laterally toward the Florida mainland.

MAGNESIUM CONTENT

As can be seen from figures 22–32 and table 15, the calcite in the sediments contains different average amounts of magnesium. The magnesium seems to occur mainly in two ranges of composition in the calcite, 0 to 5 mole percent and 11 to 16 mole percent. Nearly all the cores contain both high- and low-magnesian calcite, and the combination of the two determines the average magnesium in the calcite.

Most of the calcite in the Bahama Bank sediments contains over 10 mole percent magnesium and concentrates mainly in the 11- to 15-mole-percent range. In the clay fraction the high-magnesian calcite is always dominant, even to the exclusion of low-magnesian calcite in a few samples. In the silt and sand fractions, high-magnesian calcite generally predominates but is absent in some fractions of a few samples.

Table 15 shows low-magnesian calcite to be up to about 26 percent of the calcite in the sediments, 10 to 19 percent being prevalent. This means a general range of 0 to 3 percent low-magnesian calcite and concurrently 6 to 12 percent high-magnesian calcite in the total sample. The only places where high-magnesian calcites are not dominant are locally toward shore or at the bottoms of cores that penetrate to bedrock. At such places, magnesium-free or magnesium-leached (?) calcite lowers the average magnesium content and permits predominance or increase of the low-magnesian calcite.

Samples from the area west of the southern part of Andros Island have a higher calcite content than those from other parts of the bank. Because most of the calcite is high in magnesium, the total magnesium in this area is higher than that of any other part of the bank. The total magnesium of sediments from the Straits of Florida increases westward from the banks because of a higher calcite content, but there is no definite trend, laterally or with depth, for the average magnesium in the calcite.

SOURCES OF CALCITE, MAGNESIAN CALCITE, AND TRACE MINERALS

CALCITE

Most of the bank sediments consist of aragonite needles or aggregates. However, skeletal hard parts form a fair part of the larger sized material.

Seven cores were scanned by Ruth Todd and Doris Low for foraminiferal composition (table 12). 2 nearshore cores (*A11* and *E9a*), 3 midbank cores (*G3*, *F7*, and *D3*), and 2 outer-bank cores (*A2* and *B8*) were examined. All contained appreciable foraminiferal fractions, and specimens of the common species analysed by X-ray diffraction were all found to be calcitic. These range in diameter through the silt and sand sizes and presumably account for much of the calcite in those fractions. In the midbank and outer-bank cores studied, the sand-sized *Archaias angulatus* (Fichtel and Moll) are very abundant, as are the much smaller valvulinids and the miliolids. In the inner-bank areas *Elphidium, Buccella,* and *Rotorbinella* seem to be the most common. Cloud estimates the foraminiferal tests to constitute about 3 percent of the total sediment, but they may range much higher in some areas.

Although Foraminifera are probably the largest source of skeletal calcite, gastropod shells from the sediments and along the western shore of Andros Island were also found on examination by X-ray diffraction to contain some calcite. *Cerithium algicola* Adams, *Batillaria* (*Lampanella*) *minima* Gmelin, and *Cerithidea costata* (da Costa) all show small amounts of calcitic interlayering in the mainly aragonitic shell, as described for other species by Lowenstam (1954b).

A sample of rock from Andros Island, shown by chemical analysis to be 99.56 percent $CaCO_3$, was described by Illing as a gray calcite-cemented limestone formed by the recrystallization of aragonitic sediments (Illing, 1945, p. 23, 48–49). This description would apply to most observed samples of either the bedrock beneath the unconsolidated sediments or comprising the island and cay rocks. Similar material from the bottoms of cores which reached bedrock west of Andros Island was found by X-ray diffraction to be nearly pure calcite with little or no aragonite. This then could be a reason for large increases in calcite in sediments from the bottoms of cores or near shore.

A slightly higher than normal calcite content in the cores from the region of stations *E8*, *E9*, and South Bight could be accounted for by more calcitic elements in the shelly fauna of this area, and nearness to land and rock floor. The trend toward a slight increase of calcite with depth in the cores may be a simple function of more detrital material.

In the sediments of the Straits of Florida, aragonite needles are common, but none of the ellipsoidal pellets so common to the banks area were seen. Calcitic tests of Foraminifera and pteropods are predominant in the sand sizes, increasing in abundance toward the Florida mainland. The sample from *GS*γ contains over 60 percent Foraminifera (fig. 11) while the sample *GSx* near the bank has about 33 percent foraminiferal remains. Calcitic coccoliths 2 to 20 microns in diameter account for much calcite in the silt and clay sizes of the straits samples. This organic calcite tends to increase the ratio of calcite to aragonite greatly over that of the banks area, especially westward from the bank edge, where calcite increases to nearly 50 percent in both silt- and clay-sized fractions (fig. 19). Aragonite needles in the straits sediments concurrently decrease in volume westward.

MAGNESIAN CALCITE

The fact that the magnesium content of the calcite seems to fall principally into two ranges, 0 to 5 mole percent and 11 to 19 mole percent may well be a function of faunal and detrital sediment composition—the combination of the two determining the magnesium content of the sediments in different parts of the bank area west of Andros Island.

Studies by Chave (1954a, 1954b) of the magnesium content of shells of various faunal groups have shown that three major factors have an effect on the amount of magnesium in solid solution in their skeletal parts. These factors are skeletal mineralogy, the phylogenetic level of the various organisms, and the temperature of the water in which the organisms live. Other factors such as depth and salinity of water and age or size of the individual shell may have a lesser effect on the magnesium content. Therefore the organisms inhabiting an area could greatly influence the chemical composition of the sediments in that environment.

Chave (1954a, p. 282) found that in shells composed entirely of aragonite the magnesium content was generally less than 1 mole percent. This suggests that the average magnesium content of the sediment anywhere on the bank area is not seriously affected by magnesium in solid solution in the aragonite but is instead a function of the calcite content.

Foraminifera are relatively abundant in the bank sediments. According to Chave's (1954a, p. 274) calculations, at water temperatures of 20° to 30°C (Bahama Banks water averages across the upper half of this range) the weight percent of $MgCO_3$ in Foraminifera ranges from about 12 to 17 percent. This figure represents about 14 to 18 mole percent of magnesium.

Various species of Foraminifera were picked for analysis from a number of areas over the banks, and all except *Elphidium* contained from 15 to 18 mole percent of magnesium. *Elphidium* fell within the range of 0 to 7 mole percent magnesium. According to the preliminary study of foraminiferal distribution by Todd and Low, Elphidiidae are common across the banks and abundant near shore. Because they range in size from silt to fine sand, they probably account for some of the low-magnesian calcite in those fractions. Further work is planned to determine if this exception to Chave's data applies only to this particular species.

A number of mollusks were ground to pass 200 mesh and analyzed for magnesium content with the X-ray diffractometer. They were composed mainly of aragonite but with calcitic interlayers as mentioned previously. Magnesium content in the calcite of about half of the gastropods and half of the pelecypods fell within each range (0 to 5 percent or 11 to 19 mole percent). Because of the variable ratio of calcite to aragonite in the shells of these two classes, Chave (1954a) did not try to correlate water temperature with their magnesium content. In the Bahama Bank specimens, apparently no "straight line" correlation exists. However, too few samples were analyzed to determine the relationship.

X-ray diffractometer studies of fragments of bedrock from below the unconsolidated sediments west of Andros Island show them to be composed of calcite with little or no magnesium in solid solution. At least, any magnesium present was in quantities too small to be determined by the diffractometer method. The combination of such bedrock calcite, plus low-magnesium Foraminifera, and other low-magnesian calcite of organic origin could account for the total low-magnesian calcite in the sediments. Cloud thinks it conceivable that some of the near-shore low-magnesian calcite may have been precipitated chemically from waters wherein the ionic product $Ca^{++} \times CO_3^{--}$ was reduced below the saturation level for aragonite.

Variations in faunal assemblage could account for a relatively higher magnesium content in the silt west of the bights of central Andros Island (southern part of area studied) than in the silts west of the more northerly parts of the island. Changes of magnesium content with depth could also be attributed to faunal variations through time. The shells of other organisms would contribute to the high- or low-magnesium carbonate, depending on their phylogenetic position in the scale. The consistently low-calcite content of the total samples would tend to correlate with the relative paucity of shell-bearing organisms in the Bahama Banks sediments.

It is known that a large part of the calcite is of organic origin, wherein the different types of organisms secrete taxonomically distinctive quantities of magnesium at a fixed temperature. Such origin probably accounts for most of the magnesium present. To carry this logic one step farther, Chave (1954b) has found that a leaching action over a long period of time will remove magnesium from high-magnesium shells and possibly concentrate it at other places, perhaps even in the crystal form of dolomite. Fossils in the Pleistocene Lomita marl member and Timms Point silt member of the San Pedro formation of California were found to have lost much of their magnesium, apparently to form dolomite in the nearby matrix. No dolomite was found in the Bahaman sediments, but this lack may be due to an insufficient aging period for these sediments. Leaching or diffusion of the magnesium has not as yet been sufficient to move it from the organism of its origin. However, the failure to detect magnesium in the bedrock samples studied may be due to its being removed by leaching during subaerial exposure in late Wisconsin time.

TRACE MINERALS

Quartz in small quantities is found at all depths and in all areas of the Bahama Banks. Microscopic examination has shown some of it to be euhedral. A wind-blown origin has been suggested by some workers, but some of it could as easily be of authigenic origin. Supposedly authigenic euhedral quartz crystals are not uncommon in older limestones and dolomites such as the Beekmantown dolomite of Virginia (Carroll, 1959, p. 129). Possibly recrystallization of siliceous spicules or radiolaria supplied a nucleus around which secondary crystallization formed the euhedral quartz.

The quartz seems to be most plentiful where there is a high-calcite content, especially low-magnesium calcite. Samples taken close to shore such as *D1a* and *E9a* have higher quartz content than those farther out. Thus, part of this quartz may be derived from Andros Island, although such origin would only push the problem back a step.

The mineralogy of the insoluble residues from the bank area west of Andros Island is compared with that of the residues from the Straits of Florida in table 16. The occurrence of hydrous mica in both areas is to be expected because of its conspicuousness in most marine sediments of the world. Grim (1953) has stated that the alkaline environment of the sea favors the formation of "illite" (hydrous mica) or chlorite clay minerals rather than kaolinite. In addition it has been shown that the presence of Ca^{++} tends to block the formation of kaolinite.

The presence of hydrous mica, chlorite, and vermiculite in the sediments west of Andros Island is logical when the environmental conditions are considered. However, the same environmental conditions are supposed to preclude the occurrence of the kaolinite that is also found as traces in samples from all areas of the bank. This suggests that the kaolinite might have been transported to the area from an outside source. All samples from the Straits of Florida also contained kaolinite, which may have been transported by the Gulf Stream from areas to the south and west, or carried from the north by cold bottom currents. (See Science, v. 125, 1957, p. 981.) However, relatively large quantities of montmorillonite are also found in cores from the Straits of Florida, and since none at all is present in the bank area west of Andros Island, the likelihood of transport of the kaolinite of the straits sediments onto the banks is lessened unless, as is suggested by its occurrence as fillings of foraminiferal tests, the montmorillonite formed in place.

It is also unlikely that kaolinite in any abundance would form in place on Andros Island, as this land

TABLE 16.—*Mineral content of insoluble residues from the Bahama Banks and the Straits of Florida*

[A, abundant; P, present in moderate amounts; T, trace; U, undetected]

Sample from—	Hydrous mica	Kaolinite	Chlorite	Vermiculite	Boehmite	Quartz	Feldspar	Montmorillonite
Bahama Banks area:								
A2 top, silt	A	U	U	U	U	P	U	U
A4 bottom, silt	A	P	U	U	U	P	P	U
A4 bottom, clay	A	P	U	U	U	P	U	U
A11 bottom, clay	U	P	P	U	P	P	U	U
B4 top, clay	A	P	U	U	U	P	U	U
B4 middle, clay	A	P	U	P	T	P	U	U
B4 bottom, clay	A	P	U	P	P	P	U	U
C1 bottom, clay	T	P	P	U	P	P	U	U
C2 bottom, clay	A	P	P	U	T	T	U	U
C6 bottom, silt	U	T	P	U	P	P	P	U
C7a top, clay	A	A	P	U	U	P	U	U
C7a middle, silt	A	A	P	U	U	P	P	U
C7a middle, clay	A	A	P	U	U	P	P	U
D1a bottom, silt	A	A	U	U	P	P	P	U
D1a bottom, clay	A	A	P	U	P	P	U	U
D3 top, clay	A	A	U	P	U	U	U	U
D3 bottom, clay	T	A	U	P	P	T	U	U
D7 middle, silt	A	A	U	U	U	P	U	U
D7 middle, clay	A	A	U	T	U	U	U	U
D7 bottom, clay	U	A	P	P	P	U	U	U
E8, middle clay	A	A	P	P	P	P	U	U
E9a top, clay	A	A	P	P	P	P	U	U
E9a bottom, clay	A	A	P	U	P	U	U	U
F1 bottom, clay	A	A	P	U	P	P	U	U
G1 bottom, clay	U	A	P	U	P	U	U	U
Florida Straits:								
GSx top, clay	A	A	U	U	U	P	U	P
GSx bottom, clay	A	A	U	U	U	P	P	P
GSy top, clay	A	A	U	U	U	P	U	P
GSy bottom, clay	A	A	U	U	U	P	P	P
GSz top, clay	A	A	U	U	U	P	U	P
GSz bottom, clay	A	A	U	U	U	P	P	P
GSα top, clay	A	A	U	U	U	P	U	P
GSα middle, clay	A	A	U	U	U	P	U	P
GSα bottom, clay	U	A	U	U	U	P	U	P
GSγ top, clay	A	A	U	U	U	P	U	P
GSγ middle, clay	A	A	U	U	U	P	U	P
GSγ bottom, clay	A	A	U	U	U	P	U	P

area is composed of limestone which is, according to Illing (1954, p. 23, 48–49), 99.56 percent $CaCO_3$, 0.13 percent $(FeAl)_2O_3$, and 0.07 percent SiO_2. Therefore the island is an improbable source of the material because of its high carbonate purity and low percentage of clay-forming constituents. However, since no samples of residual soil from Andros Island have been examined for clay-mineral content, such a source cannot be positively ruled out. A red soil has been described (Mooney *in* Shattuck and others, 1905) on other islands of the Bahama group, but no soils of Andros Island were discussed. Clay mineralogy was not included in Mooney's description. If soils containing kaolinite are forming on Andros Island, then the prevailing easterly winds would favor some distribution of kaolinite over the bank area west of the island.

Another anomalous situation is the occurrence of boehmite in the sediments. Most publications indicate that boehmite is formed under conditions of low pH. This idea is out of character with the present environment. However, the boehmite is generally coexistent with kaolinite and often with a chloritic mineral. This relation holds true in the Bahaman sediments. According to Grim (1953) "* * * kaolinite is very slowly being lost in these [Pacific coast] marine sediments, probably by alteration to illite or chloritic mica." If the kaolinite is breaking down under the alkaline environment, it would probably be occurring at the bottom of the sediments where it had been exposed to such an environment the longest. This position is where the boehmite is found with chlorite and kaolinite. Therefore, if alumina were being freed in the breakdown of kaolinite, it might reprecipitate in the form of the mineral boehmite, and a chlorite or hydrous mica might be formed in place.

In a study of the soils of Guam, Carroll and Hathaway (oral communication, 1956) have found quantities of gibbsite and boehmite in conjunction with halloysite in soils forming on limestone. The original source of the silicates was nearby volcanic material. The high pH environment of the Bahaman sediments could probably result in a similar suite of minerals if any volcanic ash was deposited in them. Reed (1921, p. 170–171) states that volcanism occurred many times, from the Pleistocene to recorded history, in the Antilles, south of the Bahama Banks. Many of the eruptions from St. Kitts and St. Vincent Islands consisted mainly of ash, scoria, and fine dust. Some of this material might have been carried by the wind and deposited on the bank areas.

An alternative would be the presence of a low-pH environment at the time of the lowering of the seas in Pleistocene time. Exposure of the bank area to slightly acidic meteoric waters when the seas retreated locally might have favored formation, in place, of boehmite or kaolinite or both. When the sea again covered the bank, deposition of aragonite could have buried such kaolinite before it broke down in the alkaline environment.

A further possibility might combine the above mentioned factors. Heavy-mineral separation of seven of the samples that contained boehmite showed detrital quartz in the light fractions and the iron mineral maghemite in five samples, together with hematite. Maghemite is considered to be a weathering product of magnetite. Some distribution of volcanic ash over Andros Island and the exposed sea bottom during Pleistocene time therefore seems possible. Eventual weathering under conditions of high pH (similar to Guam) might result in small, residual, disseminated deposits of kaolinite, boehmite, maghemite, detrital quartz, and traces of feldspar. Such minerals would eventually be buried by reincursion of the sea and further deposition of aragonite. Small quantities of the same minerals formed on Andros Island might have been swept out into the banks during subsequent storms and thus incorporated in other parts of the sediment body such as the near-shore locations *E8* and *E9a* top. Kaolinite, the first product in this weathering cycle, may still be forming in minute quantities on Andros Island; this possibility would account for the traces of this mineral found throughout the banks area at all depths in the sediment columns. Further work will have to be done in the area in order to solve these problems.

MICROBIOLOGY AND BIOCHEMISTRY OF THE SEDIMENTS AND OVERLYING WATER

By FREDERICK D. SISLER

A bacteriological investigation was undertaken during August 1955 through June 1956 on sediment and water samples collected from the Great Bahama Bank in May 1955 and June 1956.

The samples collected in 1955 were refrigerated until examined. The sediments were retained in the plastic tubes used as core liners to collect the material, whereas the water samples were passed through millipore filters in the field and stored in polyethylene containers. Samples of sediment and water collected in 1956 were placed directly into bacteriological media for later laboratory examination. Unless otherwise stated, the data here presented pertain to material collected in 1955.

The purpose of this investigation was to elucidate the role, if any, of micro-organisms in the precipitation and early diagenesis of the calcium carbonate sediments on the Great Bahama Bank west of Andros Island.

LABORATORY TECHNIQUES AND RESULTS

For estimation of total bacterial populations, the minimum-dilution method was employed. Nutrient medium made with a semisolid base of agar was placed in Pyrex test tubes with screw caps containing a neoprene gasket. Serial dilutions of the sample material made up in sterile sea water blanks were inoculated into the nutrient tubes which served as culture receptacles for the bacteria. After incubation at 25°–28°C, subcultures from tubes showing growth were made into various selective media to characterize the metabolic activity of the active bacterial groups. This procedure served to identify the major groups in the samples as well as to indicate the biochemical activity possibly taking place in the sediments and waters in place. Details and limitations of the minimum dilution method using selective media are discussed in earlier publications (Sisler, 1953, 1954). Bacterial counts obtained by this method are expressed as exponents of the base 10. For sediment samples the counts are for 1-gram samples, and for water, 1-milliliter samples. Thus a count of 10^3 denotes a minimum of a thousand bacteria per gram of sediment or per milliliter of water. Because of the relative instability of bacteria in stored samples, the determination of bacterial populations in absolute numbers would have little meaning.

During the course of these investigations, repeated isolation of bacteria from a core at station *It′*, near previous station *G4*, revealed a diminution of the total count over a period of a year's storage amounting to less than 1 log (a factor of 10) in 3 months. Unless otherwise stated, the data presented on bacterial populations represent isolations made from the source material during a period of less than 6 months, and within 6 to 12 months of collecting the field sample. Comparative counts between samples, therefore, are considered fairly reliable within plus or minus 1 log and significant within plus or minus 2 logs.

Embrodt reagent was used for the detection of ammonia and ammonium salts. This reagent was prepared by adding 1.0 g Na_2CO_3 to 50 ml of 5 percent $HgCl_2$ and filtering through No. 40 Whatman paper.

This reagent, when freshly prepared, was sensitive to 0.001 percent NH_4Cl in sea water of 27°/₀₀ salinity.

Determinations of dissolved oxygen, biochemical oxygen demand, and inorganic sulfur ions more reducing than sulfate were made according to techniques prescribed in "Standard Methods for the Examination of Water and Sewage" (Am. Pub. Health Assoc. and Am. Water Works Assoc., 9th ed., 1946), with modifications as described.

An iodine method was used for estimation of the reducing capacity of the sediments. Because of the unusual nature of the source material (99+ percent $CaCO_3$ dry weight), the following method was adapted and found to give reproducible results: To a weighed amount of the sample placed in a long-necked volumetric flask, standard dilute iodine solution was added in excess, and the mixture acidified with glacial acetic acid. The effervescence created by the action of the acid on the $CaCO_3$ was allowed to abate, then the mixture was brought up to known volume with distilled water. Equal parts of the cleared solution were titrated with standard sodium thiosulfate, using starch as an indicator.

For estimation of pH and Eh, the Beckman Model G meter was employed, using either 2-inch internal or 5-inch external glass and platinum electrodes.

Selective media used for characterizing the various bacterial groups are given in table 17, and the results obtained are given in tables 18 through 21.

TABLE 17.—*Media used in determination of bacterial populations*

Aerobic heterotrophs:		
Bacto-agar	g	5.0
Bacto-dextrose	g	3.0
Yeast extract	g	1.0
Bacto-peptone	g	1.0
$NaNH_4HPO_4 \cdot 4H_2O$	g	.5
Na_2SO_3	g	.1
$FeCl_3$	g	.1
Sea water ($S=36$°/₀₀)	ml	750
Distilled water	ml	250
Cellulose decomposers:		
Bacto-agar	g	2.0
Bacto-dextrose	g	.5
Yeast extract	g	.5
Bacto-peptone	g	1.0
$NH_4H_2PO_4$	g	.2
$FeCl_3$	g	.2
Sea water ($S=36$°/₀₀)	ml	750
Distilled water	ml	250
Strip lens paper in each tube		1
Gelatin liquefiers:		
Beef extract	g	3.0
Bacto-peptone	g	5.0
Gelatin	g	120.0
Sea water ($S=36$°/₀₀)	ml	750
Distilled water	ml	250
Nitrate reducers:		
Bacto-dextrose	g	4.0
KNO_3	g	1.0
KH_2PO_4	g	.2
$FeCl_3$	g	.02
Sea water ($S=36$°/₀₀)	ml	750
Distilled water	ml	250
Quasi-autotrophs: [1]		
Bacto-dextrose	g	4.0
$(NH_4)_2HPO_4$	g	.2
$MgSO_4 \cdot 7H_2O$	g	.2
$FeCl_3$	g	.2
Sea water ($S=36$°/₀₀)	ml	750
Distilled water	ml	250
Anaerobic bacteria:		
Bacto-agar	g	5.0
Bacto-dextrose	g	3.0
Yeast extract	g	1.0
Bacto-peptone	g	1.0
$NaNH_4HPO_4 \cdot 4H_2O$	g	.5
$FeCl_3$	g	.1
$Na_2S \cdot 9H_2O$	mmole	1.0
Na_2CO_3	mmole	1.0
Sea water ($S=36$°/₀₀)	ml	750
Distilled water	ml	250
pH=8.6, Eh=−130 mv		

[1] The writer defines quasi-autotrophs as organisms having the ability to live in an essentially mineral medium, but with carbohydrate added to serve as an energy source. Such organisms must synthesize their own vitamins, amino acids, and other compounds essential for metabolism and growth.

TABLE 18.—*Estimated total bacteria and gas-producing bacteria per gram (wet weight) of sediment at approximately 15 cm below sediment-water interface west of Andros Island.*

Station	Number per gram (wet weight)	
	Total bacteria	Gas-producers
A2	10^{7}	10^{3}
A3	10^{7}	10^{2}
A4	10^{9}	10^{4}
A5	10^{7}	10^{2}
A6	10^{7}	10^{4}
A7	10^{8}	10^{4}
A9	10^{8}	10^{3}
A10	10^{8}	10^{3}
A11	10^{8}	10^{2}
B1	10^{8}	10^{3}
B2	10^{7}	10^{4}
B3	10^{6}	10^{3}
B4	10^{7}	10^{4}
B5	10^{6}	10^{2}
B6	10^{8}	10^{5}
B7	10^{8}	<10
C1	10^{8}	10^{2}
C2	10^{8}	10^{2}
C3	10^{7}	10^{2}
C4	10^{8}	10^{3}
C5	10^{9}	10^{2}
C6	10^{8}	10^{8}
C7	10^{6}	<10
D1	10^{7}	<10
D2	10^{7}	10^{2}
D3	10^{7}	10^{3}
D4	10^{8}	10^{3}
D5	10^{7}	10^{2}
D6	10^{8}	10
D7	10^{7}	<10
D8	10^{8}	10^{2}
E7	10^{7}	10^{3}
E8	10^{8}	10^{2}
E9	10^{7}	<10
F1	10^{7}	10^{2}
F2	10^{7}	<10
F3	10^{7}	10^{2}
F4	10^{8}	<10
F5	10^{8}	<10
F6	10^{7}	10^{2}
F7	10^{7}	10^{2}
G1	10^{7}	10^{2}
G2	10^{6}	10^{2}
G3	10^{10}	10^{7}
G4	10^{10}	10^{10}
GSy	10^{5}	<10
Andros Island (mangrove swamp)	10^{6}	10^{3}

CHARACTERISTICS OF THE BANK WATER

Bacterial populations estimated from examination of the bank waters west of Andros Island ranged from less than 10 to 1,000 organisms per milliliter. Samples from surface and bottom water revealed homogeneous distribution of the bacteria (table 20), as would be expected in shallow waters with prevailing wind-produced turbulence.

TABLE 19.—*Distribution of total bacterial populations and gas-producing bacteria at various depth in sediments from random cores*

Station	Core depth (in cm)	Number per gram (wet weight)		Station	Core depth (in cm)	Number per gram (wet weight)	
		Total bacteria	Gas producers			Total bacteria	Gas producers
B3	3	10^7	10^2	*C7*	3	10^7	<10
	15	10^6	10^3		15	10^6	<10
	30	10^8	10^2		30	10^2	10
B5	3	10^7	10^4	*D1*	3	10^8	<10
	15	10^6	10^2		15	10^7	<10
	30	10^6	10^3		30	10^8	10
	75	10^8	10^8	*D6*	3	10^8	10
C6	3	10^6	10^4		15	10^8	10
	15	10^8	10^8		30	10^2	10^2
	30	10^7	10^3				

TABLE 20.—*Distribution of bacterial populations in water at selected stations*

Station	Position in water	Estimated minimum number of bacteria per milliliter
A2 [1]	Surface	10^3
	Bottom	10^3
B3 [1]	Surface	10^2
	Bottom	10
C6 [1]	Surface	10^2
	Bottom	10^2
C7 [1]	Surface	<10
	Bottom	<10
D6 [1]	Surface	10^2
	Bottom	10^2
It' [2]	Surface	10
A1' [2]	Surface	<10

[1] Samples collected on millipore filters, refrigerated, and examined several months later.

[2] Samples taken in place and inoculated directly into nutrient medium.

TABLE 21.—*Biochemical characteristics of representative types of bacteria isolated from top 15 cm of sediments west of Andros Island*

[Plus and minus signs denote presence or absence of indicated bacterial type]

Station	Laboratory code	Total bacteria per ml	Cellulose decomposers	Gelatin liquefiers	Ammonia producers	Quasi-autotrophs	Gas producers	Remarks
A3	A3A	10^7	—	—	—	—	—	Aerobe.
A11	A11A	10^8	—	—	+	+	—	Facultative aerobe.
B3	B3D	10^7	—	—	—	—	—	Aerobe.
B3	B3G	10^8	—	—	—	—	—	Aerobe.
B3	B3H	10^8	—	—	—	—	—	Facultative aerobe.
B3	B3Q	10^6	—	—	+	—	—	Aerobe; strong ammonia producer.
B5	B5H	10^2	—	—	—	—	—	From water sample; facultative aerobe; forms white colonies on agar.
B5	B5I	10^2	—	—	—	—	—	From water sample; facultative aerobe; forms yellow colonies on agar.
B5	B5J	10^2	—	—	—	—	—	From water sample; aerobe; forms cream-colored colonies on agar.
C1	C1A	10^7	—	—	—	—	—	Aerobe.
C6	C6C	10^2	—	—	—	—	—	Aerobe.
C6	C6D	10^7	+	+	—	—	—	Aerobe.
C6	C6F	10^4	—	—	—	—	—	Microaerophile.
C6	C6I	10^4	—	+	—	—	—	Aerobe; produces blue pigment.
C6	C6J	10^4	—	—	—	—	—	Microaerophile; produces orange pigment.
C6	C6K	10^6	—	—	+?	+	—	Aerobe.
C6	C6N	10^4	—	—	+	—	+	Facultative aerobe; vigorous gas producer.
C6	C6P	10^3	—	+	—	—	—	Facultative aerobe.
C6	C6W	10^7	—	—	—	—	—	Aerobe.
C7	C7B	10	—	+	—	—	—	Aerobe; produces yellow-green pigment; agar digestor.
C7	C7E	10^7	—	—	—	+	—	Facultative aerobe; produces olive-green pigment.
C7	C7H	10^6	—	—	—	?	—	Facultative aerobe; strongly thigmotactic.
C7	C7I	10^6	—	—	+	—	—	Facultative aerobe; produces yellow pigment.
D1	D1F	10^2		+	+?	—	+	Facultative aerobe; produces black pigment; agar digestor.
D1	D1G	10^8	—	+	—	+	—	Aerobe; agar digestor.
D1	D1C	10^2	—	—	—	—	—	Aerobe from water sample.
D5	D5A	10^7	—	+	—	—	—	Facultative aerobe; produces blue pigment.
D6	D6I	10^2	—	+	—	+	—	Aerobe.
D8	D8A	10^8	—	—	—	—	—	Preferential anaerobe.
E9	E9A	10^7	—	—	+	+	—	Aerobe.
F1	F1A	10^7	—	—	—	—	—	Microaerophile; grows poorly on agar surface.
F4	F4A	10^8	+	—	—	?	—	Aerobe; forms yellow pigment.
G2	G2A	10^6	+	+	+	+	—	Microaerophile; iridescent.
G4	G4A	10^{10}	+?	—	—	+	+	Facultative aerobe; produces hydrogen and carbon dioxide gas in dextrose medium.
G4	G4B	10^{10}	—	—	—	+	—	Aerobe.
GSy	*GSyA*	10^5	—	—	—	—	—	Facultative anaerobe.

The paucity of bacterial numbers and species in the waters as compared with the biota of the underlying sediments suggests that waterborne bacteria are biochemically insignificant. In addition, those few species that were isolated and studied in this survey have shown no striking biochemical characteristics such as might indicate a pronounced influence on the carbonate equilibria if they were abundant. These findings are in agreement with those of Bavendamm (1932) and Black (1933a), who considered the paucity of waterborne organisms to preclude their role in carbonate precipitation. Previously Lipman (1924, 1929a) reached a similar conclusion on the basis of his observations of the low numbers of bacteria in sea water.

Perhaps the most significant biological process taking place in the water mass over the bank is that of photosynthesis. From light-dark-bottle tests conducted during daylight hours on June 11, 1956 in water west of Andros Island, it was estimated that the rate of oxygen production was 1.5 milliliters per liter per hour. A light-meter reading taken on the bottom at 11:00 a.m. registered 30 Weston units.

Assuming the principal photosynthetic reaction to be

$$6\ CO_2+6\ H_2O\rightarrow C_6H_{12}O_6+6\ O_2,$$

then CO_2 (as CO_2, H_2CO_3 or HCO_3^-) is being converted into organic matter at the rate of 1.5 ml/l per hr during daylight. The night endogenous rate of O_2 uptake was 0.1 ml/l per hr, leaving a net gain for a 24-hour period of 16.8 ml/l of O_2 produced, or 16.8 ml CO_2 per l converted to organic matter (taking yearly average 12 hours daylight, 12 hours darkness, $1.5\times12-0.1\times12=16.8$).

Since light and dark bottles were placed on the bottom for the above described test, it can be assumed that the productivity rate of the entire water column above was equal to, or greater than, the figure obtained.

CHARACTERISTICS OF THE BANK SEDIMENTS

In contrast to the overlying water, an examination of the bottom sediments from samples taken during May 1955 revealed a great variety and abundance of organisms (tables 18, 19). Gas-producing bacteria were detected in most samples inoculated into semisolid nutrient agar. From table 18 it can be seen that total bacterial population at various depths in the sediments from 47 stations ranged from 100,000 to 10 billion per gram wet weight. Although bacterial populations of billions per gram in sediments have been reported previously (ZoBell, 1946 a, b), such figures are rare. It would seem, therefore, that the finer grained sediments west of Andros Island are unusual in their ability to support such a large bacterial population.

The observation that most samples contained gas producers would indicate a high concentration of fermentable organic matter. This is supported by the high productivity figure obtained from the light- and dark-bottle experiments as well as the high biochemical oxygen demand (BOD) values given in table 22.

TABLE 22.—*Biochemical oxygen demand of water and sediment west of Andros Island*

Source station	*BOD after 6 days*[1] *at 30° C (in ppm)*
Sediment from core 15 cm deep:	
A3	120
A11	200
C1	160
C6	340
D5	140
D8	370
F4	270
G2	310
G4	330
GSy	180
GSy	140
Surface water:	
A1′	.5
It′	.5

[1] Sediment samples represent 1 percent dilutions. Water samples were undiluted and were allowed to flow directly into Winkler bottles on the bottom. BOD represesents the oxygen (in parts per million) required during stabilization of the decomposable organic matter by aerobic bacterial action.

Evidence of biochemical heating also suggests that the organic matter in the sediments is being rapidly fermented. Temperature measurements taken with a mercury thermometer of recent core material from station *It′* showed a slight increase in temperature of the mud from adiabatic temperature (0.2°C after 2 days at 30°C). A poisoned control sample failed to increase in temperature. Such a temperature increase within the sample containing living bacteria is indicative of rapid oxidation of organic matter (ZoBell and others, 1953). Cloud's May 1955 observations of sediment, water, and air temperatures at various stations, however, revealed no consistent temperature differences such as might be considered indicative of important biogenic heating of the sediments in place.

Because analysis of gas from a bacterial culture at station *G4* (pl. 9*C*) showed large amounts of hydrogen and carbon dioxide (table 23), a trap was devised to capture any gas that might be escaping from the sea bottom in this area when station *It′* (near *G4*) was occupied in June 1956. A clear-glass funnel 30 cm in diameter was fitted with a glass test tube by means of a tightly taped hose coupling. The funnel was filled with sea water at the sediment-water interface, inverted over and forced part way into the sediment on the bottom, and weighted down with a lead belt. Visual observations by Cloud at intervals during a 24-hour period revealed no free gas in the test tube. It thus appears that the bacterially generated gases either recombine chemically within the sediments about as quickly as formed, or are not generated in sufficient quantity to exceed the absorption capacity of the water. An accident with the trap prevented sampling of the water beneath it to test for absorbed gases.

TABLE 23.—*Mass spectrometeric analysis of gas evolved in bacterial culture from sediments at station* G4

[Analysis by V. H. Dibeler, Mass Spectrometry Section, Natl. Bur. Standards]

Gases	*Percent*
H_2	63. 4
N_2	4. 6
O_2	. 4
CO_2	26. 3
H_2O (vapor)	5. 3

Table 18 lists several stations, (*A6, B4, B6, C6, G3,* and *G4*) where the gas-producing bacteria in the sediments were the predominant species. Because of the possible significance of these gas producers, it should be noted that station *C6* was the site of a whiting when occupied in 1955, and that *G3* and *G4* were near station *It'*, which was a whiting site in 1956. However, no consistent correlation was observed between high populations of either total bacteria or gas producers and whitings.

A total of 36 pure cultures were isolated from random sediment samples. These cultures were considered to be different species at the time of isolation, based on their morphology, pigmentation, and appearance in the initial culture media.

Table 21 lists some biochemical characteristics believed pertinent to the carbonate-precipitation problem. Cultures from 6 stations (*A11, B3, C6, C7, E9, G2*) produced ammonia. Of these, stations *A11, B3,* and *E9* included ammonia-producing bacteria in sufficient numbers to be biochemically significant. Mud from station *B3*, at the site of minimum alkalinity and maximum salinity and greatest cumulative $CaCo_3$ loss from the overlying waters, includes a strong ammonia producer. The water column itself includes 10^4 per liter of an ammonium-producing *Micrococcus* at station *G4* (pl. 9*E*). It should be pointed out, however, that the ability to produce ammonia by bacteria does not necessarily indicate that much ammonia is actually being produced in place by these organisms. If it were produced in quantity, its effect should be to raise the pH, which does not happen, according to Cloud's field data, in either sediments or overlying water. Terminal pH readings taken of many cultures after several weeks incubation in the various media listed in table 27 also indicates that the net effect of the microbial flora in the sediments is to lower the pH in place.

The gross biochemical picture presented in the sediments thus appears to be that of decomposition of organic matter, principally carbohydrate material, with evolution of gas and a reduction of pH. A great variety of biochemical reactions is presumably taking place in the sediments. Possibly the most significant for carbonate precipitation, however, are the fermentation processes and accompanying influences on the carbon dioxide equilibria.

Perhaps second in importance to fermentation is that of the reduction of sulfates. Although few sulfate-reducing bacteria were found in the sediments, iodine titrations of the calcareous mud indicated that sulfate was being reduced, probably to intermediate compounds more oxidized than sulfide. A determination of the total sulfites in a mud sample from station *G4* based on the volumetric method revealed over 1,000 ppm Na_2SO_3 or equivalent. Tests for free sulfide in various sediment samples were only weakly positive; they indicate incomplete reduction of sulfate. Eh measurements of the sediment at the time of collection did not indicate a highly reducing environment such as is characteristic of the high sulfate-reducing bacterial population responsible for the production of sulfide in most marine environments.

SULFATE-REDUCING BACTERIA OF THE MANGROVE SWAMPS

One core (east coast core No. 4) from the intertidal zone up Fresh Creek estuary, bordering an area of mangrove growth on eastern Andros Island, was examined for bacterial flora. Using the minimum-dilution technique, an estimated total population of 10^6 organisms per gram was observed, with a count of 10^4 sulfate-reducing bacteria per gram. This core showed a much higher count of sulfate reducers than any of the bank sediments. This one examination would appear to substantiate the conclusion drawn by Bavendamm (1932) that if sulfate-reducing bacteria should play a key role in the precipitation of $CaCO_3$ their main scene of action would be the mangrove swamps.

INTERPRETATION

A summary of the hypotheses for the bacterial precipitation of $CaCO_3$ by various investigators is given in table 24, and ZoBell (1946b) adequately reviews the published record on the case for bacteria.

TABLE 24.—*Possible mechanisms for* $CaCO_3$ *precipitation through microbial activity as postulated by various investigators* [1]

Reaction	*Authors*
$(NH_4)_2CO_3 + CaSO_4 \rightarrow CaCO_3 + (NH_4)_2SO_4$	Murray and Irvine (1889).
$Ca(NO_3)_2 + 3H_2 + C \rightarrow CaCO_3 + 3H_2O + N_2$	Drew (1911, 1912, 1913, 1914).
$Ca(HCO_3)_2 + 2NH_4OH \rightarrow CaCO_3 + 2\ H_2O + + (NH_4)_2CO_3$	Kellerman and Smith (1914).
$Ca(COOCH_3)_2 + 4O_2 \rightarrow CaCO_3 + 3CO_2 + 3H_2O$	Berkeley, (1919).
$CaSO_4 + 4H_2 \rightarrow 4H_2O + CaS$ $CaS + CO_2 \rightarrow CaCO_3 + H_2S$	Bavendamm (1932).

[1] See also the works of Baier (1937), Kellerman (1916), Lalou (1955), Molisch (1925), Nadson (1928), Smith, C. L. (1940), Smith, N. R. (1926), and ZoBell (1946).

Although the production of ammonia by bacteria would presumably enhance the precipitation of $CaCO_3$ as a result of increased pH, bacterial tests indicate the magnitude of this reaction in the bank sediments west of Andros Island to be inconsequential, and the field observations of Cloud show no increase in pH in any of the bank waters. Similarly, the sulfate reducers can have no important independent effects. Thus, the writer endorses the view of Bavendamm (1932) that no single species of bacteria could be solely responsible for $CaCO_3$ precipitation. Rather, bacteria may be considered as biochemical agents which can influence the carbon dioxide and calcium equilibria in a variety of ways, depending upon the environment. In the area here reported on, it is suggested that rapid photosynthesis of carbohydrate in the water column, followed by the almost equally rapid fermentation into CO_2 in the sediment and its subsequent evasion into the waters above, is a likely biochemical influence on $CaCO_3$ precipitation. These processes coupled with the partial reduction of sulfate, appears to be the principal role that micro-organisms may play in the precipitation of $CaCO_3$ in this region.

The conclusions of the present work, then, are as follows:[2]

1. Concerning the possible role of bacteria in $CaCO_3$ precipitation west of Andros Island, the large bacterial populations of the sediment in contrast to those of the water suggest the former as most likely to affect $CaCO_3$ equilibria. However, proof is lacking that bacteria are in any large degree responsible for the precipitation observed.
2. Rather than a single species or group of microorganisms playing a part in $CaCO_3$ precipitation, the total assemblage should be considered as a single interacting complex.
3. Bacteria, rather than causing the direct precipitation of $CaCO_3$ as chemical catalysts or otherwise, seem most likely to influence such precipitation indirectly through their biochemical activity.
4. Chief among the biological and biochemical processes taking place west of Andros Island are those of photosynthesis in the water column and fermentation in the sediments, the latter generating CO_2 which to some extent probably leaks upward into the water.
5. The reduction of sulfate in the sediment through microbial action could conceivably be instrumental in contributing excess calcium ions. The present studies, however, although barely touching on the mangrove swamp environment, support the previously published view that sulfate reduction to sulfide is important only in or bordering mangrove swamp sediments.
6. It is not likely that bacteria would act as nuclei for the precipitation of $CaCO_3$ since their cell magnitude is approximately the same as the aragonite needles found in the sediment and water. However, the thigmotactic characteristics of bacteria could act to form agglomerates of $CaCO_3$.

SUGGESTIONS FOR FUTURE WORK

1. Although laboratory tests indicate that the bacteria of the sediments are producing gas and cores recently obtained show gas evolution, additional field observations are needed to estimate the magnitude, type, and effects of gas being produced in place.[3]
2. Additional field observations and laboratory studies are required on bacterial activity in the mangrove swamps for comparison with that in waters and sediments over the banks.
3. Studies should be made of the role of free or nascent gas on carbonate deposition and diagenesis.
4. Preliminary suggestion of biochemical heating within the sediments should be followed up for confirmation and subsequent estimation of magnitude.
5. Further studies are needed on the biochemical aspects of pure cultures of bacteria isolated from carbonate sediments as a possible aid to better understanding their influence on the environment of limestone deposition and diagenesis.
6. The Great Bahama Bank may afford a site of unusual interest for investigation of petroleum genesis. The highly saline waters, high organic productivity, and abundance in the sediments of microorganisms capable of producing hydrogen gas suggest further studies of conditions possibly leading to the formation of petroleum hydrocarbons. The significance of hydrogen gas in relation to petroleum genesis has been discussed by ZoBell (1947).

CHEMICAL ANALYSES OF THE WATER

By Henry Kramer

Water samples collected in 1955 and available for chemical analysis were mostly of 210-ml total volume for surface and bottom water, with only a few 500-ml samples. The interstitial waters were usually represented by only 40- to 60-ml samples. This limitation

---

[2] After these conclusions were reached, C. E. ZoBell called the writer's attention to the possible existence of microspheres or microenvironments within the sediments. The conditions within such small environments, of the order of no more than a few microns or several millimeters, may be quite unlike conditions in the surrounding sediment or water and may favor precipitation and early diagenetic changes of calcium carbonate. The above, then, favors the concept of local dynamic equilibrium between solution and precipitation of calcium carbonate within the sediments as discussed under post-depositional effects by Cloud.

[3] The significance of gas in marine deposits has been previously discussed by Sisler and ZoBell (1950, 1951a, 1951b).

in size dictated the methods of analysis. Some of the procedures are capable of greater precision under more favorable circumstances, but all were adequate to indicate variations in composition.

The results of these analyses, combined with field determinations by Cloud and Rezak and footnotes by Cloud, are given in table 25. Methods are discussed below.

Special analyses of selected large samples collected in 1956 are given in a preceding section (table 4).

RELIABILITY OF THE DATA

Sodium, potassium, lithium, and strontium were determined with the Beckman flame photometer, with photomultiplier detector using an oxyhydrogen flame.

Sodium was determined at 588 mμ by diluting the sample 500 times and making measurements in the 20- to 30-ppm range; bracketing with standards containing 1 ppm Ca, 1 ppm K, 4 ppm Mg, and 6 ppm SO_4. Under good conditions the method is accurate to ±3 percent. A range of about 4 percent was observed in analyses reported.

Potassium was determined at 768 mμ by diluting the sample 50 times and making measurements in the 5- to 10-ppm range; bracketing with standards containing 10 ppm Ca, 250 ppm Na, 40 ppm Mg, and 60 ppm SO_4. The accuracy is ±5 percent, with an apparent range to 6 percent in samples reported.

Strontium was determined by precipitating Ca and Sr as the oxalates in a 25-ml fraction; igniting to the oxides, dissolving the residue in 1+99 HCl and diluting to 10 ml. The determination was carried out at 461 mμ by bracketing with strontium standards in the 15- to 25-ppm range containing 1,250 ppm Ca. Accuracy is ±5 percent.

Lithium was determined at 671 mμ by diluting the sample 5 times and making measurements in the 0- to 1-ppm range; bracketing with standards containing 100 ppm Ca, 400 ppm Mg, 100 ppm K, 2,500 ppm Na, and 600 ppm SO_4. The accuracy is ±10 percent.

Calcium and magnesium were determined volumetrically with ethylenediaminetetraacetic acid (Versene) using suitable indicators. Murexide is used for calcium and Eriochrome Black T for the magnesium. Accuracy is ±2 percent under good conditions. Comparison with gravimetric analyses and chloride ratios indicates a systematic discrepancy of about −10 percent for calcium and +4 percent for magnesium in reported analyses, run by visual titration and listed as reported in table 25. The problem of calcium analysis in sea water is discussed in a following section by James Carpenter.

Silica was determined colorimetrically by reduction of the silica molybdate complex with aminonapthol sulfonic acid to a "heteropoly blue." Accuracy is ±5 percent.

Phosphorus (soluble) was determined colorimetrically by reduction of the phosphomolybdate complex to molybdenum blue with stannous chloride. Accuracy is ±5 percent.

Chloride was determined gravimetrically as silver chloride. Accuracy is ±0.2 percent under good conditions. Apparent discrepancies as much as 2 to 4 percent were observed in present results.

Sulfate was determined gravimetrically as barium sulfate. Accuracy is ±1 percent under ideal conditions. Apparent discrepancies up to 4 percent and even as high as 9 percent were observed in present results.

Total alkalinity was determined by titrating with sulfuric acid to a definite pH. Alkalinity, for the most part, represents the bicarbonate concentration and, to a minor extent, the concentration of carbonate, borates, phosphates, and silicates. Accuracy of the method is ±2 percent, but gaseous exchange may introduce discrepancies. Results not agreeing within 3 percent between field and laboratory are rejected in Cloud's discussions and graphs.

Boron was determined colorimetrically using carminic acid. Accuracy is ±5 percent.

Laboratory pH and Eh measurements were by John Chandler on a Beckman pH meter, Model GS, using glass-calomel and platinum-calomel couples, respectively. For Eh measurement the potential of a saturated calomel electrode at the measured temperature was added to the measured reading.

DESCRIPTION OF METHODS USED

SODIUM

REAGENTS

Sodium chloride, 1 ml=2 mg Na.—Fuse 6 g NaCl in a platium crucible, and cool in a dessicator. Grind, dissolve 5.084 g in water, and dilute to 1 l in a volumetric flask.

Calcium chloride, 1 ml=2 mg Ca.—Ovendry 6 g of $CaCO_3$ at 105°C. Cool, weight 4.994 g into a 250-ml beaker; add 20 ml of water; cover with a watch glass, and carefully add 9.0 ml of HCl. Dilute to 1 l in a volumetric flask.

Magnesium chloride, 1 ml=2 mg Mg.—Ovendry 8 g of $MgCO_3$ at 105°C. Cool, weigh 6.936 g into a 250-ml beaker, add 20 ml of water; cover with a watch glass, and carefully add 14 ml of HCl. Dilute to 1 l in a volumetric flask.

Potassium chloride, 1 ml 2=mg K.—Ovendry 5 g of KCl at 105°C. Cool, weigh 3.814 g of KCl; dissolve in water, and dilute to 1 l in a volumetric flask.

Sulfuric acid, 1 ml=1 mg SO_4.—Dilute 5 ml of concentrated H_2SO_4 to 900 ml with water (about 0.2*N*). To standardize, weigh out duplicate 0.4392-g portions of NBS $Na_2C_2O_4$ in a platinum crucible. Ignite in the muffle at a dull red heat; raise the temperature gradually until the salt is entirely white, but do not fuse (contents may be used if fused, but subsequent solution is difficult.) Cool, wash into a 250-ml Erlenmeyer flask with boiled distilled water. Titrate the Na_2CO_3 with the approximately 0.2 *N* H_2SO_4 using methyl orange indicator. Adjust the strength of the H_2SO_4 until the ignited oxalate portion (above) requires 40.00 ml of the acid. The acid will then be 0.1639 *N*. This acid is used subsequently for the bicarbonate titration. In order to get 1 ml of acid equivalent to 1.00 mg SO_4^{--}, dilute 63.50 ml of the 0.1639 *N* H_2SO_4 to 500 ml with distilled water in a volumetric flask.

Prepare 0-, 20-, 25-, and 30-ppm Na standards, each containing 1 ppm Ca, 1 ppm K, 4 ppm Mg, and 6 ppm SO_4. For example, in the preparation of 1 l of the 30 ppm Na standard, pipet 15 ml of the Na standard, into a 1-l volumetric flask, followed by 0.5 ml of the Ca standard, 0.5 ml of the K standard, 2 ml of the Mg standard, and 6 ml of the SO_4 standard, and dilute with 1 l of water. Store in a tightly sealed bottle if used over longer time.

FLAME PHOTOMETER PROCEDURE

Dilute 20 ml of the sea-water sample to 100 ml in a volumetric flask. This solution is also used for the chloride, sulfate, potassium, and lithium determinations.

For sodium dilute 5 ml of this solution to 500 ml in a volumetric flask. (Total dilution 1:500.)

Instrument settings: O_2-10psi, H_2-5 psi; slit width, about 0.05 mm; monochromator sensitivity at midpoint 5.0; photomultiplier, 1 position (least sensitive); zero suppression, off; blue-sensitive phototube, 22-megohm resistor; wavelength for sodium 588 mμ. While aspirating the 30-ppm Na standard, adjust the wavelength dial to get maximum emission with minimum slit width, simultaneously making the 30 ppm read 100 percent transmission. The 25-ppm Na standard will then read about 85 percent transmission, and the 20-ppm Na standard about 72 percent. Bracket the sample with suitable standards, making 3 readings on the upper standard, 3 on the sample, and 3 on the lower standards. If the readings do not agree to ± 1 percent, rerun. If there is drift in the readings, correct by resetting the upper standard using the fuel gage; the slit-width knob is not used.

Make calculations by assuming a straight line between the upper and lower sodium standards and multiplying by the dilution factor of 500.

POTASSIUM

REAGENTS

Prepare 0-, 5-, 10-ppm K standards, each containing 250 ppm Na, 10 ppm Ca, 40 ppm Mg, and 60 ppm SO_4. See sodium for preparation.

Sample preparation: dilute 5 ml of the 20/100 dilution to 50 ml with distilled water in a volumetric flask. (Total dilution 1:50.)

FLAME PHOTOMETER PROCEDURE

Instrument settings: wavelength 768 mμ; red-sensitive phototube (photomultiplier off); 10,000-megohm resistor in the circuit; and slit width about 0.15 mm. Other settings same as for sodium.

The procedure is similar to the sodium determination. With the 10-ppm set at 100 percent transmission, the 5 will read 55 percent and the blank about 5 percent.

LITHIUM

REAGENTS

Lithium chloride, 1 ml=1.00 mg Li.—Ovendry 7 g of LiCl at 105°C, and weigh out 6.109 in a closed weighing bottle. Transfer to a liter volumetric flask, and dilute to volume with water.

Prepare 0-, 0.5-, and 1.0-ppm Li standards, each containing 2,500 ppm Na, 100 ppm Ca, 400 ppm Mg, and 600 ppm SO_4.

FLAME PHOTOMETER PROCEDURE

Instrument settings: wavelength 670.8 mμ; blue-sensitive phototube; 22-megohm resistor; slit width about 0.05; full photomultiplier sensitivity. Other settings the same as for sodium. If there is clogging of the burner capillary, a large capillary bore burner may be substituted.

In determination use the 20 to 100 dilution—with the 1-ppm Li standard set at 100 percent transmission, the 0.5 ppm Li will read 60 percent transmission and the 0 will read 20 percent.

STRONTIUM

REAGENTS

Strontium chloride, 1 ml=1.00 mg Sr.—Ovendry 2.0 g of $SrCO_3$ at 105°C for 1 hour. Dissolve 1.685 g in 5 ml of 1+1 HCl and dilute to 1 l with distilled water.

Pipet a 25-ml aliquot of the sample into a 150-ml beaker, add 5 ml of 1+1 HCl and 2 to 3 drops of methyl red indicator. Add 0.5 g $(NH_4)_2C_2O_4$, heat to boiling, and neutralize with (1+1) NH_4OH until the indicator is just yellow; add 1 to 2 drops in excess, and digest on the steam bath for 1 hour. Filter while warm through a 7-cm 42 Whatman paper, and wash the precipitate 3 times with 1 percent ammonium oxalate. Ignite the paper and residue at 800°C in a platinum crucible. Dissolve the residue in 5 ml of 1+99 HCl, and dilute to 10 ml in a volumetric flask with distilled water. Prepare standards of 0-, 15-, 20-, 25-ppm Sr, each containing 1,250 ppm Ca.

FLAME PHOTOMETER PROCEDURE

The most sensitive strontium line is at 460.7 mμ, and the instrument settings are full photomultiplier sensitivity and slit width about 0.05 mm. With the 25-ppm Sr standard at 100 percent transmission, the zero will read about 8 percent. Samples are bracketed between the standards prepared in 5-ppm increments.

ALKALINITY

Alkalinity is determined volumetrically with standard 0.0164 N H_2SO_4 using a Beckman, pH meter model 2H. With a 50-ml sample the titer ran in the range of 7 ml. Waters were filtered prior to alkalinity determination.

CHLORIDES

Determined gravimetrically as silver chloride after precipitation with $AgNO_3$. Dilute 20 ml of the sample to 100 ml in a volumetric flask and take a 10-ml fraction. This will give a precipitate weighing about 200 mg. Bromide and iodide, in trivial amounts, are included in this determination, reported as Cl^-.

SULFATES

Sulfates are determined gravimetrically as barium sulfate. A 20-ml sample will give a precipitate weighing about 150 mg.

CALCIUM AND MAGNESIUM

Ethylenediaminetetraacetic acid (EDTA) and its sodium salts form chelate complexes with metal cations. These complexes are colorless, and it is necessary to use suitable indicators to detect the end point. The principle of the method is that EDTA is capable of extracting calcium and magnesium from their dye complexes because the EDTA complexes are more stable than the dye complexes. Further, EDTA combines with calcium before it combines with magnesium, and at a pH of 12 the calcium is titrated in the presence of magnesium using ammonium purpurate as indicator. At a pH of 8.5 to 11, calcium and magnesium are both titrated using Eriochrome Black T as indicator. Magnesium is then calculated by difference.

REAGENTS FOR CALCIUM

Standard Ca *solution, 1 ml=1.00 mg* Ca.

Standard versene, 1 ml≅0.5 mg Ca.—Weigh 5.0 g of reagent grade disodium ethylenediaminetetraacetic acid, 0.10 mg $MgCl_2 \cdot 6H_2O$, and make up to 1 l with water.

Sodium hydroxide, 4 N.—Dissolve 40 g of pellet NaOH in about 50 ml of water. Cool, dilute to 250 ml. Store in a polyethylene bottle.

Murexide indicator.—Saturate distilled water with murexide (ammonium purpurate), and leave excess dye in the bottle. Refrigerate to allay decomposition.

PROCEDURE FOR CALCIUM

Pipet 5.00 ml of the standard calcium solution into a 25-ml porcelain evaporating dish; add 15 ml of water, 1 ml of 4 N NaOH and stir. Add 5 drops of murexide indicator. Titrate using a 10-ml microburet. Because of the subtle endpoint, excellent illumination is necessary. The titrant should be added slowly until the color changes from pink to purple. At the endpoint, no further color change should occur. The titration must be completed within 5 minutes after the addition of NaOH. Calculate the titer in terms of a calcium factor for 1 ml of versene determined against standard Ca solution.

REAGENTS FOR MAGNESIUM

Standard magnesium solution, 1 ml=1.00 mg Mg.

Indicator solution.—The dye is Eriochrome Black T—the sodium salt of 1-hydroxy-2-naphthylazo-5-nitro-2-naphthol-4-sulfonic acid. Dissolve 0.5 g of the dye and 4.5 g hydroxylamine hydrochloride in 100 ml of 95 percent ethyl alcohol.

Buffer solution.—Dissolve 67.5 g of NH_4Cl in 570 ml concentrated NH_4OH, and dilute to 1 l with distilled water. Store in a polyethylene bottle.

PROCEDURE FOR MAGNESIUM

Standardize the versene against magnesium by taking 5.00 ml of Mg standard in a porcelain dish, adding 15 ml of water, 1 ml of buffer, and 3 to 5 drops of indicator. Titrate with versene until all the red disappears and the solution becomes blue. Calculate the versene titer as a factor of 1 ml.

Standardize the versene against 5.00 mg Ca using the NH_4Cl-NH_4OH buffer and EBT indicator. The factor is calculated as follows:

$$\frac{\text{titer with murexide}}{\text{titer with EBT}}=\text{factor}$$

In running the determination, first pipet a 5-ml sample into a 25-ml porcelain dish, add 2 drops of concentrated HCl, and determine calcium as outlined for the standard.

Then pipet a 2-ml sample into a 25-ml porcelain dish; add 2 drops of concentrated HCl, and determine magnesium as outlined for the standard.

To calculate Mg in sample:

1. [Titer for 2-ml sample×2.5]—[Titer for 5-ml sample×factor]=ml versene consumed by Mg

2. ml versene consumed by Mg×titer of versene in terms of Mg=mg Mg in sample

BORON

Boron was determined spectrophotometrically using carminic acid as described by Hatcher and Wilcox (1950). There is no salt effect, and the method is very rapid and precise. A 2-ml aliquot of the sample is treated by their procedure and the absorbance is measured in 25-mm cells at 585 mμ. An absorbance of 0.5 is obtained with 10γ. It is suggested that 5γ, 10γ, and 15γ standards be carried along with each set of samples because of the instability of the carmine.

If there is sufficient sample, a potentiometric titration may be used as a control as described by Foote (1932). A glass-saturated calomel electrode as in the line-operated 2H Beckman pH meter is adequate in response.

PHOSPHORUS

Phosphorus is determined colorimetrically by reduction of the phosphomolybdate complex to molybdenum blue with stannous chloride as described by Ellis and others (1945) and Harvey (1948).

For the highest accuracy use a large volume of sea water and concentrate the phosphate by precipitation with 10 mg of aluminum as carrier, filter, dissolve the precipitate in dilute H_2SO_4 and determine colorimetrically as described above. For routine determinations, use a 100-ml sample and run directly. Using a 2.5-cm cell, 0.02 mg of P_2O_5 gives an absorbance of about 0.1. There is a salt effect in the system, so incorporate NaCl in the standard (about 0.40 g NaCl/100 ml of solution).

SILICA

Silica is determined colorimetrically by reduction of the silica molybdate complex with amino-naphthol-sulfonic acid to a "heteropoly blue" as described by Bunting (1944).

Because the SiO_2 in sea water may be in colloidal form, it is suggested that a 50-ml sample be digested for 1 hour with 0.20 g of silica-free $NaHCO_3$. In addition, the standards made from $Na_2SiO_3 \cdot 9H_2O$ should contain both NaCl and $NaHCO_3$ to counteract any salt effect. At a wavelength of 815 mμ using a 2.5-cm light path, a 50-ml sample containing 0.01 to 0.05 mg of SiO_2 will give an absorbance of 0.3 on the photometer.

THE PROBLEM OF CALCIUM DETERMINATION IN SEA WATER[4]

By JAMES H. CARPENTER[5]

The chemistry of calcium is relatively simple (Latimer and Hildebrand, 1951, p. 57–79; Moellar, 1952, p. 845–867). On the basis of atomic and physical properties, calcium is a member of periodic group IIa and more closely related to the heavier members of the series, strontium and barium than to magnesium. Among the members of this group the only common oxidation state is +2, and a trend from covalence to ionic bonding with increasing size is noted. The solubility and formation of complexes in aqueous solution reflects the close similarity of these elements. Differences in degree are found but are not large enough to be classified as quantitatively specific.

The methods for determining calcium which have been published include nearly all the common analytical techniques. The calcium in sea water has been most commonly estimated by oxalate precipitation and the precipitate either ignited to the oxide and weighed (Matide, 1950; Thompson and Wright, 1930) or dissolved in sulfuric acid and the oxalic acid titrated with potassium permanganate (Kirk and Moberg, 1933; Gripenberg, 1937). These procedures have in common the difficulties encountered in quantitative precipitation with oxalate in the presence of magnesium and strontium. The ratio of magnesium to calcium in sea water is approximately 3 on a weight basis and 5 on an equivalent basis. The ratio of strontium to calcium in sea water is approximately 0.03 on a weight basis and 0.015 on an equivalent basis.

Examination of a few of the careful studies on oxalate precipitation shows that this composition makes separation very difficult (Ingols and Murray, 1949; Holth, 1949; Gordon and Wroczynski, 1952; Kolthoff and Sandell, 1943, p. 345–360). There is marked disagreement among the recommended procedures. Compensating errors arise from postprecipitation of magnesium and incomplete precipitation of calcium as temperature conditions and digestion periods are varied. Sodium, potassium, and sulfate have an effect on the composition of the precipitate. All of the methods show some coprecipitation with equal amounts of calcium and magnesium, so that multiple precipitation is necessary. Errors arising from these extensive manipulations and solubility losses are difficult and tedious to avoid. Strontium is supposedly precipitated quantitatively with the calcium, but the opposite opinion has been expressed (Banewicz and Kenner, 1952; Chow and Thompson, 1955). Corrections for sea-water analyses have been suggested (Webb, 1938). The oxalate procedures for sea water are laborious and not susceptible to rigorous interpretation.

The use of sulfate in methanol solutions for separating calcium, strontium, and barium has been examined (Elving and Van Atta, 1950), and interference by sodium and potassium are noted. Poor separations were obtained, and the precision was several parts per

---

[4] U. S. Public Health Service research grant RG 4430 provided funds in support of a part of the work on which this discussion is based.

[5] Chesapeake Bay Institute, The Johns Hopkins University.

thousand, which is approximately the same as the better oxalate procedures.

A flame photometric procedure for calcium in sea water has been described (Chow and Thompson, 1955). The chloride, magnesium, potassium, and sulfate ions showed a negative radiation interference, and sodium ions gave a positive radiation interference. Use of the method of standard additions did not completely eliminate these interferences since emission intensity was not linear with calcium concentration. A precision of one percent was obtained.

When the careful analyses of open-ocean water by various investigators are compared on the basis of calcium to chlorinity ratios, agreement to within one percent is found (Matide, 1950; Thompson and Wright, 1930; Kirk and Moberg, 1933; Gripenberg, 1937; Chow and Thompson, 1955; Dittmar, 1884). This constancy of composition will allow calcium estimation in the open sea to be made with nearly as great precision from accurate chlorinity as by direct determination. In samples that have a greatly altered calcium to chlorinity ratio, the possible change in relative concentration of the other ions makes the use of the empirical gravimetric procedures questionable.

The determination of calcium by titration with ethylenediaminetetraacetic acid (EDTA, or versene) has been described (Betz and Noll, 1950). This reagent is not specific for calcium and reacts with a large number of metals, so that separations or masking reagents are necessary. The determination of calcium in distilled-water solutions has been examined by this writer. The reaction between calcium and EDTA has a log stability constant of approximately 10. The effect of this value on the determination may be examined with the following relationships for the titration:

$$\mathrm{Ca^{++}+EDTA \rightleftarrows CaEDTA} \qquad \mathrm{K}=\frac{[\mathrm{CaEDTA}]}{[\mathrm{Ca}][\mathrm{EDTA}]}$$

Let $M_0=$ original calcium ion concentration
$M =$ calcium ion concentration during the titration
$T =$ added EDTA concentration

Neglecting volume changes the titration may be described as—

$$\mathrm{K}=\frac{M_0-M}{M\cdot(T-M_0+M)} \text{ or}$$

$$M=M_0-T+\frac{M_0-M}{\mathrm{K}M} \qquad (1)$$

For the case of complete reaction; that is, infinite K, equation (1) reduces to a straight-line relationship with M equal to zero at T equal to M_0, which may be taken as the theoretically perfect system. The last term of equation (1) is an expression for the error. The titration is most readily performed by measuring M near the end point and estimating the end point from a plot of M versus T. The slope of the expected curve may be found by taking the first derivative with respect to T of equation (1).

$$\frac{dM}{dT}=\frac{-\mathrm{K}M}{2\mathrm{K}M-\mathrm{K}M_0+\mathrm{K}T+1} \qquad (2)$$

Evaluation of the error which will result from the deviation of the curve from the desired minus one slope may be most easily made by consideration of the equivalence point T equal M_0. The slope at this point is larger than at any place in the region T less than M_0, and use of this slope will give a maximum value of the error for the estimation made with a number of points in the region T less than M_0. Substitution of T equals M_0 into equations (1) and (2) and translation of the resulting expressions into an increment of T gives—

$$\Delta T=\sqrt{\frac{1}{\mathrm{K}^2}+4\,\frac{M_0}{\mathrm{K}}}$$

For the case of M_0 equal to 0.003 molar and log K equal to 10, the error will be 0.04 percent of M_0, so that the titration will be accurate to this extent if the end point is estimated with values of M in the region T less than M_0.

The spectrophotometric titration of calcium with EDTA has been studied (Sweetser and Bricker, 1954) and confirms the above calculation. Solutions as dilute as 0.00003 molar were titrated and very sharp end points were found. Ultraviolet absorption at 222 mμ was used to determine the excess EDTA.

A photometric procedure for calcium using ammonium purpurate has been examined (Williams and Moser, 1953) and found to have a very high sensitivity. The absorbency index of the calcium purpurate complex is 10^4/moles/l/cm. At pH 11.3 and a purpurate concentration of 5×10^{-5}, Beer's law was found to hold up to 1.2 ppm calcium. This procedure is readily adapted to photometric titration. The use of a titration cell which allows a reference solution to be used for compensation of the decomposition of the purpurate ion with time and a light path length of 25 mm is necessary for high precision. The use of a weight buret to add 97 percent of the EDTA and a microburet for the final increments allows T to be determined with a precision of 0.01 percent or better. When six or more determinations of M are made in the region T equals 0.97 M_0 to T equals 0.99 M_0 and a straight line is fitted to these values, standard error of estimates of 0.001 ml are found. For solutions containing approximately 4 mg of calcium and using 0.005-molar EDTA for the titration, a precision of 0.01 percent was found for repeated titrations of the same stock solution.

If the standardization of the EDTA can be done with this same precision and accuracy, the calcium content of the distilled water solutions may be determined with confidence. It is very difficult to obtain calcium salts that do not contain impurities of this magnitude, in particular other members of periodic group IIa. Drying of the salt also presents a problem unless fused in an inert atmosphere. The use of copper metal has the advantage that very pure electrolytic copper is readily available and is not hygroscopic. Purpurate ion forms a complex with copper and spectrophotometric titration at 450 mμ may be used. Repeated titrations of copper standards with EDTA give a standard deviation of 0.02 percent, which is comparable to the confidence in the values of the atomic weights of calcium and copper.

The separation of calcium from the other constituents of sea water has been examined by the writer. The difficulties found in precipitation are outlined above. Ion exchange has been used for the separation of calcium from magnesium in limestones and dolomites (Campbell and Kenner, 1954). Elution with HCl was used and 500 ml of 1.07 N HCl was necessary to elute 1 mg of magnesium. Titration with EDTA was used, and the visual end point was indistinct with such large volumes. The separation of calcium, strontium, and barium using ammonium lactate as an eluting agent has been described (Lerner and Rieman III, 1954). Larger amounts of calcium may be taken. However, the lactate interferes with the EDTA titration and oxalate precipitation was used for the calcium determination after separation. Lerner and Rieman state that the precision is not limited by the ion exchange separation and that the gravimetric procedure was the limiting factor.

Ion exchange separation using ammonium acetylacetonate as an elutant has several advantages over the above procedures. Ten mg of magnesium can be eluted from a 8- by 80-mm column of Dowex 50 (100 to 200 mesh, 8 percent cross linkage) with 35 ml of 0.2-molar ammonium acetylacetonate at a flow rate of 0.5 ml per min. No calcium will appear in the effluent until 250 ml of this solution has passed through the column, so that a very clean separation is effected. Four mg of calcium can be removed from this same column with 27 ml of 1.0-molar ammonium acetylacetonate. No strontium will appear in the first 60 ml of the effluent. One mg of strontium can be quantitatively removed from this column with 50 ml of 2-molar ammonium chloride. The members of periodic group IIa that occur in sea water in appreciable quantities are separated by taking up a sample on the column and eluting with two different concentrations of the same reagent. In practice the sample size is adjusted so that the above quantities of the elements are present on the column and 50 ml of 0.2-molar ammonium acetylacetonate are used to ensure complete elution of the magnesium and 50 ml of 1.0-molar ammonium acetylacetonate are used for the calcium elution. When pure calcium solutions were titrated before and after uptake on the column and elution, recovery was complete to 0.02 percent of the calcium present.

Aqueous solutions of acetylacetone are not very stable. Boiling decomposes it into acetone and acetic acid. When 50 ml of 1.0-molar ammonium acetylacetonate is heated at 95°C for 90 minutes, it is quantitatively decomposed as shown by no reaction with magnesium Erichrome Black T complex, which it readily decolorizes. The product has not been identified except with regard to its complexing ability. Ammonium acetylacetonate appears to be an ideal reagent. It forms strong complexes with magnesium and weaker ones with calcium and strontium, so that the ion exchange process is efficient, and it may be easily eliminated by heating.

The calcium determinations identified elsewhere in this report as by ion-exchange photometric titration were performed in the following manner. A sample of suitable size was weighed in an automatic pipet and transferred to the column. A bank of ten columns was used so that four duplicate samples and a duplicate blank could be run simultaneously. The magnesium was eluted with 50 ml of 0.2-molal ammonium acetylacetonate. All solutions were made up by weight. Two-molal ammonium hydroxide was prepared with redistilled water and ammonia gas. The acetylacetone was redistilled. The ammonia and acetylacetone were mixed fifteen minutes before use. The calcium was eluted with 50 ml of 1.0-molal ammonium acetylacetonate. The elutant was collected in 150-ml beakers, covered with watch glasses, and heated under infrared lamps for 90 minutes. After cooling, 1 ml of redistilled piperidine for buffering to pH 11.3 and 2 ml of a 0.002-molal ammonium purpurate solution was added. A 0.004-molal EDTA solution was added from a weight buret until a visual end point was reached, which was 97 percent of the required EDTA. The sample was transferred to the titration cell and the titration continued with a 1-ml microburet that could be read to 0.0001 ml. The values of absorbence were plotted against added EDTA and the end point determined by visual fitting of a straight line. Blanks of the order of 0.05 gms of the EDTA solution were found and duplicates agreed within ±0.002 gm. The total weight of EDTA used was 25 to 30 g; so the determination of the blank was satisfactory. The colums were washed with 50 ml of 2-molal ammonium chloride to remove the strontium and were ready for use again. The ammonium chloride was prepared from redistilled hydrochloric acid and the 2-molal ammonium hydroxide solution. The 4 samples could be run in approximately 8 hours. The EDTA was standardized against copper solutions made up by weight from copper metal.

EXPERIMENTAL PRECIPITATION OF CALCIUM CARBONATE

PHYSICOCHEMICAL PRECIPITATION FROM SYNTHETIC SOLUTION

Experiments in the precipitation of $CaCO_3$ from synthetic solution were carried out along the lines described by DeKeyser and Degueldre (1950), Zeller and Wray (1956), and Wray and Daniels (1957).

At first, sodium carbonate solutions were added to calcium nitrate solutions in varying dilution in a separatory funnel, at room temperature. All solutions were prepared in distilled water, and otherwise identical samples were run with and without addition of Sr, Ba, and Sr+Ba. The precipate was drawn off, centrifuged, dried, and identified in the X-ray diffractometer by Paul Blackmon. All precipitates gave the lattice spacing for calcite.

Next a 1-liter 0.1-molal solution of $Ca(NO_3)_2$ was prepared, and to it 1 milliliter of NH_4OH was added, bringing the pH to 9 at 30°C. To this was added 20 milligrams Sr as $Sr(NO_3)_2$. This solution, in an Erlenmeyer flask, was set on a magnetic stirrer in a steam bath at 50°C. A burette loaded with 80 ml of 1.0-molal solution of Na_2CO_3 in distilled water was arranged above the strontium-spiked calcium nitrate solution and allowed to drip into it at the rate of 2 ml/ min. The next morning all the sodium carbonate had dripped into the solution, and the temperature had increased slightly, to 53°C. A pH reading of 7 was obtained by hydrion paper (meter being out of order), but the paper seemed to be reading low, and from comparison with solutions of known pH, the pH was estimated as well above 8. The precipitate was identified by Blackmon from diffractometer spacing as mainly aragonite with a little calcite. The aragonite needles so formed averaged only a fraction over 1 micron long (pl. 4*C*). Their trace-element composition is indicated at the left side of table 26. Strontium is lower than in aragonite needles of any origin formed in sea water, but barium is about the same.

The experiment was now repeated in all details except temperature (and the quantity of Na_2CO_3). The strontium-spiked 0.1-molal $CaNO_3$ solution was set up at 24°C and pH 8.8 (from added NH_4OH), and 50 ml of 1.0-molal Na_2CO_3 was allowed to drip into it, at the same rate of 2 ml/ min. After 2½ hours the pH was found to have fallen to 8.2, and the temperature had risen to 28°C, presumably from the heat generated by the magnetic stirrer. The precipitate consisted of 1μ to 2μ rhombs, mostly calcite but partly vaterite.

These results, and those of others cited above, could be interpreted as supporting Lowenstam's (1954a, 1954b) conclusion that the polymorphic solid state of $CaCO_3$ is a simple function of temperature. If that were true, however, the temperature required for aragonite precipitation would evidently be lower in marine water than in the laboratory solutions. The implied complications are underscored by the fact that "pressures on the order of several thousand bars would be required for the equilibrium formation of aragonite at 25°C" (MacDonald, 1956, p. 744).

It seems more difficult to interpret the data from the experiments described, or those of the authors cited, as substantiating the conclusion of Zeller and Wray (1956, p. 149, 151) and of Wray and Daniels (1957, p. 2033–2034) that the coprecipitation of strontium, barium, and lead with aragonite is cause and not effect. MacDonald (1956, p. 752–754) also concludes, from thermodynamic induction, that stabilization of aragonite relative to calcite as a result of components other than $CaCO_3$ should not take place until at least 30 mole percent of such components are present. Wray and Daniels directly (1957, p. 2033), and Zeller and Wray obliquely (1956, p. 145–147, fig. 2), relate the effect of the supposedly controlling impurity ions to pH; but, as will be elaborated in a following section the same relation of aragonite to higher and calcite to lower pH seems more consistently interpreted in terms of carbonate ion concentrations and free energy of reaction.

The precipitation experiments described and referred to above are here considered proper basis for concluding that, other conditions being equal, aragonite forms at higher temperature and higher pH, calcite at lower temperature and lower pH. More than this remains to be proved.

PHYSICOCHEMICAL PRECIPITATION FROM SEA WATER

Calcium carbonate was also precipitated from natural sea water without addition of materials, and supposedly in the absence of biologic activity. Experiments were modeled on the method of Gee (1932; also Revelle and Fleming, 1934). The water was first passed through a millipore filter, which retains particles larger than 0.45 micron and which presumably excluded bacteria and microscopic algae. If any micro-organisms were left, or introduced after filtration. they could hardly have had any measurable effect on the reaction, because of the scarcity of nutrients and the absence of attachment surfaces other than the walls of the container. With the help of Dorothy Carroll and W. W. Brannock, a chain of containers was set up whereby air from an ordinary compressed air trap was filtered through a saturated solution of sodium hydroxide to take up CO_2 and then allowed to bubble through a column of sea water. The effect was to carry CO_2 out of the sea water, thereby raising pH, moving the carbonic-acid equilibria to the right, and bringing about precipitation of $CaCO_3$.

Surface water from the Straits of Florida was chosen for experiment because it was assumed to approximate the condition of water about to move over the banks. The first test on water from station *GSy* was continued for 1 week, at the end of which time a small precipitate was formed; X-ray diffraction proved this to be aragonite.

This procedure was repeated on surface water from station *GSz*, this time passing smaller bubbles of the CO_2 free air through the water at a slower rate for a longer time. A 445-ml sample of the refrigerated sea water was transferred to the end bottle, at a beginning pH of 8.0, the same as at the time of its collection a year previously. After 13 days continuous run, with two changes of NaOH, a perceptible precipitate had formed and pH had risen to 9.6 at the room temperature of 24°C. The experiment was terminated, and the precipitate separated and identified by X-ray diffractometer as entirely aragonite.

The weight of the separated precipitate from this second test was 22 mg, a quantity equivalent to 49.4 mg/l. This figure is of an order of magnitude comparable to the slightly above-average $CaCO_3$ losses indicated for bank waters by calcium and alkalinity discrepancies, although not equal to the largest such theoretical losses. If the weight of this precipitate is computed as calcium ion (19.8 mg/l) and the calcium originally present is assumed to be of the theoretical value of 425 mg/l (instead of the probably deficient analytical value of 384 mg/l), it is seen that 4.7 percent of the original calcium was precipitated. This figure is only two-thirds of the average extraction of 7.5 percent found by Revelle and Fleming (1934) using a similar method. Their values are comparable to the larger apparent bank losses.

A third test was made to see if a larger precipitate could be obtained, using 500 ml of fresh surface sea water from bank-edge station *A1′* and the technique described. Although the test was allowed to run for three weeks at an average temperature of about 26°C, only 9.5 mg of $CaCO_3$ was precipitated, perhaps because the bubbles were too large and allowed to move too rapidly. The precipitate was all aragonite, in needlelike to lath-shaped crystals 2 to 30 microns long.

A final experiment was tried, again using surface water from the same bank-edge station (*A1′*), but passing small bubbles of CO_2 free air very slowly through it for a long time. This was done in two stages at laboratory temperature (average about 20°C), by Paul Blackmon. The first stage run lasted 5 months, from September 19, 1956 to February 13, 1957. Beginning pH was 7.75, and volume of water 586 ml; pH at the end of the run was 8.83, and volume of water 517 ml. The precipitate was separated and found to give X-ray spacings showing mainly aragonite but traces of calcite. The 20 mg of precipitate obtained represents a loss of about 35 mg/l, which, as will be seen, would have brought the solution close to the apparent saturation level for aragonite. The experiment was continued with the same water for 4 more months (Feb. 13 to June 6, 1957), with evaporation to 453 ml and terminal pH 8.72. The precipitate formed from this run was determined by X-ray to consist of a mixture of calcite and aragonite. The theoretical implications of these findings are discussed in the section "Significance of the data for calcium carbonate equilibrium."

Electron micrographs by John Hathaway of experimental precipitates from sea water from straits locality *GSz* and bank locality *A1′* (pl. 4*D–E*) show a comparable range in size and form to aragonite needles from the sediments west of Andros Island (pl. 3). The precipitated needles and the needles from sediments also resemble those of known algal origin (pl. 5) except that they seem to show more of a tendency to be ragged ended.

Spectrographic analyses for trace elements (table 26) show resemblance between the experimental precipitate from sea water at station *GSz* and aragonite needles filtered from suspension in whiting water at station *C6*. Both are characterized by the presence of manganese and boron, which is lacking in analyzed needles of algal origin, as well as by a seemingly significantly higher content of iron and silica than the algal needles. On the other hand they differ from aragonite needles in the clay-fraction of the sediment in the same way. One might conclude from this that the whiting material was a physicochemical precipitate but that the sediments are algal. Without more analyses of identified precipitates made in different ways from water with different storage histories, and of whiting suspensoids, however, it seems better to defer reaching any conclusion until the whole body of available evidence can be reviewed for consistency (p. 97–98).

EVAPORATION OF SAMPLES WITH AND WITHOUT BACTERIA

Published experiments demonstrating bacterial precipitation of $CaCO_3$ generally involve the previous addition to the water of calcium salts (for example, Drew, 1911, 1912, 1913, 1914) or the cultivation of bacteria in contact with a calcareous substrate (for example, Lalou, 1957a). An experiment was devised, therefore, to test the influence of bacteria on pure sea water, with calcium-free nutrients and a noncalcareous substrate, and to compare the results of this experiment with the evolution of identical bacteria-free sea water exposed to the same conditions.

Although it is questionable whether any $CaCO_3$ was precipitated during this experiment, in either bacterial or reference waters, the effects observed bear on the problem. To bring out this bearing, and also to illustrate the method, and to eliminate some too facile conclusions that have been or might be reached, it is necessary to describe the experiment and its interpretation in some detail.

PROCEDURES

Cultures from different waters and sediments by Sisler had confirmed that bacteria are relatively few in the water but very abundant in the marine muds. (See also Drew, 1912, p. 143–144; 1914, p. 43; Lipman, 1924, p. 190.) If, therefore precipitation of $CaCO_3$ is taking place from sea water, such part as bacteria might play in it would presumably not be direct but indirect, through their effect on the chemical environment as a result of processes carried on within the sediments. It seemed essential, if the experiment was to approximate natural conditions, that a sedimentary substrate be provided beneath the experimental water. At the same time, introduction of solid $CaCO_3$ into the system would allow possibility of simple recycling such as invalidates the conclusions of some previous experiments reporting bacterial $CaCO_3$ precipitation.

Fine-grained quartz sand was, therefore, used as a substrate. This sand was leached in acid, flushed vigorously, and stored in distilled water. Just before use the sand was drained and dried, and 400 grams of it was placed in each of fourteen 2-liter battery jars, previously cleaned with distilled water. The possibility was considered that the quartz sand would be an inimical environment for micro-organisms that normally live interstitial to or attached to $CaCO_3$ surfaces. From unpublished experiments described to me by Mme. Jeanne Debyser, however, it seems very unlikely that this would be true for time intervals no longer than this experiment lasted.

Sea water collected a week previously from midbank whiting station *It′* was added to 7 of the battery jars containing the washed and dried $CaCO_3$-free sand and water from bank-edge station *A1′* was added to the other lot of 7, each jar getting 1.5 liters. Five of the 1.5-liter aliquots in each batch of 7 were passed through millipore filter[6] papers to exclude bank water organisms; and 2 in each batch were unfiltered, raw sea water. Bacteria were added by Sisler to 3 samples of the filtered water in each batch as 1 milliliter of a mixed enrichment culture from surface mud collected a week previously at station *It′*.

To 1 each of the remaining 2 pairs of filtered and unfiltered water which had not been bacterially inoculated and to each bacterially inoculated sample, nutrients were also added by Sisler as a mixture of dextrose, yeast extract, and peptone (0.5-g/l concentration) with traces of sodium, and iron salts (0.08-g/l concentration). Calcium salts were excluded, and yeast extract lacks the CO_2-generating properties of yeast cells. A bacteriostatic agent[7] was added to the two nutrient-inoculated control samples in each batch.

Thus each of the 2 batches of 7 samples from water at stations *A1′* and *It′* included the following components: (a) 3 samples of bacterially inoculated nutrient-enriched filtered sea water: (b) 4 control samples of which 2 each were filtered and 2 unfiltered, 1 each of these having nutrient and bacterial repressant added, the other pair being the raw filtered and unfiltered water. The level of the water in each jar was marked on the outside with a grease pencil.

Following 15 hours dark incubation under cover and beneath a hood at room temperature, lids were removed and a battery of six 250-watt infrared lamps were turned on about 60 cm above the open jars. The beginning temperature was 26°C, and the lights were turned off whenever the temperature rose above 32°C, and during the night.

RESULTS

A volume reduction of 12.5 to 14 percent (190 to 210 ml) took place in a week's time, and the experiment was terminated. Triple lots of water from each sample were passed through a millipore filter for independent replicate analysis. Determination of pH and alkalinity were run on the first set the same day it was filtered, and titrations for chloride and calcium were made the following day—in duplicate, or in triplicate where the first pair varied outside narrow limits. My systematically low visual versene titra-

---

[6] Previous experience had indicated no appreciable change of pH or alkalinity of such water on filtration, although considerable differences occurred with long aging between filtered and unfiltered waters owing to biologic generation of CO_2 in the latter.

[7] This was the sodium salt of 1-hydroxy 2-pyridine thione, 2-pyridinethiol, 1-oxide at a concentration of 0.025 g l, prepared by Sisler as an aqueous solution and added at a concentration based on results with nonmarine bacteria by Dr. A. G. Norman, of the University of Michigan. The dosage used was increasesed by a factor of 10 over the minimum inhibitory dose for *Escherichia coli* (0.0025 g l).

tions for calcium were corrected upward percentagewise to a pair of curves based on analyses by Carpenter's ion-exchange photometric titration method. Results are graphed in figure 33, where calcium values are believed to be within two percent of true values. As chloride controls the graph, it was double checked by independent duplicate analyses and specific gravity. The points are thus believed to be arranged in the right sequence with regard to one another and the line of no apparent calcium change.

The significance of the calcium changes seen, however, is closely related to pH and alkalinity. The pH of the starting waters was low to begin with, having fallen to 7.8 in the water from station *It'* and to 7.9 in that from station *A1'*, probably owing to biologic generation of CO_2 in the week-old, then unfiltered, water (fig. 33). It fell off further in varying degree, in every one of the experimental samples.[8] Alkalinity also varied systematically, both upward and downward, in differently treated groups of samples.

From comparable starting conditions, each batch of seven samples became segregated into an identical threefold grouping as regards pH and alkalinity—(a) the samples to which bacteria had been added; (b) the samples with nutrients and bacteriostatic agent, and without added bacteria; and (c) plain sea water, both filtered and unfiltered. In both batches the alkalinity increased in groups a and b and decreased in group c. Although pH fell in all samples, it fell more in groups a and b, with increasing alkalinity. The average group values are given in table 27 and individual values are indicated in figure 33. Groups a and b might almost be lumped as essentially similar to one another and distinct from the untreated water. This is especially so for the batch of waters from station *A1'* (fig. 34), where the relations are more systematic and plainly the reverse in the untreated waters from those in the nutrient-enriched waters. The similar reversal in the batch from station *It'* (fig. 35) is more obscure. These reversals suggest that micro-organisms of some sort (perhaps molds) were introduced into the waters, presumably from the atmosphere, and that they were able to work actively in the presence of nutrients despite the chemical repressant. In the absence or paucity of nutrients in the plain sea water, the available micro-organisms worked more slowly but still evolved CO_2 faster than had been possible in the sealed collecting container (under lower temperature and obscure light).

For practical purposes then, groups a, b, and c are equivalent to: (a) CO_2-producing micro-organisms from bank sediment and possibly from atmosphere active; (b) CO_2-producing micro-organisms from atmosphere probably active; and (c) organic activity low compared to a and b.

INTERPRETATION

Depression from starting alkalinity as great as that attained by the plain-water samples of both batches, together with increasing ionic strength as a result of evaporation, would imply precipitation of $CaCO_3$ at usual pH values. What about at the values obtaining?

Using Hindman's (1943, p. 140) simplified saturation equation: pH saturation $= -pK'\ CaCO_3 + pK'_2 + 4.69$

Computing at 30°C and 36‰ salinity (19.9‰ Cl^-), taking K' aragonite as 0.99×10^{-6} at these conditions (see later discussion), and in addition taking pK'_2 at this temperature and salinity from Buch (1951, p. 8), gives: pH saturation $= -6.004 + 8.90 + 4.69$, which is equivalent to a pH of 7.59

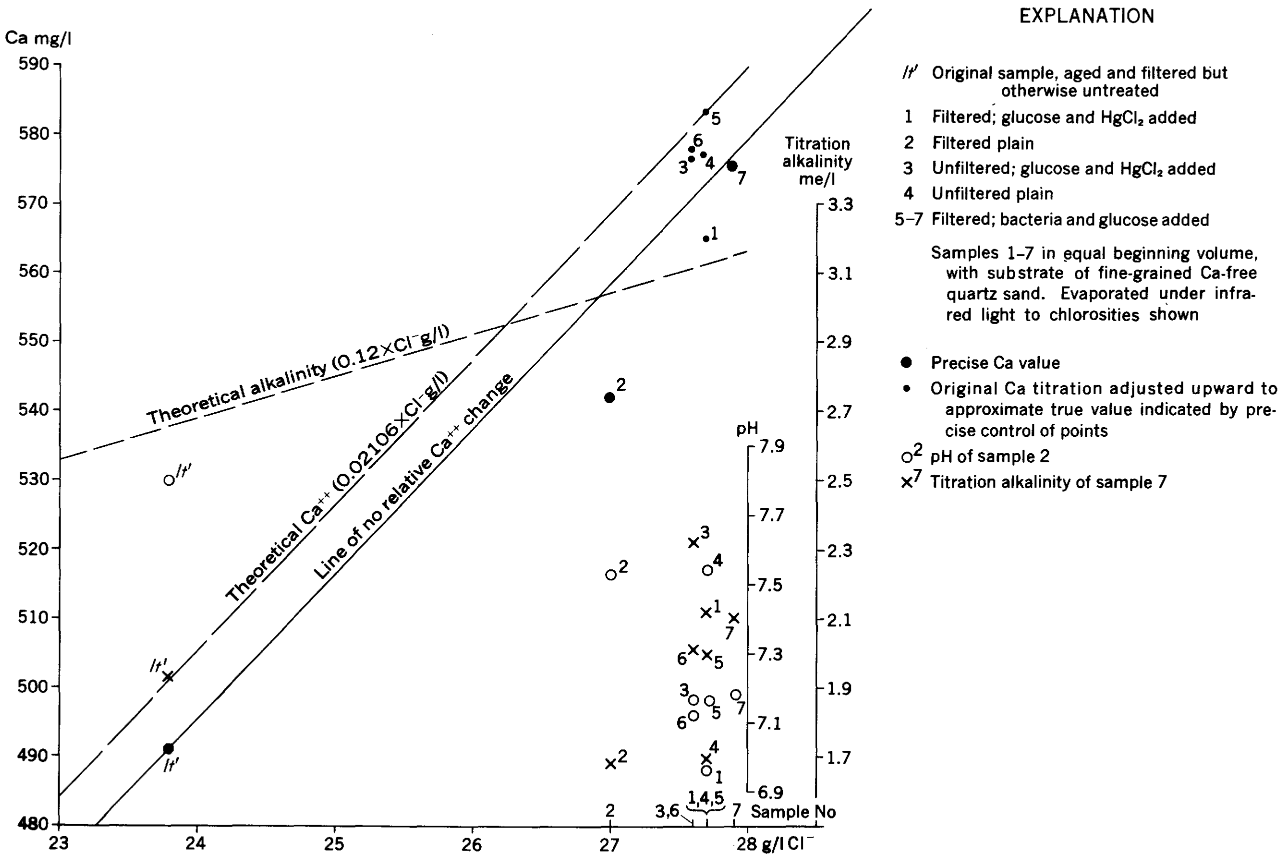
This hypothetical pH of saturation, which may be called pH_s, decreases with increasing temperature and increases with increasing salinity (also pressure, which is not involved). As the salinity effect (increasing pH_s) is the principal factor in the present computations, only the relatively high pH of groups designated c in table 27 allows chance of $CaCO_3$ precipitation. Hypothetical pH_s may be calculated at the chloride content of these pairs of samples. The average Cl^- g/l is 27.7 for that from *It'* water, and 23.6 for *A1'* water. These averages are equivalent to 26.7 and 22.9‰ Cl^- or 48.2 and 41.4‰ salinity.

TABLE 27.—*Alkalinity and* pH *of water evaporated with and without bacteria*

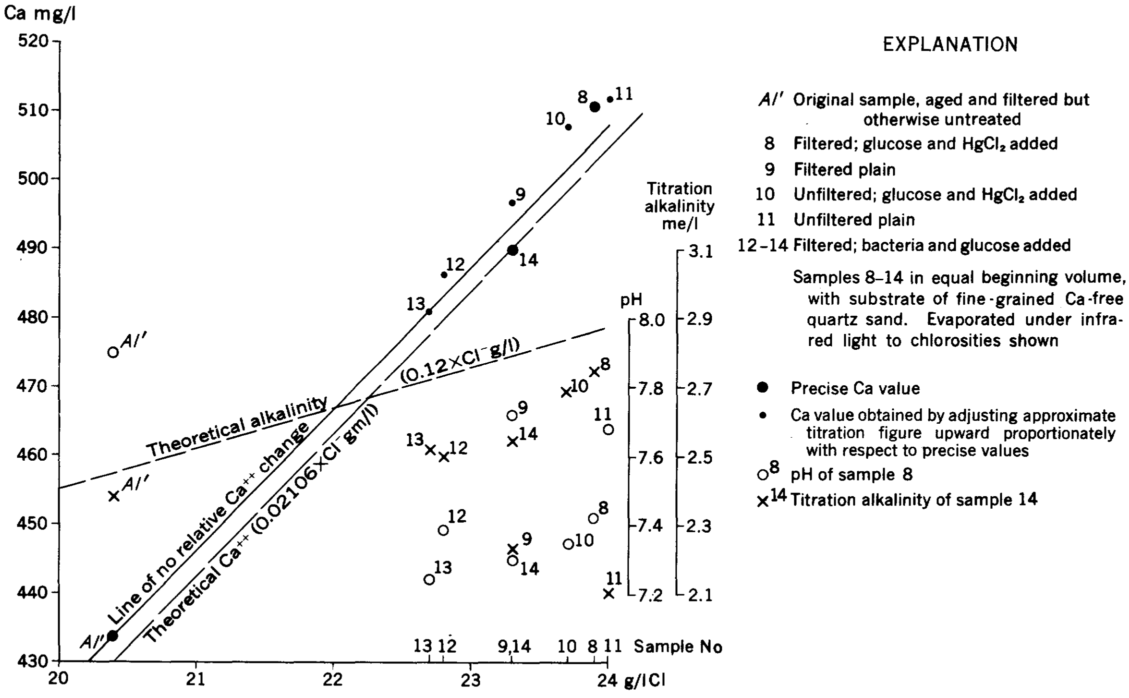
Batch	Group	pH		alkalinity me/l	
		Start	End	Start	End
It' (See fig. 35)	a, bacteria and nutrients added	7.8	7.16	1.93	2.04
	b, nutrients and repressant added	7.8	7.06	1.93	2.22
	c, plain filtered and unfiltered water	7.8	7.54	1.93	1.69
A1' (See fig. 34)	a, bacteria and nutrients added	7.9	7.31	2.38	2.52
	b, nutrients and repressant added	7.9	7.39	2.38	2.72
	c, plain filtered and unfiltered water	7.9	7.70	2.38	2.16

---

[8] HCl or H^+ not washed from the leached substrate sand probably does not account for more than 0.1 units of this pH depression, this being the approximate amount of decline in pH of the starting water after an hour's equilibration with sand and atmosphere.



B. MIDBANK WATER FROM STATION *It'*



A. BANK-EDGE WATER FROM STATION *A/'*

FIGURE 33.—Results of evaporation of midbank and bank-edge waters with and without bacteria.

Convert $\mathrm{p}K'_{\mathrm{aragonite}}$ with Wattenberg's (1933) temperature coefficient of −0.038 per part per thousand increase in salinity (reverse of direct log correction for K'). This conversion gives $\mathrm{p}K'_{\mathrm{aragonite}}$ 5.746 at 26.7$^{\circ}/_{oo}$ Cl^- and 5.892 at 22.9$^{\circ}/_{oo}$ Cl^-.

Buch's (1951, p. 8) table for $\mathrm{p}K'_2$ variations shows a decrease of 0.05 for each 2$^{\circ}/_{oo}$ Cl^- increase from 15 to 21$^{\circ}/_{oo}$. Extrapolating gives a value of 8.73 for $\mathrm{p}K'_2$ at 30° and 26.7$^{\circ}/_{oo}$ Cl^-, and of 8.83 at 26.7$^{\circ}/_{oo}$ and 22.9$^{\circ}/_{oo}$ Cl^-.

Entering the new values into Hindman's equation gives:

$\mathrm{pH_s}$ aragonite$=-5.746+8.73+4.69=7.67$ at 30° and 27.7$^{\circ}/_{oo}$ Cl^- (sta *It'*)

$\mathrm{pH_s}$ aragonite $=-5.892+8.83+4.69=7.63$ at 30° and 22.9°/N Cl– (sta. *A1'*).

The comparable apparent calcite values for $\mathrm{pH_s}$ appear to be about 7.4 in the *It'* batch and 7.35 in the *A1'* batch [using the $K'_{calcite}$ values of 0.52×10^{-6} of Wattenberg and Timmerman (1936, p. 25) and of Hindman (1943, p. 131)].

These manipulations indicate that precipitation of aragonite was possible only in the plain waters of group c from station *A1'*, where the average terminal pH of 7.70 was 0.07 above the computed saturation pH of 7.63 for aragonite at this temperature and chlorinity. The pH of the group-c water from station *It'* is below its computed saturation value for aragonite, and a temperature correction of 0.02 per °C (subtracted for increasing *T*, Hindman, 1943, p. 141) would not bring the theoretical saturation point down to the pH recorded until *T* passed 36°C. If the *It'* water, therefore, did precipitate $CaCO_3$, it presumably did so either at an improbably high peak temperature, or as calcite. The calcium values can now be considered in reasonable perspective.

When the precise calcium determinations for the experimental waters from station *It'* are compared (fig. 35), they show an apparent calcium loss of about 16 mg/l in plain filtered sea water (sample 2) in contrast to only 1.5 mg/l in the bacterially inoculated and nutrient enriched water (sample 7). However, if the calculations above are to be believed, no precipitation of either aragonite or calcite should have occurred in sample 7, and calcite only could have precipitated from sample 2. In the samples from *A1'*, where the calculations allow better prospect of precipitation, the analytical data indicate only 4 mg/l calcium loss in a bacterial sample (No. 14). In reviewing the total evidence, moreover, it is obvious that inasmuch as no calcium could have been dissolved in the absence of solid phase, no calcium points should lie above the line of no relative calcium change, as some do. The calcium values are, thus, not all accurate; in fact relatively small percentage errors in either calcium or chloride could explain maximum calcium diversion from the theoretical line of no relative calcium change. Unequivocal quantification would require repetition of a comparable experiment with very precise terminal calcium and chloride analyses, but the present results give a good enough approximation to warrant their review in advance of opportunity for repetition.

In the first place, these results are good enough to make it almost certain that no aragonite was precipitated in any sample and likely that no calcite was precipitated either. Most significant, however, the chemical state of the bacterially inoculated waters at the end of the experiment was less favorable to precipitation of $CaCO_3$ than plain sea water exposed to the same conditions (table 27). Bacterial generation of CO_2 resulted in terminal pH far below the saturation values at which precipitation of either calcite or aragonite was likely, even at the high concentrations of the experimental waters. Of course, if solid $CaCO_3$ were already present at such a stage, it would presumably be taken into solution and thus be available to reprecipitate if and when the pH increased to or above saturation value. It seems likely that such solution and reprecipitation is what happens in the essentially closed-system experiments described by Mlle. Claude Lalou (1957a, especially p. 235–236; 1957b) where first depression and then increase of pH occurs in water above sediments rich in calcium carbonate and beneath an organic surface film that inhibits gas evasion.

The opaque whitish discolorations frequently mentioned in discussions of supposed bacterial precipitation of $CaCO_3$ were also observed in the experiments discussed. During and after the experiment, and even after all of the waters were filtered, it was evident that the bacterial samples were cloudy and the others not. It was also noticed that the samples with nutrient and bacterial repressant included nearly clear, gelatinous looking streamers which Dean Cowie, of the Carnegie Institution, has suggested (oral communication, 1956) might have been molds. A filtrate from bacterial sample 5 from *It'* was recirculated through the millipore filter to see if the cloudiness could be diminished, but it showed no change. A sample of the cloudy bacterial water was also acidified under a Tyndall beam without visible evolution of gas or clearing of sample. Evidently the cloudiness is not the result of suspended $CaCO_3$.

EXPERIMENTAL CONSOLIDATION OF CALCIUM CARBONATE SEDIMENT

By Eugene C. Robertson, Lynn R. Sykes, and Marcia Newell

About 130 short-period experiments were performed on calcium carbonate sediment from the banks west of Andros Island to gain a first understanding of physical factors involved in the diagenesis of such sediment, principally its consolidation. During consolidation, sedimentary particles are brought together compactly, solidified, and strengthened. The conditions were controlled with only rough precision, and they included the following: Pressure, temperature, time, composition, and concentration of fluid and of solid, particle size, and permeability of supporting pressure cylinder. As described in preceding sections of this paper, the sediments employed were pelletal limemuds and muddy pellet sands of clay and silt size which consisted mainly of aragonite.

Bruno Sander (1936) concluded from field studies that in the diagenesis of limestone sediment, solution, redeposition, and some crushing are important processes. Terzaghi (1940) performed two experiments on compaction of Bahaman sediments and observed an exponential relation between expulsion of water and pressure. Terzaghi (1940, figs. 2, 3) found that increase of pressure causes a decrease of void ratio (volume of voids divided by volume of solids). Her plots of void ratio versus logarithm of pressure show concave curvature to the log pressure axis, and she concluded from this that the grains began to crush. However, for a short-period test, the initial water content is so important in determining the final compaction rate that either convex or concave plots could occur, and her conclusion is probably in error.

The technique for the present experiments was to apply a constant load to an essentially natural-state sample of sediment weighing about 200 gm (about 40 percent water) and contained in a sintered alundum, porous, filter cylinder, 5 cm inside diameter by 10 cm long. The pressures on the experimental sample ranged from 30 psi to 500 psi and were applied by directly loading the steel pistons or by using a lever-arm press with a mechanical advantage of 8 to 1. The pressure on the top piston was known within about 2 percent of true value, but the friction and nonuniformity of pressure distribution in the sediment reduced the accuracy of the pressure estimates to about 10 percent. The amount of compaction was about the same for slow (>1 hr) as for rapid (<2 min) loading; and loading was usually carried out over a period greater than 10 minutes to avoid breaking the porous cylinder by high radial stress due to initial hydrostatic pressure.

Experiments were run at temperatures of from 30°C to 450°C by heating the porous cylinder and mud with an external furnace; measurements were made by means of a thermocouple placed inside the bottom steel piston. Variation of sediment temperature during the average experiment was within 10 percent of the measured value. Duration of experiments ranged from 1 hour to 4 days. The density of each product was measured to about 10 percent accuracy.

The effects of certain variables were found to be neglible in consolidation. Porous cylinders with a range of permeability from that of fine sand (5 darcys) to coarse sand (275 darcys) were used to support and drain the samples, but no observable effect of external permeability was found with all combinations of the other variables. For a small variation in grain size, no important effect on consolidation was observed; sediments having a median grain-size of 0.066 mm and 0.004 mm were used. For intervals ranging from 3 hours to 4 days, there was no significant effect of time on consolidation; but as these intervals are very short relative to geologic time, the effect of time on other factors considered cannot be dismissed.

Chemical tests were made by Cloud on the interstitial water squeezed from 5 samples by pressures of 30 psi, 100 psi, 200 psi, 300 psi, and 400 psi, each kept at room temperature for 3 hours. The average of the 5 sets of analyses show pH increase of about 3 percent (from normal 7.35 to 7.6), chloride increase of about 18 percent (from normally 24,400 mg/l to 28,700 mg/l), and calcium increase of about 50 percent (from normally 490 mg/l to 740 mg/l). The increase in pH can be explained by evasion of CO_2 and that in chloride by simple evaporation of H_2O during each run. The increase in calcium, however, was accompanied also by an apparent increase in its ratio to chloride, from 0.0201 in the interstitial water to 0.0258 in the expelled water; the implication is that some calcium went into solution under experimental conditions. Graphing of the data revealed no consistent relation between the pressure and pH, chloride concentration, or calcium content.

The density of the product shows an anticipated increase with increase of pressure for each temperature value used for times up to 4 days. The effect of heating on consolidation of the sediment for pressures from 30 psi to 500 psi is a surprising decrease in the final density. The final density is about 20 percent lower for 4-day runs at 300°C than for those at room temperature. This difference in density of the products is due to nothing more than an exchange of air for water in the void spaces of the material; sediment tested at room temperatures had a higher density because of the water remaining in the void spaces after the experiment.

For all pressures up to 500 psi over periods of time as much as 4 days and for temperatures less than about 350°C, the solidification of the sediment can be destroyed by immersing it in water; it then falls apart upon rubbing between the fingers. Limemuds and muddy limesands subjected to higher temperatures did not break down so completely in water; they disintegrated to coarse aggregates, formed apparently by cementation of the initial grains. At the higher temperatures, also, aragonite inverted to calcite.

Aragonite is metastable under all conditions of pressure and temperature used in these experiments; at room temperature, a pressure of 60,000 psi is required for aragonite to be stable. Calcite is the stable phase. The change from the initial 90 percent aragonite and 10 percent calcite to 100 percent calcite is directly proportional to temperature, pressure, and time; complete inversion occurs at 450° C in 1 hour under 30 psi and at 380° C in 20 days under 500 psi. The effects of water-vapor pressure and dissolved salts were not evaluated, although undoubtedly they are important.

A penetrometer, such as is used in testing soils, showed a maximum bearing capacity of 2,500 psi for samples heated at 300° C under 500 psi for 4 days. The bearing capacity is about 400 psi for other samples heated at 110° C under 200 psi for 1 day.

Efforts to consolidate the Bahaman sediments studied were inconclusive for the conditions reported. Experiments are being continued, however, in the same range of temperatures and pressures but for longer periods of time to investigate the consolidation of the mud in more detail and to ascertain more completely the conditions for inversion of the original aragonite to calcite. The first dense calcite rock to be produced was from aragonite mud kept at 5,000 psi (350 kg per cm^2) and 200° C for 27 days (pl. 7*H*).

ORIGIN OF THE SEDIMENTS

THE PROBLEM

The sediments west of Andros Island were originally thought to be detrital. Alexander Agassiz (1895, p. 52–54) attributed them to the attrition of eolian deposits on Andros Island, and Miller and Shattuck (*in* Shattuck and others, 1905, p. 16) extended a similar explanation to Bahaman and Floridian carbonate sediments generally.

Dall (*in* Dall and Harris, 1892, p. 101), however, had even earlier suggested chemical precipitation as an explanation for fine-grained Floridian carbonate sediments; and this hypothesis was revived and extended to the Bahamas, in a physicochemical sense, by Vaughan (1914a). In the meanwhile, Drew (1911; 1912; 1913; 1914) had proposed a bacterial origin for the fine-grained limemuds. Thus the bacterial and physicochemical hypotheses came into prominence at about the same time, and they have persisted as the principal rival views.

By the time of Vaughan's final paper on the subject, he had come to the conclusion that "the results of the different investigators are accordant" and that precipitation of $CaCO_3$ was partly the product of bacterial action, partly the result of a variety of purely physicochemical processes (Vaughan, 1924, p. 57). Maurice Black (1933a) reached essentially the same conclusion with a different emphasis. From the work of Bavendamm, he underscored the importance of the mangrove swamps and a bacterial mechanism.

Drew insisted until his untimely death that denitrifying bacteria were the principal or only precipitating agents and that they acted directly upon the open bank waters. N. R. Smith (1926) concurred with Drew on bacterial mechanism and place but preferred sulfate reducers. Bavendamm (1932) had earlier concluded that sulfate reducers did the work, but in mangrove swamps on Andros Island, from which the sediments washed to sea. Thorp (1936) and Lipman (1924; 1929a) each rejected the bacterial hypotheses as quantitatively inadequate; and C. L. Smith (1940) concurred with this conclusion and proposed a purely physicochemical precipitation mechanism that was believed to operate mainly or wholly over the open banks.

It remained for Lowenstam (1955) to inject a new element with his emphasis on the possible significance of algally secreted aragonite needles, earlier reported by Pobeguin (1954, p. 85–86, figs. 33, 38). Lowenstam concluded that only in the Bahamas "is there any legitimate reason to attribute at least some needles to chemical precipitation." Lowenstam and Epstein (1957) later suggested that the O^{18}/O^{16} ratios of Great Bahama Bank sediments and algae indicate that even there the sedimentary needles are primarily of algal origin.

Since 1950, also, some investigators have returned to the view that the deposits under study are detrital from previously formed deposits on Andros Island, or elsewhere.

Vigorous disagreement thus exists over a variety of hypotheses, in which the gross variables are mechanics and site of origin. Are the needles bacterial, algal, of other direct or indirect biologic origin, a physicochemical precipitate, or of complex origin? If bacterial or algal, are they from one or several kinds, and what kinds? Do they originate essentially where found, or are they transported from some other area?

This section is concerned with these questions and with an effort to quantify the factors involved. It begins with the introduction of evidence believed to prove that the great bulk of the deposit formed where found. Then an estimate is made of the fraction of direct biological origin. Finally an attempt is made to identify and evaluate the various more strictly chemical effects that may be involved; including bacterial and other secondary biochemical effects, as well as purely physicochemical factors.

EVIDENCE THAT THE DEPOSITS FORMED WHERE FOUND

The first step in considering site of origin is to inquire whether and where systematic variations of the ionic components of calcium carbonate have occurred, and how persistent any patterns found may be. Owing to the important earlier work and meticulous reporting of C. L. Smith (1940), it was possible, with minimum effort, to confirm and refine the general pattern of chemical changes outlined by him and to determine that this is regular and persistent (figs. 3–6).

The results also show that large parallel losses of Ca^{++} and CO_3^{--} take place within the water body above the sediments—changes of the right order of magnitude to account for all sediments formed during the present cycle. After reviewing the evidence for this conclusion, consideration will be given to evidence that has been held to favor the origin of the same sediments by transport from adjacent areas.

SYSTEMATIC ANOMALIES IN THE WATER CHEMISTRY, AND APPARENT RATE OF SEDIMENTATION

In normal sea water the concentration of the principal ions bears a constant ratio to chloride, which is not altered by simple concentration or dilution. Figure 34, however, shows that the ratios of calcium and carbonate[9] to chloride in the bank water west of Andros Island do not remain constant but decrease markedly with increasing concentration. According to the relations graphed, 1.0 me/l of Ca^{++} and 0.97 me/l of CO_3^{--}, measured as titration alkalinity (A_t), has disappeared from the water between the surface of the Straits of Florida and the inner banks. These losses represent 50 mg/l of $CaCO_3$. There is a peculiar complication in bank edge calcium, which will be discussed shortly, but this does not affect the essence or the general regularity of large $CaCO_3$ removal from the bank waters.

Figure 35 shows the same effect in more detail, although not so neatly. In general, continuous calcium and alkalinity loss with increasing salinity occurs along traverses from bank edge to shore (*A* to *D*). Roughly static conditions obtain parallel to shore. Kinks in the Ca^{++}/Cl^- profiles may reflect mixing of different water masses; and there is a strong hint that maximum loss is toward bank center.

The exact values for total $CaCO_3$ withdrawal are uncertain because of incongruous fluctuations of analytical calcium values between bottom and surface of the Straits of Florida and the bank edge. These fluctuations may reflect in part analytical difficulties, in part calcium pick-up and complexing at bank edge, and in part the uncertain ancestry of waters at the surface of the straits and the edge of the bank. The analytical problem is illustrated by table 28, and James Carpenter discusses and presents an improved method of calcium determination in a preceding Section. Figure 36, however, shows that over the bank itself the apparent calcium loss indicated by different methods is fairly consistent and averages close to 35 mg/l.

TABLE 28.—*Determinations, by different analysts and methods, of* Ca *in filtered samples of sea water collected June 13, 1956, from midbank* (It′) *and bank-edge* (A1′) *stations*

Station, analyst (A, B, or C), and method	Date in 1956 that sample was—		Ca (mg/l)
	Filtered	Reported	
Sta. *It′*, whiting:			
C, gravimetric triple precipitate with $(NH_4)_2C_2O_4$.	June 18	July 17	[1] 490
A, versene, photometric after isolation by ion exchange.	June 29	July 16	490.8
B, versene, photometric on raw filtered sample.	June 29	July 2	473
C, versene, photometric on raw filtered sample.	June 18	July 17	483
C, versene, visual on raw filtered sample.	June 18	July 17	473
Sta. *A1′*:			
C, Gravimetric triple precipitate with $(NH_4)_2C_2O_4$.	June 18	July 17	[2] 435
A, versene, photometric after isolation by ion exchange.	June 29	July 16	433.4
B, versene, photometric on raw filtered sample.	June 18	July 2	435
B, versene, photometric on raw filtered sample from same water after precipitation of 7.6 mg/l $CaCO_3$.	June 29 [3] and July 13.[4]	July 16	435
C, versene, photometric on raw filtered sample.	June 18	July 17	429
C, versene, visual on raw filtered sample.	June 18	July 17	418

[1] Sr subtracted from original 495 mg/l.
[2] Sr and Ba subtracted from original 439 mg/l.
[3] Before precipitation of 7.6 mg/l $CaCO_3$.
[4] After precipitation of 7.6 mg/l $CaCO_3$.

Ratios of chloride to sulfate, magnesium, and strontium were also calculated and graphed to see whether they showed any changes that might correlate with calcium and carbonate fluctuations. The ratio to sulfate was constant and regular. The ratio to magnesium fluctuated around a mean about 4 percent lower than normal, indicating no important changes and reflecting difficulties experienced with the standard EDTA titration for magnesium and calcium. The ratio to strontium averaged lower over the banks than

---

[9] As reflected by alkalinity, or excess base, which is a measure of the total weak (titratable) anions that balance the excess of strong cations over strong anions in sea water. Although the greatly preponderant alkalinity anion at the pH of sea water is HCO_3^-, a decrease of alkalinity value directly measures CO_3^{--} loss.

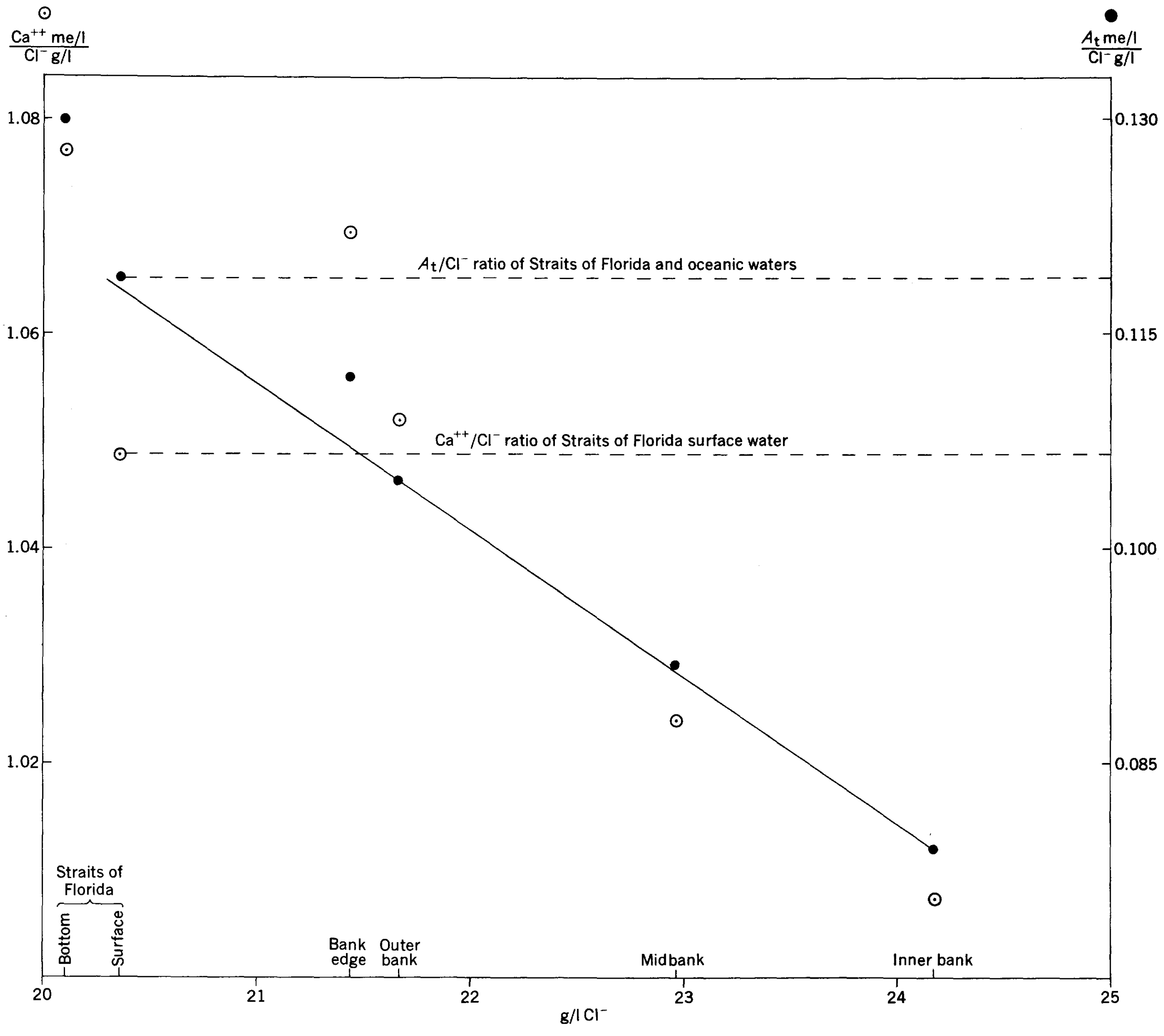


FIGURE 34.—Ratios of combining equivalents of calcium and alkalinity to chloride plotted against increasing chloride.

in the straits waters, presumably reflecting slight withdrawal by inclusion in the crystal structure of aragonite. Documentation of these facts is not important enough for present purposes to warrant publication of the graphs.[10]

Some peculiarities of the $CaCO_3$ loss are illustrated by figure 37. From the relatively constant salinity and regular relations of Straits of Florida water, the percentage variations of chloride, calcium, and alkalinity (reflecting CO_3^{--} changes) depart markedly from one another over the banks. Despite the relative and nearly equivalent loss of both Ca^{++} and CO_3^{--} implied by chloride ratios, however, the calcium per unit volume actually increases slightly with increasing salinity, while alkalinity decreases drastically along the same traverses. The explanation for this seeming anomaly is that alkalinity, although subtracted in the same proportion as calcium, is taken from a smaller initial concentration. The systematic nature of the variation stands out, with emphasis on the greater regularity of the alkalinity profiles as compared with those for calcium.

Different ways of computing possible $CaCO_3$ losses from the water were tried (table 29) to see whether they gave generally consistent or conflicting results and whether one could be chosen above others as a

---

[10] The low general Sr^{++}/Cl^- ratio, however, is of interest. It was only 0.00034 in the surface waters of the Straits of Florida, which supports the conclusion of Carpenter (doctoral dissertation at the Johns Hopkins University) that the ratios in ocean-water for Sr^{++}/Cl^- and Ca^{++}/Cl^- should be revised from 0.0007 and 0.02106 to 0.0004 and 0.02126.

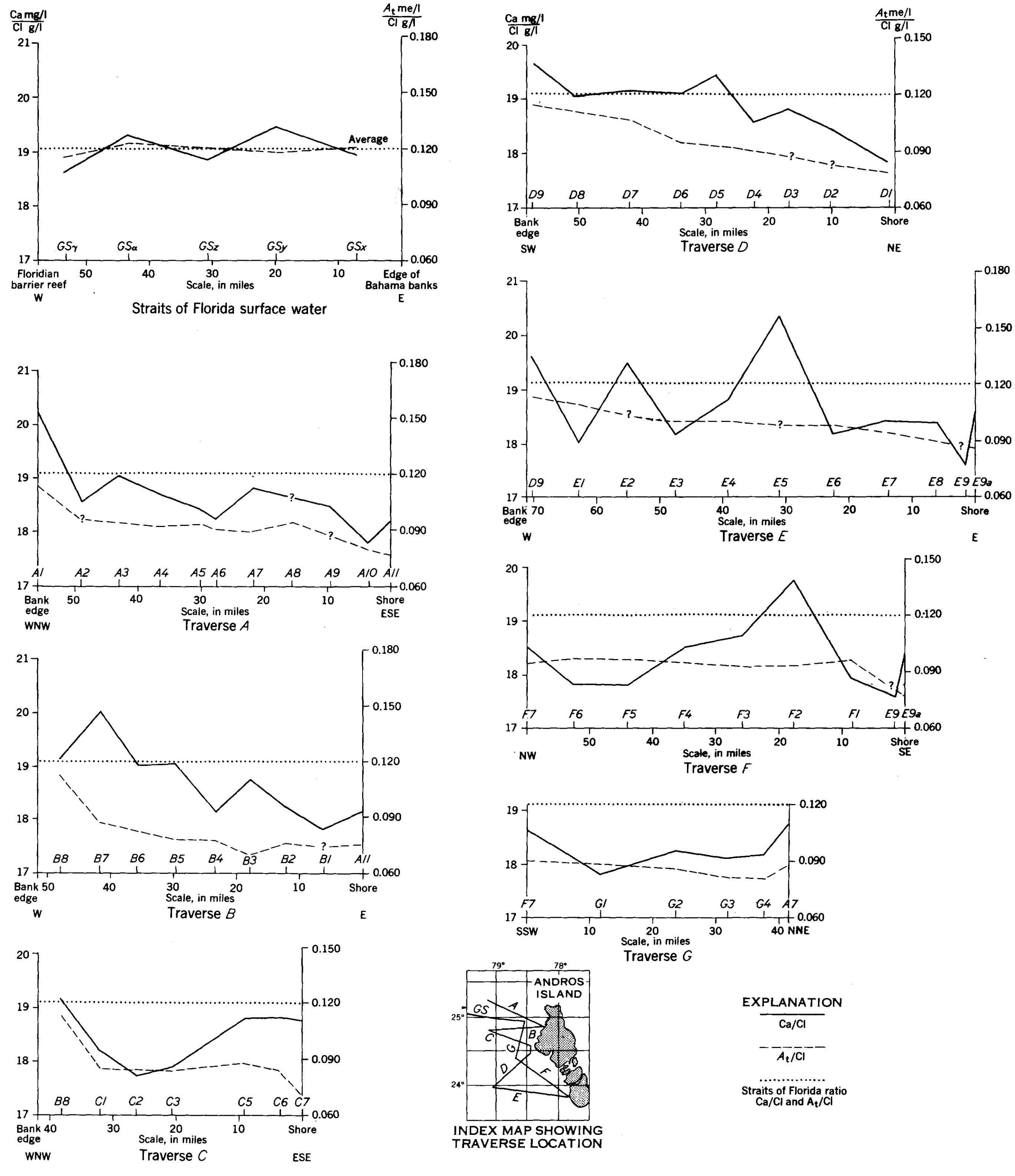
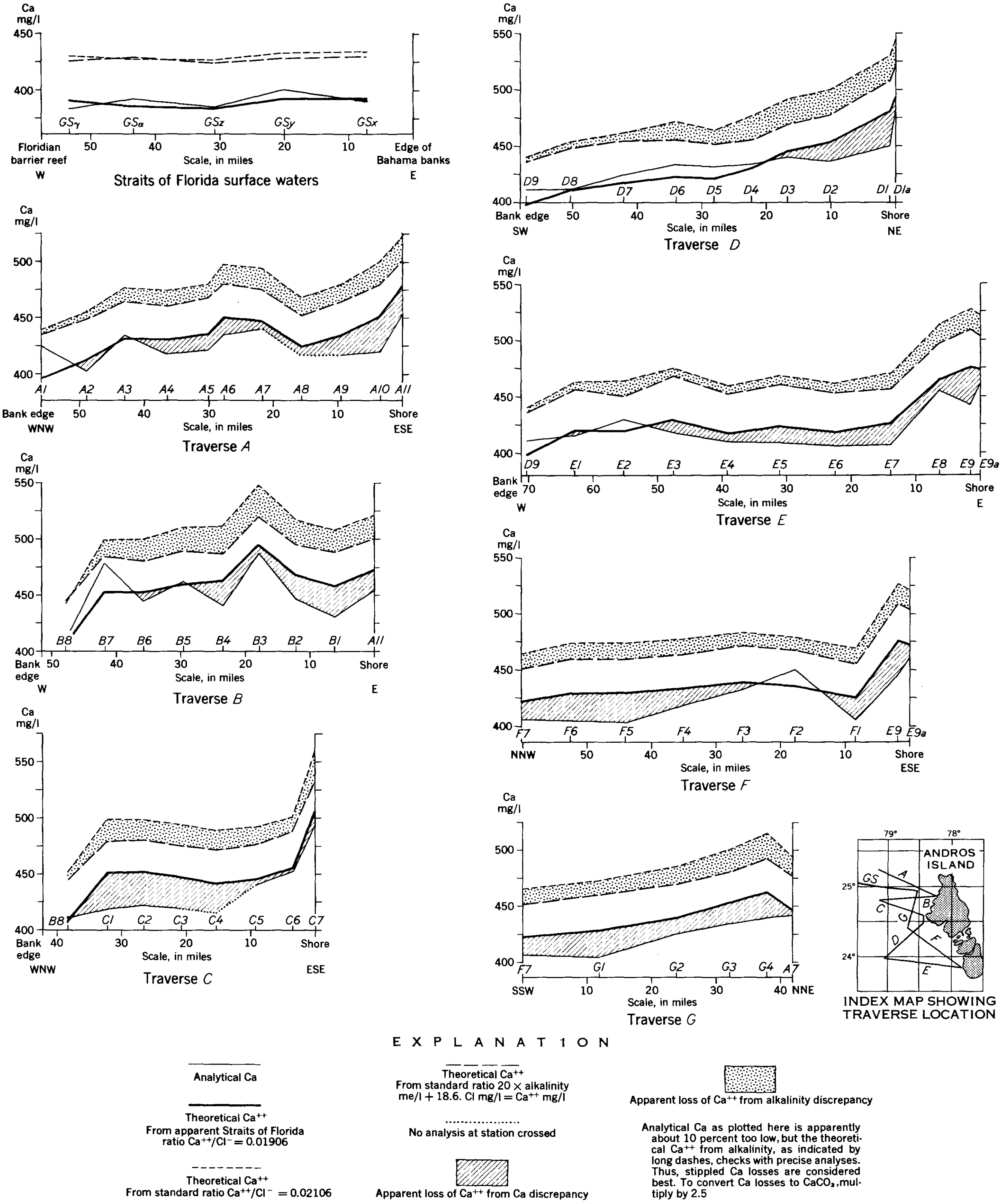


FIGURE 35.—Ratios of calcium and titration alkalinity to chloride along lines of traverse west of Andros Island, May 1955.



Analytical Ca as plotted here is apparently about 10 percent too low, but the theoretical Ca++ from alkalinity, as indicated by long dashes, checks with precise analyses. Thus, stippled Ca losses are considered best. To convert Ca losses to $CaCO_3$, multiply by 2.5

FIGURE 36.—Apparent calcium losses along lines of traverse west of Andros Island, May 1955.

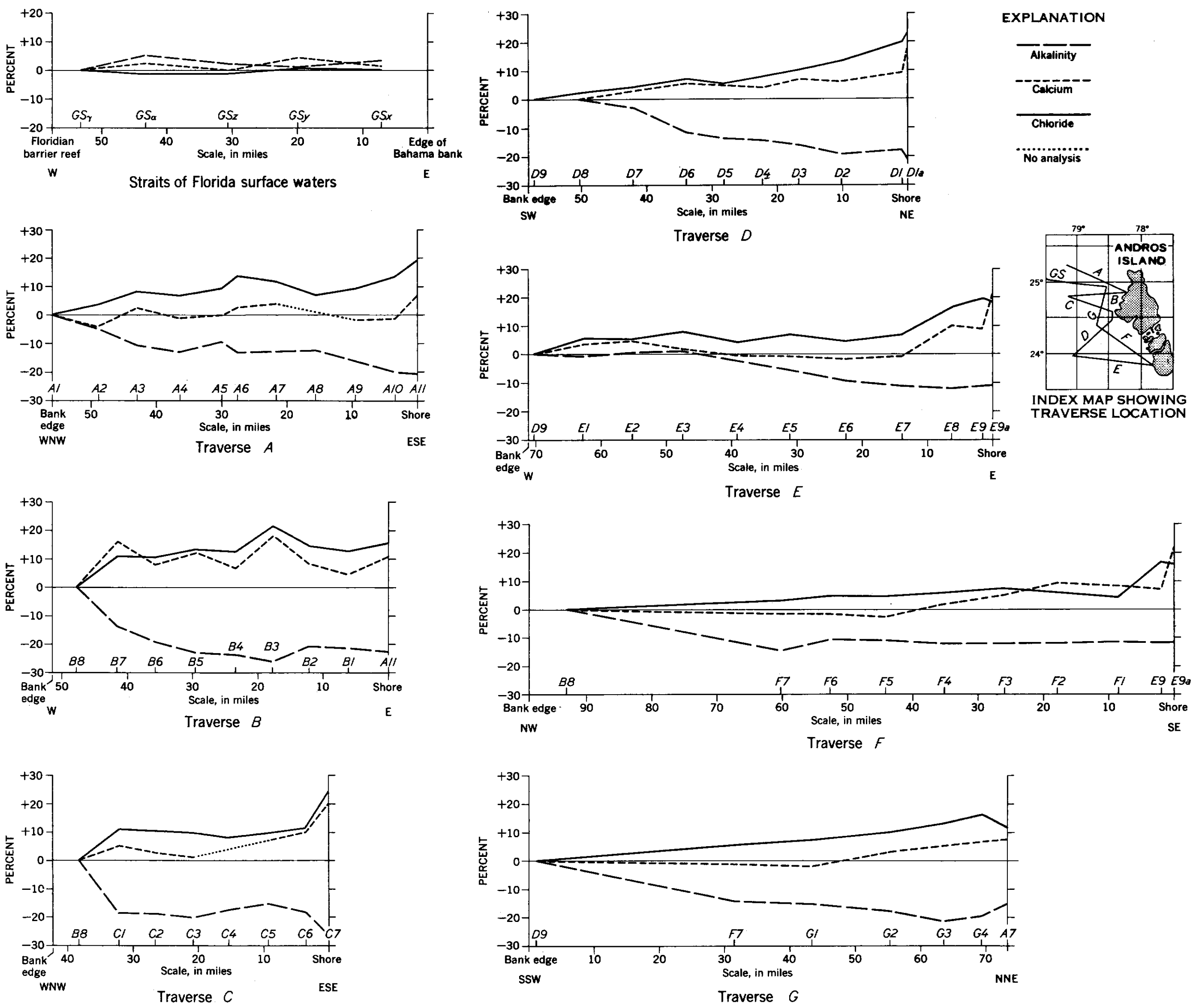


FIGURE 37.—Percentage variation in calcium, alkalinity, and chloride in waters west of Andros Island, May 1955.

means of quantifying results, if consistent. Leaving aside local anomalies, the results are closer than might have been expected from such crude methods. They indicate a range of average $CaCO_3$ loss over the whole area studied in May 1955 of 26 to 41 mg/l, with the 35 mg/l value from alkalinity discrepancy close to the mean of all values. In any case, alkalinity differences are probably the most accurate means of estimating calcium loss, because the few precise calcium values for bank waters coincide with those predicted from the ratio of Wattenberg (1936):

Ca^{++} mg-atom/l=½ alkalinity me/l×0.465 Cl^- mg/l, within the limits of alkalinity and chloride error.

The pattern of $CaCO_3$ sedimentation suggested by alkalinity variations (and broadly confirmed by analytical calcium) is shown in figure 38. This pattern reconciles fairly well with the distribution of sediment thickness and aragonite muds (figs. 9, 10). The peak in cumulative $CaCO_3$ loss at station *B3* and the closer spacing of the contours of uniform loss toward the western apex of Andros Island suggest these to be sites of maximum rate of $CaCO_3$ withdrawal; although it is also implied by data to be presented that precipitation is generally accelerated just over the bank edge and diminishes toward shore with exhaustion of the system. Thickness of sediment varies not only with reference to rate of precipitation, but also with volume of overflowing water from which precipitation can take place and with movement of sediment seaward from the site of primary origin. Moreover, regardless of what mechanism may cause its withdrawal, apparent losses of calcium carbonate from the water provide a

Table 29.—*Apparent precipitation of* $CaCO_3$ *indicated by calcium and alkalinity discrepancies (all calcium is figured as* Ca^{++}*ion)*

Traverse and station	Local calcium discrepancy [1]		Discrepancy between theoretical calcium from chloride ratio alone and from chloride + alkalinity [2]		Alkalinity discrepancy [3]		Regional calcium discrepancy [4]	
	Theoretical less analytical Ca mg/l	$CaCO_3$ mg/l	Ca from chloride ratio less Ca from chloride and alkalinity	$CaCO_3$ mg/l	Theoretical less titration alkalinity mg/l	$CaCO_3$ mg/l	Theoretical less analytical Ca mg/l	$CaCO_3$ mg/l
A1	−27	−68	4	10	0.15	8	−25	−62
2	10	25	7	18	[5].34	[5] 17	13	32
3	− 3	−8	13	32	.60	30	3	8
4	10	25	14	35	.73	36	15	38
5	12	30	12	30	.62	31	17	42
6	16	40	17	42	.76	38	24	60
7	5	12	17	42	.74	37	12	30
8	[5] 8	[5] 20	16	40	.60	30	[5] 13	[5] 32
9	18	45	[5] 17	[5] 42	[5].76	[5] 38	25	62
10	32	80	19	48	.96	48	40	100
11	19	48	22	55	1.11	56	26	65
Average *A*		23		36		34		37
B8	−4	−10	−2	−5	0.15	8	−8	−20
7	−26	−65	15	38	.76	38	−19	−48
6	6	15	19	48	.89	44	13	32
5	−1	−2	22	55	.95	48	8	20
4	23	58	24	60	1.06	54	32	80
3	8	20	28	70	1.34	67	20	50
2	21	52	22	55	1.04	52	30	75
1	28	70	[5] 20	[5] 50	[5].99	[5] 50	37	92
Average *B*		17		46		45		34
C1	18	45	19	48	0.87	44	25	62
2	30	75	19	48	.88	44	37	92
3	28	70	19	48	.89	44	35	88
4	[5] 27	[5] 68	17	42	.78	39	[5] 38	[5] 95
5	5	12	17	42	.77	38	12	30
6	2	5	13	32	.88	45	9	22
7	11	28	29	72	1.41	70	24	60
Average *C*		43		47		45		64
D9	−12	−30	4	10	0.11	6	−10	−25
8	0	0	5	12	.18	9	3	8
7	−6	−15	5	12	.29	14	−2	−5
6	−7	−18	16	40	.57	28	−2	−5
5	−10	−25	13	32	.58	29	−6	−15
4	13	32	[5] 20	[5] 50	[5].65	[5] 32	3	8
3	2	5	[5] 23	[5] 58	[5].77	[5] 38	9	22
2	16	40	[5] 23	[5] 58	[5].89	[5] 44	23	58
1	30	75	23	58	1.04	52	41	102
1a	8	20	23	58	[5] 1.20	[5] 60	19	48
Average *D*		9		39		31		20
E1	4	10	7	18	0.26	13	8	20
2	−11	−28	[5] 13	[5] 32	[5].24	[5] 12	−7	−18
3	11	28	6	15	.28	14	16	40
4	8	20	7	18	.28	14	11	28
5	15	38	[5] 8	[5] 20	[5].40	[5] 20	20	50
6	13	32	9	22	.45	22	17	42
7	19	48	14	35	.55	28	24	60
8	11	28	18	45	.81	40	20	50
9	33	82	[5] 19	[5] 48	[5].87	[5] 44	44	110
9a	13	32	18	45	.85	42	22	55
Average *E*		29		29.8		25		44
F7	15	38	13	32	0.59	30	19	48
6	24	60	14	35	.54	27	29	72
5	26	65	14	35	.54	27	31	78
4	15	38	14	35	.59	30	20	50
3	5	12	12	30	.65	32	11	28
2	−15	−38	12	30	.60	30	−10	−25
1	20	50	14	35	.54	27	25	62
Average *F*		32		32		29		45
G1	24	60	[5] 12	[5] 30	[5].65	[5] 33	29	72
2	14	35	16	40	.78	39	20	50
3	19	48	19	48	.94	47	26	65
4	23	58	22	55	.96	48	36	90
Average *G*		50		43		42		69
General average		26.2		38.4		34.8		41.4

---

[1] Theoretical Ca in mg/l from apparent Straits of Florida ratio Ca/Cl=0.01906. Because the result is given in mg/l Ca, and $Ca+CO_3=CaCO_3$, the difference listed × 5/2 (mol. wt $CaCO_3$÷at. wt Ca) equals discrepant $CaCO_3$. Precipitation is indicated except for negative values which indicate analytical Ca in excess of that predicted from ratio used.

[2] Higher value is theoretical Ca in mg/l based on standard ratio Ca/Cl=0.02106; from this is subtracted lower theoretical Ca in mg/l=40.08 × (1/2 alkalinity me/l+0.465 Cl gm/l). Conversion to $CaCO_3$ as for column "Local calcium discrepancy."

[3] Theoretical alkalinity in me/l from Straits of Florida ratio of titration alkalinity me/l÷Cl g/l=0.12. Because result is in milliequivalents, and $2HCO_3^- \rightarrow H_2O+CO_2+CO_3^=$, the difference listed × 50 (1/2 mol. wt $CaCO_3$) equals discrepant and apparently precipitated $CaCO_3$.

[4] Theoretical Ca in mg/l from standard ratio Ca/Cl=0.02106 less 40 mg/l to allow for average discrepancy in Straits of Florida water, less approximate analytical Ca. Procedure and results otherwise as for column "Local calcium discrepancy."

[5] Analytical values of Ca or alkalinity interpolated.

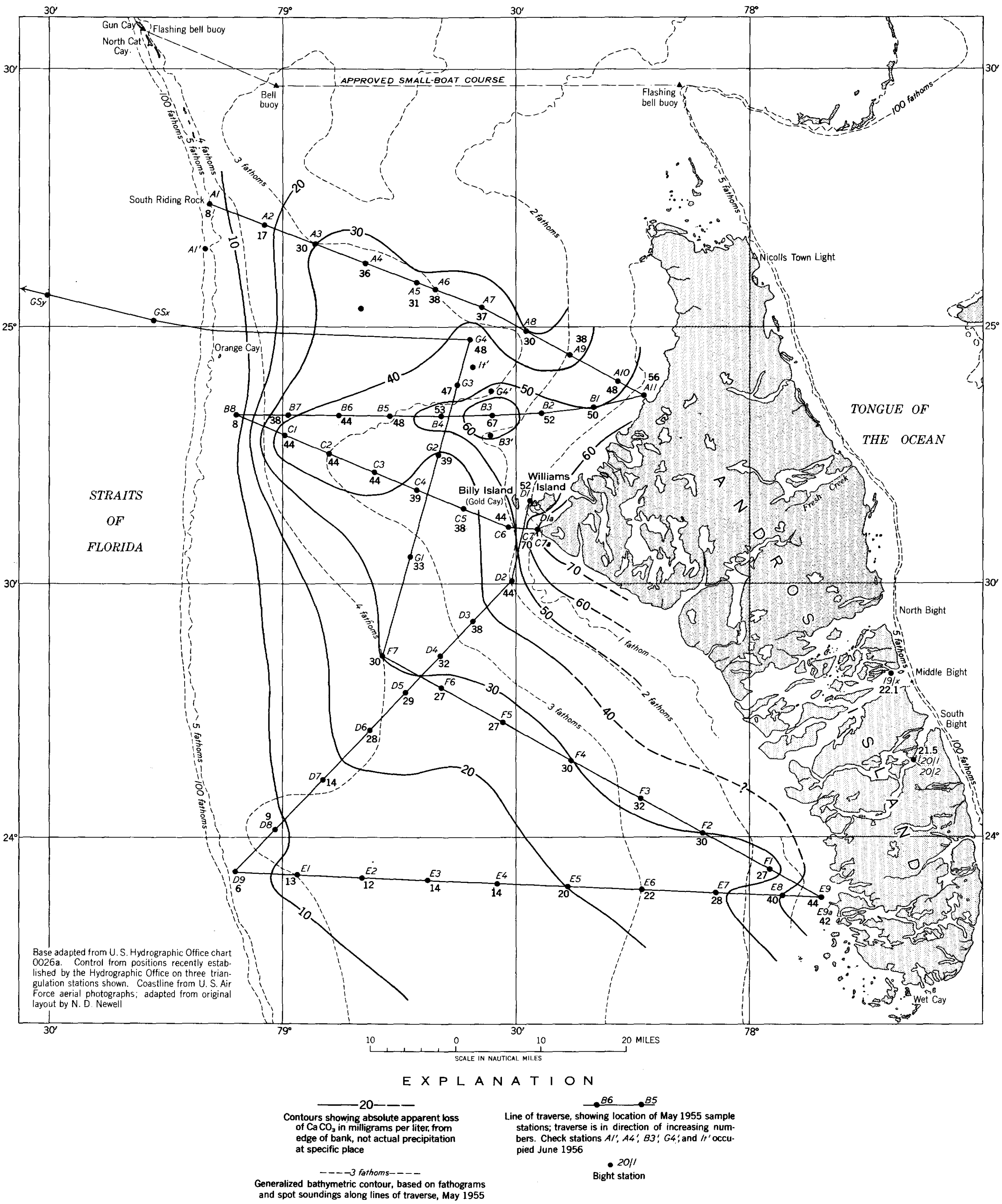


FIGURE 38.—Areal distribution of cumulative apparent $CaCO_3$ withdrawal determined from difference between theoretical and titration alkalinity west of Andros Island, May 1955.

key whereby total nondetrital sedimentation may be approximated.

In comparison with the average loss from bank waters of 35 mg/l $CaCO_3$ found in the latter half of May 1955, C. L. Smith (1940, p. 181) found a range from 22 to 59 mg/l and an average of 38 mg/l loss. The close correspondence of averages is surely fortuitous, for his April 1939 value is 50 mg/l, and the stations for which he computed losses are all at inshore or midbank localities, where maximum cumulative withdrawal would be registered. Moreover, to arrive at a fair judgment of depositional rate it is necessary to consider the total effect on a given mass of water during its entire stay on the bank, as well as the frequency of turnover.

Although the situation is certainly much more complex, it may be visualized in terms of what happens to a given liter of water in transit from bank edge to the western shore of Andros Island. Reference to figure 3 suggests that in May 1955 the initial liter would, on an average, have been reduced by evaporation to about 80 percent of its starting volume, with a concurrent increase in salinity to about 45°/₀₀, by the time it reached Andros Island. The apparent along-shore loss of 60 mg /l $CaCO_3$ suggested by figure 38 thus represents a relative loss of only 48 mg/l from the original water or about 5 percent of its original calcium. This figure is close to the 53 to 54 mg of $CaCO_3$ which, it is calculated later, can be precipitated from a liter of water of original salinity 36°/₀₀ in the temperature range of 28° to 29.3°C before moving into the calcite field, a transition which mineralogical data indicate happens rarely if at all in the area studied. Although surface water temperatures rise from June to October (fig. 39), so that precipitation may then more generally reach the absolute maximum, this is probably compensated by increased calcium loss over the Straits of Florida. Allowing for the annual cycle of temperature and wind variations, the following values are taken as approximating average maximum losses of $CaCO_3$ from 1 l of Straits of Florida water during a complete trip across the bank to Andros Island: mid-April to mid-November, 48 mg/l; mid-November to mid-April, 22 mg/l (from C. L. Smith's Dec. 1939 to Jan. 1940 minimum). The average annual rate of loss thus figures as roughly 37 mg/l.

To convert this estimate of average loss per liter to an annual rate of deposition requires estimating also the volume of new sea water that annually flows across the banks. Of course, what is left after evaporation of water that flows on to the bank must also flow off, but residual current values presumably take account of this and other local complications in water movement. Measurements of residual current velocities by C. L. Smith (1940, p. 154–156, figs. 46, 49) indicate between 1 and 2 months as the time required to move a mass of water clear across the bank west of Andros Island. Rate of flow naturally varies with the seasonal winds, and not all unevaporated onflowing water makes the complete round trip. The sluggish midbank currents and high salinities observed in May 1955 and June 1956, for instance, suggest a minimum rate, whereas the winter salinity decrease indicates more rapid exchange. Data available are insufficient to warrant trying to quantify all these and other imponderables, especially for the rough approximation sought, but it is believed that use of an average turnover time of 2 months is consistent with the several compensating factors. This amounts to a complete change of water six times a year, which in the 13,000-square-kilometer area of accelerated precipitation averages about 6 meters deep.

Since flow of water as well as withdrawal of $CaCO_3$ is essentially continuous across the bank, the yearly exchange may be treated as if it consisted of a succession of six static water masses each uniformly undergoing its average cumulative loss of 37 mg/l $CaCO_3$ and then being replaced by the next. Below an average square meter of each such mass of bank water is 6 cubic meters or 6,000 liters of water. The precipitate from such a volume of water at the rate of 37 mg/l is 222 grams of $CaCO_3$. Divided by the specific gravity of the dry mud, converted to volume per unit area, and multiplied by six, this is equivalent to a rate of 0.48 mm per year of dry sediment or 1.1 mm per year of wet, allowing an average of 55 percent of total sediment column for water.

An unknown amount of the primary sediment is, of course, returned to the Straits of Florida by the winnowing action of return currents and local turbulence, especially from the outer banks. Considering such recycling, the very rough estimate of 1.1 mm per year as the rate of deposition is unexpectedly consistent with the earlier described accumulation rate of 0.8 mm per year of wet bank sediment, based on radiocarbon age estimates. The accumulation rate of 0.8 mm per year for sediment plus interstitial water is equivalent to about 0.38 mm per year of limestone with a bulk density of 2.7, allowing for addition from the interstitial water. It compares with an average rate of accumulation in the region since Cretaceous time of 0.36 mm per year of a presumably more porous rock (Newell and Rigby, 1957, p. 64).

Considering the many assumptions necessary to make such estimates and the thinning of the sediments away from bank center, it would be unwise to stress the remarkable and probably fortuitous agreement between deposition rate, accumulation rate, and rate of limestone buildup. Nevertheless, in reviewing the estimate from water chemistry, it also seems clear that the observed changes are of the right order of magnitude and frequency to more than account for the unconsolidated sediments found, in the time available for their formation and without addition of material from outside sources.

The loss of $CaCO_3$ implied by the chemical changes observed in the bank waters could, of course, be directly biologic, physicochemical, the chemical product of a biologically altered environment, or by some combination of these means. It makes no difference to the water in what way it loses $CaCO_3$—whether to communities of calcareous organisms or by some other equilibrating mechanism.

EVIDENCE RELATING TO TRANSPORT FROM OTHER SITES OF ORIGIN

Andros Island itself is the extraneous source most commonly suggested for the bank sediments, the rationale being either that the primary genetic mechanism can work only there or that distribution patterns require it. Bavendamm (1932) reasoned that the limemuds are most logically attributed to the activities of sulfate reducing bacteria. Inasmuch as these are uncommon in the bank sediments but abundant in the mangrove swamps he suggested that the sediment is precipitated in the mangrove swamps and thence transported to sea. Without specifying primary mechanism, Newell, Rigby, Whiteman, and Bradley (1951, p. 15) favored Andros Island as a major source of bank sediments to the west on the basis of previously published reports by others that terrestrial mollusks are "more or less coextensive with the deposit" and that the greatest thickness of mud is near the western shoreline of the island. Newell and Rigby (1957, p. 60–61), while admitting contributions from other sources, believed, on similar grounds, that bankward transport from Andros Island is important. Later, however, apparently persuaded by differences in radiocarbon ages of bank and island sediments, Newell, Imbrie, Purdy, and Thurber (1959, p. 223) concluded that "All the facts support the theory * * * that most * * * of the mud is inorganically precipitated from sea water." Indeed the chemical evidence described above and the radiocarbon evidence together present seemingly insurmountable difficulties to the detrital hypothesis, but in order to deal with this hypothesis positively it seems desirable to consider also the evidence that has been advanced in its favor.

The alleged bankwide dispersal of terrestrial mollusks is a keystone of the detrital hypothesis. Surface and core sediments examined for mollusks during present studies, however, revealed none of the distinctive terrestrial and mangrove-swamp mollusks beyond one-fourth of a mile westward from the shore of Andros Island (table 3), and even normally intertidal shells were not found in any abundance more than 5 miles from shore. The "strays" at stations *F2* and *G3* were 2 meters beneath the present sediment top, on the old rock floor. To be sure this inspection was not exhaustive and by no means proves the absence of land or mangrove-swamp shells at great distances from shore. Nevertheless, the distribution tabulated does not favor mass transport seaward of the island sediments, and no comparable data favoring such transport have been published by its advocates.

Reports that sediments are much thicker near the western shore of Andros Island than farther westward over the bank are also advanced in favor of the detrital hypothesis, although it is not clear why. In any event, evidence from coring indicates that the general maximum thickness of sediments is near the center of the bank. The authenticity of deep muds on the land is, of course, not questioned. The sites at which thick muds were found alongshore and inland during the heroic pioneering work of Black (1933b), Drew (1914), and C. L. Smith (1940, p. 149) may be filled Pleistocene sinks, crevasses, or old stream courses. Mooney (*in* Shattuck and others, 1905, p. 171), however, reports that the "white marl" which "covers the western half" of Andros Island "has a depth of from 1 to 3 feet, and is underlain by the same material solidified." Shattuck and Miller (*in* Shattuck and others, 1905, p. 15) state that the lake deposits are generally thin over fossiliferous marine beds. And probing and coring near shore during present fieldwork revealed rock bottom within a few inches or feet at all places.

To be sure, radiocarbon dating (table 13) and contained organic remains show that the thicker sediment in the low scarplet at station *C7a* belongs to an early marine stage of the present sedimentary cycle, and this sediment is now being eroded and redeposited. Comparison, however, of present shoreline features plotted from airphotos (figs. 3–9) with those shown on U.S. Hydrographic Office Chart 26a, based on British surveys from 1836 to 1848, shows some surprising local correspondences both in general outline and in specific details that would seem especially susceptible to change in soft sediments undergoing significant erosional attack (or growth for that matter).

As for movement of sediment from the interior of Andros Island, shoreline tidal channels are dark on the airphotos and the only one examined was relatively deep and crystal clear. From the air the lakes appear mainly very shallow, as was reported by C. L. Smith (1940, p. 149), and they lack well-defined drainage systems (pl. 1*A*–*B*). At an annual rainfall of 45 to 50 inches a year (table 1) on such low terrane, transfer of

$CaCO_3$ from rock to lake sediment and thence seaward could hardly be a quantitatively important source for the bank sediments, regardless of how much limemud may exist in the lakes. Two stations occupied by C. L. Smith (1940, p. 184) in shallow salt lakes indicated little calcium deposition there, and Newell and Rigby (1957, p. 61, pl. 16, fig. 2) found the muds of fresh-water lakes on eastern Andros to be calcite, rather than aragonite as in the bank sediments.

Derivation of the bank sediment by the flushing out of new precipitates from the mangrove swamps at the western side of Andros Island also faces severe difficulities. Even at the bank edge the mean tidal range is only 74 centimeters (table 1), and it is probably much less in the mangrove swamps which were covered by only 2 or 3 decimeters of water at highest tides observed. The volume of water involved, and of $CaCO_3$ available for precipitation from it, thus appears to be small; and the general sluggishness of water movement suggests that its rate of renewal is very slow. Its transporting power is low because of the quiet tidal movements, the baffle of the mangrove roots, and the interference of beach ridges (pl. 1*C–D*, station *A11*). The sea water adjacent to the swamps is, in addition, of a chemical state that implies large previous loss of $CaCO_3$ (fig. 6), although additional precipitation might be favored by sulfate reduction. Finally the surface sediment of the mangrove swamps was everywhere observed to be protected by a rubbery gelatinous mat of blue-green algae. This mat so firmly adheres to even relatively coarse sediment that it is an effective sediment binder, facilitating buildup and opposing loss.

The effect of occasional catastrophic storms has also been considered as a possible cause of seaward movement of sediments from Andros Island. Aerial observation in May 1955, however, showed no storm breaching of the western beach ridges; and as mentioned above, comparison between old maps, and recent aerial photographs show strikingly close parallelism in the configuration of certain western shoreline features which happen to be identifiable because of their complexity. Both because of subaerial alteration and the above-mentioned deposition of calcite in the fresh-water lakes, layers or masses of sediment showing high calcite ratio might be expected over the banks if mass transport from land were important. Mineralogical studies, however, show only a general slight increase of calcite toward shore, the base of the sediment cores, and the seaward bank edge. From this it seems that mass movement of sediment seaward is not important—either because the shallow banks themselves, or the mangrove swamps, or both, tend to damp storm waves and inhibit wave attack on the shoreline muds.

From all viewpoints, therefore, Andros Island is an improbable source for the bulk sediments to its west. Certainly it supplies some small fraction of detrital material to the banks, but its principal function in relation to western bank sedimentation appears to be that of providing a windbreak, in the semistagnant lee of which are generated the special conditions that precede the deposition of aragonite mud.

In view of the chemical changes within the area and the sluggish water movements described, it would be gratitutous to debate the possible significance of current transport of materials from bordering sites of marine sedimentation.

The remaining question at this place, then, is how to estimate the actual amount of detrital (or recycled) $CaCO_3$ sediment that has found its way from Andros Island to the banks at the west. The only identifiable detrital elements of the sediment west of Andros are the fragments of low-magnesian bedrock calcite which, together with certain organogenic components and possibly traces of chemically precipitated calcite, constitute the approximately 5 percent low magnesian calcite in it. Such detrital calcite, to be sure, can represent only part of the 5 percent low magnesian calcite fraction, and, in addition, some of the aragonite is necessarily recycled. Thus any estimate of total detrital fraction is arbitrary, but, from the considerations reviewed, a figure of 5 percent seems a reasonable guess and 10 percent a maximum.

EVIDENCE FOR A DIRECT BIOLOGICAL SOURCE

Calcium carbonate sediments may be termed biogenic where they originate either as direct biologic precipitates within or about animal or plant structures, or as a secondary effect of biochemical alteration of the aqueous environment. The immediate discussion concerns only that fraction of the deposits that can be recognized in some way as of direct biologic origin. The secondary biological effects are discussed in a following section, together with the physiochemical effects, from which it is difficult to separate them.

SKELETAL FRACTION OF ANIMAL ORIGIN

Identified skeletal grains (table 8) account for about 11 percent of the bank sediment west of Andros Island; and, altogether, somewhere between 15 and 25 percent of the total is probably of skeletal origin. This estimate compares with Illing's (1954, p. 17) figures of 12 percent skeletal grains and 23 percent total skeletal content for the southeastern bank area, where conditions appear to be more favorable for the growth of a shelly fauna.

Excluding the 4 percent algal fraction leaves an estimated 7 percent of the recognizable skeletal debris as of molluscan, foraminiferal, or other animal origin. In view of the rarity of important triturating organisms and the subdued abrasive forces, this figure presumably should not be much increased. Probably not much more than about 8 percent of the total mass of sediments under consideration is skeletal material of nonalgal origin, although, by subtraction of algal maximum from total maximum, as much as 13 percent might be so categorized. This skeletal fraction includes both aragonite and calcite (Pobeguin, 64–65) and probably accounts for most of or all the high-magnesium calcite in the sediments, as suggested by Blackmon.

SECRETION BY PLANTS

Identified algal fragments represent about 4 percent of the surface sediments west of Andros Island, and about the same proportion seems to hold at depth (fig. 6). These are sand-sized grains of which more than 75 percent belong to the green codiacean alga *Halimeda*, probably even in areas where the small algal fraction or minute grain size makes separation as a discrete category unrealistic. The algal fragments are most abundant toward the bank margins. Not only do the living plants (especially *Halimeda*) seem to undergo numerical increase in this direction, but also the highly porous condition (pl. 6*A–B*) and relatively large size of the *Halimeda* particles may increase their susceptibility to saltative downslope transport within the bank area until such time as they are covered by fine sediments. At the bank margins the more abundant *Halimeda* fragments tend to become infiltrated and smoothly coated with precipitated aragonite. They are there heavier, and lodge more firmly among the coarser debris, while any accompanying fine fraction tends to be winnowed seaward.

The total algal $CaCO_3$ fraction, however, is certainly larger than the identified 4 percent, because most of the precipitating species simply disaggregate on death and decay to yield aragonite needles (pl. 5) and structureless aggregates. Under the impetus of Lowenstam's (1955) provocative views, therefore, an effort was made to quantify the algal contribution to aragonite needle formation.

Special attention had been paid to collecting algae and estimating their abundance while diving at the different stations occupied in 1955. These observations had already indicated that one site was about like another as far as the algal biomass was concerned, except for an increase toward the bank margins. Therefore, a midbank station near the scene of apparent maximum $CaCO_3$ extraction (*It′*) was chosen for quantitative study in 1956, and an area of bottom 5 meters square was staked off here. Comparison with previous impressions indicated that the bottom at Station *It′* was somewhat richer in algae than the bank area in general and that the staked square was richer in *Halimeda* and *Batophora* and poorer in *Penicillus* and *Avrainvillea* than is the case at the average bank station. As far as *Batophora* is concerned this impression is probably incorrect, for numbers of this inconspicuous little dasycladacean attach to the basal and largely buried creeping rhizomes of the green alga *Caulerpa* and do not seem abundant until the latter is collected. With these qualifications, the analysis of total algal biomass and sediment production given in table 30 is considered representative of the present growing surface. It would, of course, have been more accurate to do several sites and compare results. The interest being in orders of magnitude, however, and the general algal population appearing to be as uniform as it does in this region, the time and labor involved in achieving such refinement was considered unwarranted in view of other work to be done.

First the algae were collected from the area staked out. Except for *Caulerpa* and *Batophora* every visible specimen was taken. This required a number of return dives, waiting between each for the stirred up mud to clear enough for the next collecting run. Rooting out all the *Caulerpa* rhizomes proved to be more of a task than anticipated. However, it is estimated that half of the caulerpas were collected, and therefore half the batophoras, and allowance is made for the difference in table 30. After the water cleared following removal of algae, the *Thalassia* population was estimated. Roughly one-fiftieth of the thalassias were taken for sediment study (plus a small collection for nutrient analysis)—the fleshy roots were grubbed out along with the flimsy tops. All matters of doubt and choices of procedure were resolved in favor of maximum algal contribution to the sediments.

In the laboratory the plants were separated and counted, except *Caulerpa* which is an essentially continuous meshwork, and *Thalassia* whose total number is but a rough estimate anyhow. All plants were shaken vigorously in clean water by hand to remove as much as feasible of the extraneous sediment. The algae were then severed from their sediment entangling holdfasts, and placed in separate containers for digestion in hydrogen peroxide. It was assumed that all sediment then still clinging to them had been created by them, although much undoubtedly had simply settled from suspension to the outer surface. When all of the organic matter seemed to be digested, the samples were washed, thoroughly broken up by vigorous mechanical stirring for 15 to 20 minutes and weighed. A mechanical analysis was then made.

TABLE 30.—*Biomass and sediment analysis of total sessile flora from 25 square meters of bottom at station* It′

Genus	Number of individuals collected	Estimated total number of individuals	Dry weight of plants collected, above holdfast (in grams)	Estimated total dry weight of whole population, above holdfast (in grams)	Dry weight of holdfast plus entangled sediments (in grams)	Mechanical analyses of holdfast sediment				Mechanical analyses of sediment from plant above holdfast			
						Total	Sand	Silt	Clay	Total	Sand	Silt	Clay
Flowering plants:						*Grams*	*Grams*	*Grams*	*Grams*	*Grams*	*Grams*	*Grams*	*Grams*
Thalassia	200±	10,000±	31.0	[1] 1,500	None					[1] 500	[1] 116	[1] 241	[1] 143
Brown algae:													
Laurencia	5 (bunches)	5	2.1	3	None					1.12	.59	.21	.32
Green algae:													
Avrainvillea	41	41	30.4	31	62	51.93	13.86	10.89	27.18	21.09	2.86	10.47	7.76
Batophora	1,100	2,200	44.0	[2] 88	None					[2] 71.24	[2] 26.80	[2] 24.32	[2] 20.12
Caulerpa	Mesh of runners	Mesh of runners	14.0	[2] 28	[2] 16	[2] 6.52	[2] 1.90	[2] 3.60	[2] 1.02	[2] 15.70	[2] 6.02	[2] 7.40	[2] 2.28
Halimeda	111	111	238.0	240	700	482.44	196.52	84.82	201.10	215.60	175.70	18.11	21.79
Penicillus	17	17	2.8	3	12	11.08	4.62	4.19	2.27	1.79	.96	.22	.61
Rhipocephalus	22	22	13.0	13	35	33.13	12.19	13.45	7.49	9.38	3.27	4.51	1.60
Udotea	35	35	1.6	2	20	19.43	7.22	4.02	8.19	.72	.26	.24	.22
Valonia?	10	10	2.6	3	None					2.10	.50	.60	1.00
Total algae	1,341+	2,441+	348.5	411	845	604.53	236.31	120.97	247.25	338.74	216.96	66.08	55.70
a Holdfast and algal sediment, percent						100	39	20	41	100	64	20	16
b Holdfast fractions represented by *Halimeda*, first breakdown, do						80	83	70	81				
c Algal fractions above holdfast represented by *Halimeda*, first breakdown, do										64	81	27	39
d All plants exclusive of algal holdfasts, grams										839	333	307	199
e All plants exclusive of algal holdfasts, first breakdown, percent										100	40	36	24
f Plant fractions represented by *Halimeda*, first breakdown, do										26	53	6	11
g *Halimeda* size fractions redistributed from percent analysis of crushed sample, grams										215.6	89.6	95.6	30.4
h Algal fractions above holdfast redistributed to allow for crushed *Halimeda* values, do										338.7	130.9	143.5	64.3
i Plant fractions exclusive of holdfasts, redistributed to allow for crushed *Halimeda* values, do										839	247	384	208
j Algal sediment, redistributed to allow for crushed *Halimeda* values, percent										100	39	42	19
k Plant sediment, redistributed to allow for crushed *Halimeda* values, do										100	29	46	25
l Plant fractions represented by *Halimeda* after crushing, do										64	36	25	15
m Algal fractions above holdfast represented by *Halimeda* after crushing, do										64	68	67	47
n *Halimeda* sediment above holdfast, first breakdown, do										100	82	8	10
o *Halimeda* sediment above holdfast, after crushing, do										100	42	44	14

---

[1] Weighed amount × 50, to adjust for field estimate of total population.

[2] Twice weighed amount to adjust for field estimate of total population.

The data were tabulated in various ways for inspection, and possibly significant percentages were computed (table 30). The initial disaggregation by leaching of organic matter and vigorous stirring of residues broke up most of the samples pretty thoroughly, but the *Halimeda* looked so heavy in the sand fraction that an 8.6-gram sample was crushed and ground lightly in a mortar for several minutes and a new mechanical analysis made. The effect was to halve the sand fraction, and concurrently to increase silt by a factor of five and the clay sizes by one-third.

It might be supposed that such information could be interpreted in terms of algal growth rates. Some dasycladaceans are known to grow rapidly, because *Acetabularia* estimated to be 2.5 cm long and having terminal disks 5 mm in diameter were seen in November 1954 at the trailing edge of a Miami speedboat that had been cleaned and scraped 3 months previously, and because the rapid growth and regeneration of this genus makes it a favorite among plant geneticists. The lime-secreting codiaceans also are capable of rapid growth, for Finck (1904, p. 146) recorded the six weeks' growth of a specimen of *Halimeda* at Funafuti as "some three inches" high and representing 14 grams of calcareous matter. Rate of algal growth and secretion of $CaCO_3$, however, is apparently erratic, and dependent on local conditions. I have observed, at Key West, many square miles of nearly waist-deep and presumably rapidly growing *Halimeda* thickets, but in the lagoon west of Saipan repeated observation (but no measurement) of sites of dense but low *Halimeda* carpeting showed no noticeable growth increase over an interval of 8 months during 1948 and 1949. In addition to the apparently wide local variation, growth rates have not even been recorded for most of the lime-secreting species; and, above all, the algal flora west of Andros Island does not give the impression of vigorous growth. A more concrete basis, therefore, was sought for estimating the volume of algal sediment.

The data can be interpreted, however, in terms of abundance of recognizable *Halimeda* fragments in the sand fraction of the whole sediment, if certain assumptions are made. Those on which the present attempt at quantification is based are (a) that the ratio of *Halimeda* to other algae is roughly uniform bankwise and that the sample studied is not misleadingly far from the mean, (b) that the crushing and mortar grinding of the *Halimeda* fraction approximates the disaggregation achieved under natural conditions, (c) that the percentage estimates of *Halimeda* in the sediment (fig. 11) are reasonably representative and of the right order of magnitude, and (d) that the sediment entangled in the holdfast system was previously deposited and may be disregarded as not significantly affecting conclusions. These assumptions are based as far as possible on observation and numerical estimates, but they are, of course, subjective. *Halimeda* is the obvious key for this method of interpretation because of its volumetric dominance, its sure and rapid identification, and its importance as a contributor of aragonite needles. For computing purposes the previously listed estimate (table 8) that sand-sized *Halimeda* fragments represent 3+ percent of the total sediment is taken as 3.5 percent and used as a numerical value for what will be called the *Halimeda* ratio. Inasmuch as this estimate is for the total sediment column, it includes the time factor.

If sediment from all plants is included, the size breakdown after crushing and grinding of *Halimeda* is 29 percent sand, 46 percent silt, and 25 percent clay (table 30, line k). *Halimeda* itself, however, represents only 36 percent of the sand fraction (table 30, line l). On the basis of these data, the *Halimeda* ratio would imply that the total fraction of the bank sediment is 35 percent—10 percent sand $\left(\frac{100}{36}\times 3.5\right)$, 16 percent silt $\left(\frac{46}{29}\times 10\right)$, and 9 percent clay $\left(\frac{25}{29}\times 10\right)$.[11] The individual components of the sand fraction are known, however, and the preponderating *Thalassia* residues consists almost entirely of skeletal material of animal origin and fecal pellets. The bulk of the material from this plant, therefore, consists of sediments secondarily entrapped in its enveloping fleshy roots and encrusting microorganisms, and the estimates for total plant fraction have no significance for primary origin.

For algae alone, after crushing and grinding of *Halimeda*, the fractions of sand-, silt-, and clay-size are 39 percent, 42 percent, and 19 percent of the total; and 70 percent of the algal sand is *Halimeda* (table 30, lines j and m). The *Halimeda* ratio (sand fraction) then implies, by similar manipulations to those used above, that 12.5 percent of the total bank sediment is of algal origin—5 percent sand, 5 percent silt, and 2.5 percent clay. If we stick to the original estimate (table 8) of roughly 4 percent algae in the sand fraction, the fractions would be scaled down to 4, 4, and 2 percent, respectively, and total algal fraction to 10 percent.

Estimates of aragonite-needle abundance in the experimental algal sediments range from 60 to 100 percent of the clay and 20 to 50 percent of the silt. Rounding these estimates upward to 100 and 50 percent, and using the proportional percentages above, gives about 4 to 5 percent of the total sediment as aragonite needles of plant origin by the *Halimeda* ratio. By allowing 40 percent permanent loss of silt and clay through pel-

---

[11] Of the individual multipliers within parentheses, 3.5 is, of course, the *Halimeda* ratio, and 10 is the percentage of total plant sand in the bank sediment.

leting activities, the actual proportion of aragonite needles of algal origin on this line of reasoning comes close to 2.5 to 3 percent of total sediment. Of course, at a place where *Halimeda* grows as vigorously as at Key West, Fla., all the reportedly few aragonite needles could easily be of algal origin.

As discussed elsewhere, an attempt was made, through electron micrography and spectrography of the minor elements, to find clues to distinction of algal aragonite needles from those chemically precipitated in sea water. It was found that the algal needles have a trace-element composition similar to those in the bulk sediment, but slightly different from a sample filtered from whiting waters and one forced to precipitate from Straits of Florida water in the laboratory (table 26). Electron micrographs, on the other hand, hint that the aragonite needles of known algal origin may be generally better formed and less likely to have ragged ends than those of the bulk sediments, the whiting filtrate, and the forced precipitate. The evidence of the trace-element spectrography is inconclusive because effects on the water of filtration, storage in polyethylene, and precipitation procedures need to be evaluated; because data are available on only one sample each of whiting and known sea-water precipitate; and because the same evidence concurrently favors chemical precipitation in the whitings and an algal origin for the bulk sediments beneath them. Likewise, the interpretation of shape from electron micrography is too subjective and inconclusive to be helpful.

Impressive arguments for algal origin of the sedimentary needles are advanced by Lowenstam and Epstein (1957). They show that adjusted oxygen isotope ratios for sedimentary needle carbonate lie near the middle of the much wider spread of similar ratio values for different kinds of algal aragonite, while ooids and grapestone clusters studied by them have isotope ratios that cluster in a narrow range at one extreme of the algal ratios. Their preferred interpretation of these facts is that the ooids originated through physicochemical precipitation in equilibrium with sea water at temperatures of 24.0° to 25.7°C, whereas the sedimentary aragonite needles are in isotopic disequilibrium with the surrounding water, like needles of algal origin. It is to be noted, however, that the δO^{18} values for the probable main source of algal needles, *Halimeda*, are consistently lower than for other algae or for the sediments themselves (op. cit. fig. 5). The fact, also, that the same isotopic ratios obtain for the cores of the ooids as for their enveloping concentric laminae (op. cit. p. 372, footnote) seems contradictory to the general conclusion of Lowenstam and Epstein. The commonest type of ooid core in this region is a fecal pellet, created by bonding of whatever fine sediment was ingested by the pellet maker, and most especially by sedimentary aragonite needles where they are present. In some ooids it also seems likely that the concentric shells themselves may have been created by organic bonding of successive layers of previously precipitated sediment around the nuclear surface rather than by new inorganic secretion. The two-stage buildup of the ooids is underscored by the different radiocarbon ages of nuclei and outer shells at some localities (Thurber and others, 1958).

Lowenstam and Epstein (1957, p. 373) themselves point one way out of this dilemma where they indicate that equilibrium temperatures for the sedimentary aragonite needles would have to range between 27.6° and 31.7°C. Fortunately, data are available with which to evaluate the occurrence and prevalence of water temperatures within this range for the area of interest. The average monthly sea surface temperatures of Atlantic Ocean water near Andros Island (Fugilister, 1947) give the minimum duration and values of temperatures in the required range—between 27.5° and 28.5°C from June to October. Increase of both temperature and duration is required, however, to accommodate more detailed local data than was incorporated in Fugilister's estimates.

Average temperature of the water west of Andros Island in middle and late May 1955 was 28.4°C (table 5). At midbank in mid-June 1956 it was 29.5°C. The average for August in Middle Bight is 29.7°C, with an average local oceanic high of 28° to 29°C in October (Smith, C. L. 1940, p. 156–158). Temperature of surface water in the Straits of Florida at lat 25°33′ N. exceeded 30°C during August and parts of July and September between 1953 and 1956, with a high of 31.4° in August (Bsharah, 1957, p. 204–206). In the Middle Bight of Andros Island, which is flushed twice daily with the cooling waters of tidal onflow from the Tongue of the Ocean, daily observations at 8:00 a.m. through the year 1939 show a water-temperature range of 28° to 30°C from June to October (fig. 39). The sluggish water west of Andros Island presumably reaches still higher temperature averages, for air temperatures rise as high as 36.7°C at Nassau in June (table 1) and tidal exchange is trivial.

In figure 40, therefore, a curve of probable average temperature of bank water west of Andros Island, is derived by upward adjustment from a curve summarizing Fuglister's oceanic temperature data to take account of the foregoing local temperature data, as well as seasonal wind changes. This curve suggests that average bank-water temperatures west of Andros Island spread through the O^{18}/O^{16} equilibrium range of 27.6° to 31.7° C during an interval of about 6½ months from April to November. It was earlier estimated that

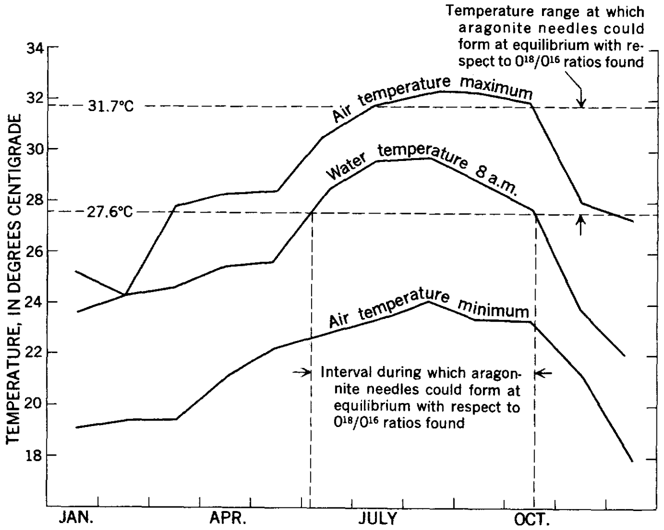


FIGURE 39.—Early morning water temperatures at Middle Bight, Andròs Island, through the year 1939, compared with equilibrium temperature range estimated by Lowenstam and Epstein (1957) for oxygen isotope ratios found in sedimentary aragonite needles.

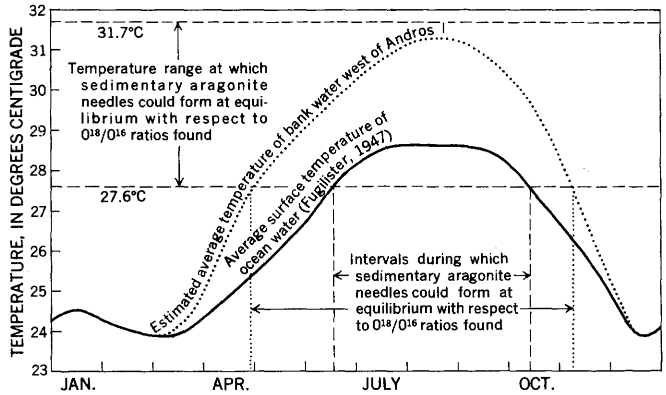


FIGURE 40.—Average monthly surface temperatures of Atlantic Ocean near Andros Island, and adjusted probable temperatures of bank waters compared with equilibrium temperature range estimated by Lowenstam and Epstein (1957), for oxygen isotope ratios found in sedimentary aragonite needles.

about three-fourths of the primary sediment is deposited during this interval. Allowing also for the fact that even higher water temperatures are probably reached at times and places in this area of intense evaporation, and for the uncertain basis of their large salt correction (op. cit. p. 372), the O^{18}/O^{16} equilibrium temperatures found by Lowenstam and Epstein for sedimentary aragonite needles cannot be accepted as proof of an algal origin. There is, moreover, no evident conflict between equilibrium formation for both needles and ooids, inasmuch as the latter seem to form mainly toward the eastern and northern bank edges, and around the Tongue of the Ocean, in better circulated, and probably partly upwelled, and cooler waters.

Because of the isotopic data, however, consideration has been given to the possibility that the local algal fraction of the sediment might be supplemented by transport of aragonite needles from areas of algal growth to the north or south. Four general observations are pertinent to this question. Currents moving into the area west of Andros Island from the banks to the north and south are weak. The marginal water where seen to the north on one occasion from the air and two occasions from a boat appears relatively clear of suspended matter as compared to the opaque, whitish water west of Andros Island proper. The same marginal water does not seem to support a particularly abundant algal flora. And apparent loss of $CaCO_3$ based on water chemistry is much greater in the area of study than at its margins—ample, in fact, to account for all sediments here, whatever the mechanism of its removal.

Finally, it is germane to ask why aragonite needles are not volumetrically important components in areas of truly rich growth of dasycladacean and tropical codiacean algae, if the Bahaman needles are prevailingly of algal origin.

For the foregoing reasons the preferred estimate for the proportion of algal sediments west of Andros Island is the 10 to 12.5 percent based on the *Halimeda* ratio. Lumping all of this as skeletal and adding to it the possible 7 to 8 percent of animal origin gives inferred limits of 17 to 20 percent of the total sediment as of skeletal origin. This figure is close to the previously and separately reached crude estimate of 15 to 25 percent.

A round figure of 20 percent is taken as reasonable, therefore, for total sediment of skeletal origin. If we add to this roughly 5 percent of detrital origin, 75 percent is left to be accounted for in some other way.

EVIDENCE FOR A CHEMICAL SOURCE

Although, in fact, the entire mass of nondetrital sediments is chemical in origin, it is convenient to consider under this heading only the more strictly chemical processes that take place within the bank waters at large and to exclude those that take place within organisms. In this sense the chemical effects involved may range from those closely connected with bacterial metabolism on the one hand, through the more remote effects of photosynthetic consumption of CO_2 or intermediate sources of it, to the purely physicochemical factors of evaporation, temperature increase, and pressure changes. Subtracting, now, the roughly 25 percent of the sediment that can be accounted for by direct biological or detrital processes leaves 75 percent to be explained by such indirect biochemical or physicochemical precipitation.

It will probably never be possible to isolate and quantify satisfactorily the results of all such processes in the field. On the other hand, information now available does make possible some degree of quantification and better labeling of the remaining problems.

POSSIBLE BACTERIOLOGICAL MECHANISMS

Microbiological effects most frequently suggested as a cause of $CaCO_3$ precipitation are those of the nitrate- and sulfate-reducing bacteria. The effects proposed are usually indicated to be nucleation, or physiological reactions that affect water chemistry or alter previously deposited materials.

Drew, principal champion of the nitrate-reducers, experimentally fed them calcium succinate and other calcium enriched nutrients and got mainly concretionary precipitates identified by F. E. Wright (Drew, 1913, p. 505–506; 1914, p. 31, 43) as probably calcite [12] and gypsum. Lipman (1924, p. 188) criticized this work on the basis that many different marine bacteria precipitated $CaCO_3$ when tested in Drew's media, but none, not even Drew's *Pseudomonas*, did so in sea water alone. C. L. Smith (1940, p. 184) objected that formation of ammonia as a result of nitrate reduction should raise the pH, whereas in fact a slight decrease of pH characterizes the bank waters. Such a decrease in pH was also observed during present work. Bacterial ammonia production, nevertheless, was observed by Sisler in cultures from six localities (three high enough to be biochemically significant), and one culture from the important bank center station *B3* showed a strong ammonia producer at a concentration of 10^6 individuals per gram wet weight of sediment (table 21). Inasmuch as field observations show no increase of pH in either overlying or interstitial water, it must be assumed that the effects of whatever ammonia is produced in nature are cancelled by some other reaction within the sediments.

Sulfate-reducing bacteria (Bavendamm, 1932; Smith, N. R., 1926) might lead to precipitation of $CaCO_3$ if neutralization of hydrogen ion during sulfate reduction were coupled with bacterial or other introduction of CO_2 leading to generation of HCO_3^- and H^+ in accordance with the sequence $CO_2+H_2O \rightleftharpoons H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$. This process could increase CO_3^{--} and lead to $CaCO_3$ precipitation thus:

$$8e+SO_4^{--}+8H^+ \rightleftharpoons S^{--}+4H_2O \text{ (sulfate reduction)}$$

$$CO_2+H_2O \rightleftharpoons H_2CO_3 \rightleftharpoons H^+ + HCO_3^- \text{ (CO}_2\text{ addition)}$$

$$8HCO_3^- \rightleftharpoons 8H^+ + 8CO_3^{--} \text{ (hydrogen uptake)}$$

$$8e+SO_4^{--}+8HCO_3^- \rightleftharpoons S^{--}+8CO_3^{--}+4H_2O \text{ (combined reaction)}$$

$$8CO_3^{--}+8Ca^{++} \rightleftharpoons 8CaCO_3 \text{ (precipitation)}$$

The odor of H_2S in many sediment samples led to the expectation that sulfate reducers would be found and that a mechanism such as outlined might be operating. Sisler's studies, however, showed sulfate-reducing bacteria to be rare and sulfide to be present only in traces too small for mass spectrographic detection. In addition, chemical analyses show that the ratio of sulfate to chloride remains essentially constant in both bank and sediment waters, indicating no appreciable withdrawal of sulfate. If, then the sulfate-reducing bacteria are indeed important precipitating agents, it would seem, as Bavendamm concluded, that the mangrove swamps should be their working sites. They are known to be abundant in the muds and are presumably present in the waters of the mangrove swamps; they, in fact, may contribute to $CaCO_3$ precipitation there. Data were not obtained during the present study that would permit the testing and possible quantification of this effect. However reasons were advanced at the beginning of this section for considering the mangrove swamps unimportant as a source for the bank sediments.

Kellerman (*in* Vaughan, 1914b, p. 228–229) made some observations that imply significance for the CO_2 couple in bacterial precipitation. He and his associates at the U.S. Bureau of Plant Industry found first that Drew's procedures and calcium-enriched media gave rapid $CaCO_3$ precipitation with bulk bacterial samples from the Florida Keys but that no precipitation whatever occurred in plain sea water with the same bacteria. Precipitation did occur when CO_2 was introduced to the bacterial medium. Experimenting with Kellerman's reaction, with introduction of calcium sulfate and bacterially produced ammonium carbonate, Vaughan (1914b, p.22) produced a spherulitic precipitate and then formed concentric shells of $CaCO_3$ around the spherulites, but apparently by the reaction: $CaSO_4 + (NH_4)_2CO_3 \rightleftharpoons CaCO_3 + (NH_4)_2SO_4$. What may have happened in Kellerman's own experiments with plain sea water (assuming that no excess calcium was present as sediment or nutrient) is that, with or after formation and dissociation of carbonic acid, bacterially induced neutralization of H^+ caused HCO_3^- and then CO_3^{--} increase, leading to $CaCO_3$ precipitation as described in the preceding paragraph. Most experiments reporting bacterial precipitation of calcium carbonate, however, involve the presence of calcium-rich nutrients or sediments which apparently go into solution upon bacterial or other lowering of pH and then combine with carbonate ion as the pH rises again—most commonly to form calcite.

Mlle. Claude Lalou (1957a, especially p. 235–236, 261–262; 1957b) called on increase in alkalinity and eventually CO_3^{--} as a secondary effect of bacterial CO_2 production to bring about precipitation of micro-

---

[12] In view of the propensity of bacteria to bring about a lowering of pH, it might be expected that reactions induced would generally lead to precipitation at lower ionic-product levels and thus result in calcite instead of aragonite. Pobeguin (1954, p. 60) also indicates that bacterial $CaCO_3$ is mainly calcite.

crystalline calcite, radial spherulitic aggregates of aragonite, and, in late stages, traces of a mineral identified by X-ray powder pattern as dolomite. If this supposed dolomite is analytically certain and not a high-magnesian calcite or protodolomite, proof is needed that it could not have been carried to the surface as detrital particles by gas bubbles rising from slightly dolomitic sediment beneath. Indeed the possible significance of Lalou's experiments for the problems under discussion is largely nullified by the fact that they were carried out in tanks containing glucose-enriched sea water over bacterially rich calcareous muds obtained from Villefranche Bay, along the Mesozoic limestone and dolomite coast of southeastern France. Formation of a surface film over the stagnant and bacterially active waters retarded evasion of CO_2 and other bacterially evolved gases. In consequence pH fell drastically. Later, with rise of pH to values as high as 8.4, a precipitate of $CaCO_3$ formed, in or under the surface scum. Two effects seem possible here. Perhaps bacterial neutralization of H^+ caused the late stage pH increase and precipitation as apparently visualized by Lalou, and as suggested in the preceding paragraph. Or, because of the experimental circumstances mentioned, $CaCO_3$ may have been dissolved from the muds as pH fell. followed by later equilibration and precipitation as pH rose again, upon exhaustion of excess nutrients and diffusion through the surface film of accumulated gases. The occurrence of much of the precipitate in spherulitic form (as if around now collapsed gas bubbles) in or under the surface film lends credence to the latter mechanism.

Sisler found, during the present study, that bacteria were not sufficiently abundant in the bank water to affect seriously the precipitation of $CaCO_3$. They were, however, extremely abundant in the sediments beneath. Gas producers, especially of CO_2, were active in culture, and one laboratory sample of gases made by bacteria from station *G4* (pl. 9C) proved to be 67 percent light hydrogen (Cloud and others, 1958) and 28 percent CO_2 (table 23).

It became important, therefore, to determine if possible what gases are being generated in place, and an attempt was made to do this in 1956 at station *It'*. Although abundant oxygen was generated in a few hours in stoppered ½-liter Winkler bottles in the water at the shallow sea floor, a clear funnel a foot in diameter, inverted and anchored over the sediment, showed no gas accumulation in a catching tube at the end after, or at any time during, the 24 hours it remained in place. Evidently excess oxygen is taken up at the sediment-water interface as fast as it is generated in the basal water, and such bacterial gas as may escape from the sediment and not be utilized biologically is in solution or goes into solution immediatly. Plans to remove a sample of the water from beneath the funnel for analysis of dissolved gases failed when it was accidentally tipped over, and time was not available to repeat the experiment. It is not known, therefore, how much, if any, CO_2 may have been evaded in excess of photosynthetic take-up, inasmuch as up to about 30 millimolls per liter may accumulate in aqueous solution before appearing as a separate gas phase. Observed evasion of gases from sediment cores implies that absorption or exchange in the bottom water plays some part in the total gas-equilibrium picture but does not prove or quantify this.

These observations do suggest, however, that despite some exchange across the depositional interface, the systems water and sediment (including interstitial water) show a large degree of chemical independence in the area of limemud deposition.

How precipitation of $CaCO_3$ might occur under the influence of known reactions by bacteria from the banks' sediments is as follows:

1. Bacterial $CO_2+H_2O\rightarrow H_2CO_3\rightarrow H^++HCO_3^-$
2. Bacterial or other H^+ neutralization, combined with residual enrichment of HCO_3^- and increased pH
3. Dissociation of $2HCO_3^-$ to $H_2O+CO_2+CO_3^{--}$, reflected or accelerated by pH increase
4. $CO_3^{--}+Ca^{++}\rightarrow CaCO_3$.

Production of CO_2 alone cannot increase carbonate ion, because the dissociation $H_2CO_3\rightarrow H^++HCO_3^-$ produces as many hydrogen ions as alkalinity ions, and reduction in pH decreases the CO_3^{--} component of alkalinity (fig. 7).

It seems certain, however, that bacteria could bring about $CaCO_3$ precipitation if, and wherever, they can neutralize H^+ and produce CO_2 at the same time. The place where such reactions might occur to the greatest extent is within the sediment. It is in the interstitial waters too that we find the highest alkalinity values, as well as the low pH which largely cancels their effect on the carbonate equilibria.

The effect of transfer of such interstitial alkalinity increases to the overlying waters should be measurable as the difference between a larger $CaCO_3$ loss computed from the ratio of calcium to chloride and a smaller loss computed from the ratio of titration alkalinity to chloride, assuming both are accurately determined. There is a suggestion in the present data (table 29) that this might be as much as 15 percent of the total $CaCO_3$ loss from bank waters. This percentage is viewed with reservations for four reasons. First, the average local $CaCO_3$ loss from bank waters indicated by ratios of calcium to chloride alone is very close to the total loss from straits to bank shore as indicated by essentially congruent calcium and alkalinity discrepancies (fig. 34). Second, variation in the ratio of alkalinity to chloride is strikingly regular. Third, an effect on the overlying water would depend on upward diffusion of interstitial waters of high alkalinity or of alkalinity ions, rather than the gases themselves, and such diffusion of the interstitial water at least is apparently extremely slow in the mud areas where the high interstitial alkalinities are found. Finally the slight lowering of pH in the overlying waters, concurrently with alkalinity depression, suggests possible bacterial effects that would work against, rather than with, precipitation of $CaCO_3$.

For these reasons, and because of the chemically distinct interstitial environment which they create and inhabit, the bacteria are believed to be much more important for diagenesis than for precipitation of bulk sediments. At most bacterial effects could hardly contribute more than about 15 percent of the total original sediment. For the reasons given, moreover, it is considered that a more realistic value would be much less than 15 percent and perhaps none at all.

OTHER SECONDARY BIOCHEMICAL EFFECTS

Changes in CO_2 content of the water caused by respiration and photosynthesis are probably the only important secondary biochemical effects still to be considered. From pH, Eh, and other evidence we may safely assume that photosynthetic production of O_2 equals or exceeds respiratory generation of CO_2 and that the focus of interest in this system is CO_2 uptake. The reverse effect, anyhow, would not differ from bacterial CO_2 production, which was discussed in the preceding section.

It has been experimentally demonstrated that aragonite needles similar to those of the bank sediments can be precipitated from biologically inactivated Straits of Florida or bank waters by forcing the evasion of CO_2. Therefore, $CaCO_3$ should be precipitated from the more concentrated bank waters by anything that would withdraw or cause evasion of CO_2, thereby increasing the CO_3^{--} fraction of the alkalinity complex. Photosynthesis is one of the identifiable mechanisms by which such a result is achieved, either by direct uptake of CO_2 or through the use of H_2CO_3 or HCO_3^- (Baas Becking, 1956, p. 417; 1958; Hood and others, 1959).

Phytoplanktonic O_2 production estimated at the high rate of 1.5 ml/l per daylight hour was found by Sisler in stoppered Winkler bottles left at the shallow sea floor near station *It′* for varying intervals in 1956. To such extent as this photosynthetic uptake may combine with that of the megaflora to exceed biogenic CO_2, it necessarily causes $CaCO_3$ precipitation. Inasmuch as no abundant planktonic micro-organism was identified in the plankton catch of May 30, 1955 (fig. 3), or on the millipore filter papers, autolytic nannoplankton are presumably the preponderant photosynthesizers. The only evidence of relation to the CO_2 cycle is that from the funnel observations described in the preceding section. These observations indicate that rapid equilibration of photosynthetic oxygen takes place at the sea floor and that there may thus be a balanced local interchange of O_2 and CO_2 across the sediment-water interface.

Nevertheless, the threefold discrepancy between presumably accurate inorganic phosphorus determinations from large samples of whiting water at Station *It′* and that adjacent to it (tables 2 and 4) implies important photosynthetic effects in the very area where the high O_2 production was found. The analytical values convert to 0.30 microgram-atom per liter PO_4-P within the whiting water and only 0.10 microgram-atom per liter peripheral to it. These figures, to be sure, could be interpreted as suggesting decreased rather than increased local nutrient consumption in the whiting water; but, in view of the much smaller phosphorus values reported at other bank sites, the actual and relatively high oxygen production here, and other differences (table 6), it seems more likely that this whiting water actually is a focus of phytoplanktonic activity, whatever be the explanation for its high nutrient content. A high rate of photosynthetic withdrawal of CO_2 at such sites, either directly or indirectly, would logically cause $CaCO_3$ precipitation as a secondary biochemical effect.

To what extent the evidence suggesting photosynthetically accelerated precipitation at station *It′* may be important for other whiting waters or for bank waters in general is uncertain. The low phosphorus values of other waters analyzed do not favor an important bankwide imbalance between biogenic CO_2 and its photosynthetic removal, but quantification is not possible on the basis of available information. Evidently photosynthesis is an important factor but probably not a dominating process in bankwide calcium carbonate precipitation.

PHYSICOCHEMICAL FACTORS

The chain of evidence favoring physicochemical precipitation of some fraction of the aragonite muds has five links: (a) as was shown early in this section, congruent chemical changes of the right order of magnitude to account for all these $CaCO_3$ sediments take place within the water body above them, (b) changes of the same general nature leading to precipitation of aragonite needles have been produced synthetically in biologically inactive sea water, (c) identified direct and indirect biological mechanisms are probably not quantitatively adequate to account for all the nondetrital sediments found, (d) physicochemical effects exist in nature that are capable of producing the results seen, and (e) independent evidence indicates that such physicochemical effects do in fact augment or cause the precipitation of $CaCO_3$ in the bank area at some times and places, and perhaps generally. Because evidence favoring the first three steps in the argument has already been developed in preceding parts of this paper, the present section is concerned primarily with the existence and types of possible physicochemical mechanisms.

Evasion of CO_2, causing the dissociation $2HCO_3^- \rightarrow H_2O + CO_2 + CO_3^{--}$, may result from equilibration between water of higher and air of lower partial pressure following pressure or temperature changes of either. It could also follow some triggering action after the ionic product $Ca^{++} \times CO_3^{--}$ had passed a critical concentration for waters of a given ionic strength as a result of evaporation or temperature increase.

For available estimates of the solubility product constant of $CaCO_3$ in the sea, it seems highly improbable that the ionic product $Ca^{++} \times CO_3^{--}$ could reach levels as great as those found west of Andros Island without eventual precipitation as concentration and temperature increased. With increasing temperature of the water the ionic product that must be exceeded for precipitation to take place decreases—about 30 percent from 20° to 30°C. Increasing salinity alone improves the prospects of precipitation, as will be discussed, because the activity coefficients of the combining ions decrease with increasing ionic strength. It is possible, therefore, without extraneous effects of any sort, to explain the entire sequence of changes seen as a function of increasing concentration, temperature, and CO_2 evasion leading inevitably to precipitation as known since the experiments of Usiglio (1849, p. 185). Failure to precipitate the salts that come after $CaCO_3$ in the Usiglio evaporite series can be explained as the result of continued renewal of the parent water at about the right rate to hold the concentration in the range of aragonite precipitation. In such a system, the event that triggers the initial shift in CO_2 balance, permitting precipitation to begin, may be as subtle as a rise in temperature or barometric pressure or the locally accelerated photosynthetic activity of a microflora.

As was recognized by C. L. Smith (1940) the prior presence of stirred-up aragonite needles in the bank waters also provides nuclei which might stimulate precipitation, but precipitation from filtered water in the laboratory implies that nuclei are not essential. Anyhow, some aragonite needles are likely to be available for nucleation in all areas inhabited by *Halimeda* and certain other codiacean and dasycladacean algae.

Whether or not small atmospheric pressure changes are important, a preceding review of the white-water areas locally referred to as whitings showed no immediate correlation with turbulence of any sort, and the barometer in a whiting area showed no unusual variations. To test the possibility that low-level variations between partial pressure of CO_2 in atmosphere and water might affect precipitation, mass spectrometric analyses were obtained of air samples taken at different times of day and heights above water at station *It′* (table 31), a site of presumably active precipitation at the time. Unfortunately, the sensitivity of the method permits only the conclusion that the CO_2 content of the surface air was in the direction of mean atmospheric value.

TABLE 31.—*Percentage composition of dry sea-level air and of gas above a sediment core from station It′*

[Analyses by Vernon H. Dibeler, Mass Spectrometry Section, U.S. Natl. Bur. Standards. Values are mole percentages and equivalent to partial pressures; all samples, including reference laboratory air, were bubbled through water before analysis. Sediment core 3 ft long, collected and sealed 3 weeks before analysis. Sample removed by hypodermic syringe from small space above sediment and 1 in. of water]

Components	Laboratory air	Sea air June 12, 1956						Gas above core	Mean[1] atmosphere
		At sea surface			9 feet above surface				
		7 a.m.	11 a.m.	3 p.m.	7 a.m.	11 a.m.	3 p.m.		
CO_2	0. 3	0. 2	<0. 1	<0. 1	<0. 1	<0. 1	<0. 1	1. 2	0. 03
A	. 9	. 9	. 9	. 9	. 9	. 9	. 9	1. 0	. 94
O_2	20. 9	19. 6	19. 8	19. 8	20. 1	20. 1	20. 2	9. 7	20. 99
N_2	78. 2	79. 3	77. 4	79. 2	78. 9	78. 9	78. 8	88. 1	78. 03
H_2	------	-----	[2]1. 8	-----	-----	-----	-----	-----	. 01

[1] Volume percent dry air at sea level from Handbook of Chemistry and Physics, Hodgman ed., 1947, p. 2625.

[2] Anomalous H_2 may be instrumental contaminant.

Other evidence, however, indicates evasion of CO_2 from the water at *It′*. Air collected at the sea surface in the early morning showed more CO_2 than samples taken later in the day, when photosynthetic CO_2 uptake from bank water is effective, or at the same time 9 feet above it. In addition, computation of the partial pressure of CO_2 in the water gives values exceeding the mean atmospheric value of 0.03 percent (tables 6, 35). Assuming the correctness or parallel error of alkalinity values at and marginal to the whiting site at station *It′*, the partial pressure of CO_2 in the whiting water is one-third lower than that at its margins, while cumulative CO_2 loss is twice as great.

The mechanics of this CO_2 evasion, to be sure, are not certain. CO_2 enrichment of the water and evasion to the atmosphere is bound to occur in darkness, with halt of photosynthesis; and swarming of phytoplankton in high-phosphate whiting waters could and probably does account for the lowered partial pressure of CO_2 and high CO_2 withdrawal there. But, as noted in the preceding section, the comparatively low phosphate values of other bank waters analyzed imply that photosynthetic CO_2 uptake as high as observed at this station is probably not a persistent bankwide feature. Room is thus left for effects resulting from purely physical evasion of CO_2.

Figure 41 presents previously unpublished data compiled by C. L. Smith to show seasonal variation of specific alkalinity in bank waters. Smith's data emphasize that as the season advances from March to October the rates of alkalinity loss with rising salinity across the bank (fig. 34) increase generally at any particular salinity with rising temperature of the water. Such growing alkalinity loss presumably is due to decreasing capacity for CO_2 retention by the water as its temperature increases, leading to temporary augmentation of CO_3^{--} and thence to $CaCO_3$ precipitation. Data suggesting an average increase of 2° to 2.5°C from ocean to bank waters during the months of maximum precipitation were earlier summarized in figure 40, and for upwelled waters the discrepancy would be greater. Variation curves accompanying the discussion of equilibrium relations suggest relatively large precipitation effects from small temperature variations.

Demonstrable physical factors that affect the precipitation mechanism thus include (a) evaporation, with consequent increase in concentration and decrease in activity of the pertinent ions, (b) temperature increase of bank waters, affecting solubility of CO_2, pH, and relative concentration of carbonate ion, and (c) changes in partial pressure of CO_2 in water and and atmosphere affecting rate and direction of CO_2 exchange.

The biological factors other than photosynthesis have been quantified within limits that seem reasonable, and the photosynthetic factor is probably in large degree cancelled out by biogenic CO_2 (including that from bacterial sources). It thus seems unlikely that photosynthetic CO_2 uptake can account for more than a modest part of the approximately 60 to 75 percent of the deposits remaining after subtraction of previously considered elements.

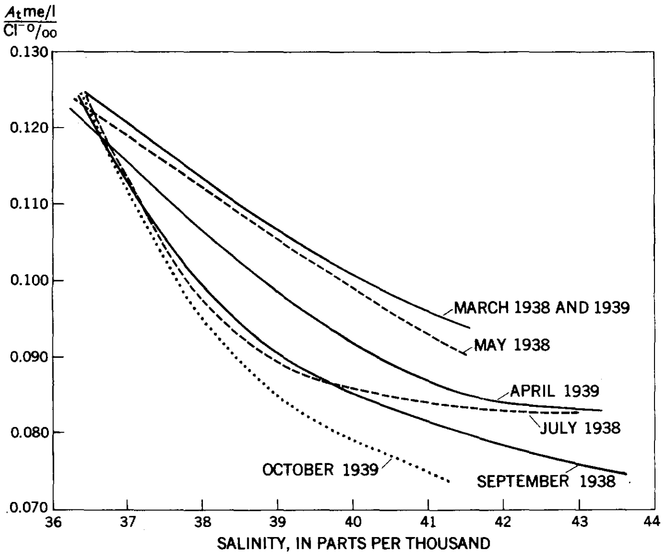


FIGURE 41.—Seasonal variation in specific alkalinity with reference to salinity in waters over the Great Bahama Bank (previously unpublished data presented for use in this report by C. L. Smith, July 25, 1957).

Therefore, by a process of elimination as well as from the independent evidence of physical effects, it becomes reasonable to impute to identified physiochemical mechanisms a large or even a preponderant fraction of the sediments. Another point favoring the importance of physiochemical factors is the general chemical regularity of the system. It works like something that, once started near the seaward margin of the banks, moves steadily toward a predictable end at sites of maximal salinity—except insofar as it may be locally retarded or accelerated by extraneous factors. This regularity seems more in keeping with the progressive chemical equilibration of a disequilibrium state than with biological drawdown of a richly stocked potential skeletal or nutrient reserve. This aspect of the system is discussed more fully in a following section on equilibrium relations.

RECAPITULATION OF INFERRED PRIMARY GENESIS

Factors that might contribute to the primary sediment have now been reviewed in detail and roughly quantified. The estimated percentages that each may represent are summarized in table 32. The present distribution of the sediment by genetic classes is estimated in table 33. The supposed primary mechanisms may now be summarized; consideration of postdepositional effects being reserved for the following section.

TABLE 32.—*Estimated percentages of primary sediment from various contributing factors*

Contributor	Minimum	Maximum	Probable
Detrital	<5	10	5
Direct biologic origin:			
Plant fraction	4	13	12
Animal fraction	7	13	8
Chemical origin:			
Bacterial	0	15	<5
Other secondary biochemical	(?)	<75	70–75
Physicochemical	>0	60–75	

First to be considered is the detrital fraction, of which the only confidently identified component is a part of the low-magnesian calcite from adjacent and former land. This component is less than 5 and probably not more than 2 percent of total sediment; but some probably small fraction of the aragonitic sediments is surely also recycled. All that has been dem-

TABLE 33.—*Estimated distribution of present sediment by genetic classes*

Sediment	Percentage
Detrital fraction	5
Identifiable skeletal fraction (plant and animal)	15
Aragonite needle fraction of algal origin	3
Durable fecal pellets from skeletal aragonite needles	2
Durable fecal pellets from aragonite needles of chemical origin	30
Aragonite needle fraction of chemical origin (physicochemical and secondary biochemical)	45

onstrated is that the detrital contribution is small, but 10 percent is suggested as a maximum and 5 percent as a probable figure for sediment of detrital origin.

Water chemistry (figs. 34, 35) strongly implies that the great bulk of the sediments originated essentially where found. Basic water properties are summarized in table 34. This summary indicates that at the bottom of the Straits of Florida the water is cold, and of relatively low pH (7.83) and high alkalinity (2.62 me/l). As the water rises to the surface [14] it warms, loses some CO_2, and undergoes a slight salinity increase as the result of evaporation. Alkalinity decreases sharply, and calcium a little, instead of increasing with salinity as would be the case with simple concentration. Water that floods the bank from the east and northeast undergoes similar changes, but with a much larger temperature gradient, especially in the summer months.

As these waters move across the bank, they undergo large salinity increases as a result of sluggish circulation and evaporation. Alkalinity continues to fall, however, and calcium does not increase as rapidly as it would if it maintained constant relations with chloride. In fact, from straits surface waters to inner bank, the decreasing ratios of alkalinity and calcium to chloride indicate large and equal loss in combining equivalents of Ca^{++} and of CO_3^{--} (figs. 34, 35). Only about 20 percent of this loss is acccounted for by direct organic precipitation as skeletal components of plants and animals. A more problematical fraction of not more than 15 percent, and probably less than 5 percent, can be accounted for by the secondary effects of bacterial biochemistry, compensating some of the absolute alkalinity loss by concurrent CO_2 production and possible hydrogen ion neutralization.

The inadequacy of identified direct biological mechanisms to account for the rate of deposition found implies that the rest of the $CaCO_3$ withdrawal is a matter of chemical precipitation. Indeed the system behaves with a regularity suggesting physicochemical equilibration, and identified physicochemical mechanisms could account for all the changes observed. It is almost certain, however, that photosynthetic uptake of CO_2 is at least locally important. How important is not known; nor is it likely that the purely physicochemical factors can ever be completely untangled from the secondary biochemical factors with which they intergrade. Isolating the bacterial effect therefore, and considering the whole sediment, leaves 60 to 75 percent, and probably closer to the higher figure, of unspecified chemical origin. This large remainder is apparently in part the result of photosynthetic CO_2 uptake, is perhaps also partly due to unidentified influences, but is probably in greatest part physicochemical.

The principal mechanism is visualized as a complex succession of repeated annual cycles of persistent evaporation, warming, loss of CO_2, and concurrent increase in the ionic product $Ca^{++} \times CO_3^{--}$ and decrease of activity coefficients of the same ions in waters which are already supersaturated, or nearly so, when they reach the bank edge. These changes take place in consequence of initial movements from depth to a warmer, lower pressure, surface layer and of lateral movement at the surface to an area of temperature increase (fig. 40) and high residual concentration. The

TABLE 34.—*Basic properties of water from classified groups of stations*

Class	Number of stations	Temperature (°C)	pH	Eh (volts)	sp. gr.	S°/oo	Cl^- (mg/l)	A_t* (me/l)	Ca^{++}mg/l†		$aCa^{++} \times aCO_3^{--} \times 10^9$
									Used	Analyzed	
Straits:											
bottom	5	22.6	7.83	0.33	1.0239	35.43	20,100	2.62	433	394	11.58
surface	5	27.9	[1] 8.04	.31	1.0238	35.93	20,360	2.43	427	388	12.13
Bank edge	6	27.8	8.17	.33	1.0251	37.97	21,435	2.39	459	417	14.58
Outer bank [2]	11	28.0	8.16	.35	1.0253	38.27	21,690	2.28	456	415	14.32
Midbank	26	28.4	8.10	.33	1.0269	40.35	22,960	2.10	470	427	11.73
Inner bank	20	28.4	8.02	.27	1.0307	42.45	24,170	1.91	487	443	8.67

[1] Low pH because 4 of 5 stations were nighttime readings.
[2] Includes bank edge.
* Titration alkalinity.
† Calcium values used in computing $aCa^{++} \times aCO_3^{--}$ are analyzed calcium plus 10 percent to allow for systematical error.

---

[14] It is certain that the bottom water directly beneath is not the parent of the surface water directly overhead. The comparison will do for illustration, however.

existence of a supersaturated condition is indicated by three lines of evidence. First, computed ionic and activity products away from sites of peak salinity markedly exceed the apparent solubility and activity product constants for both calcite and aragonite when all are compared at the same temperature, pressure, and salinity. Second, variation curves (figs. 43–46) for the ionic and activity products show a sharp drop from bank edge to outer bank and general decrease across the bank to minimal values at midbank or adjacent to Andros Island. Third, the fact that the chemical precipitate is aragonite, rather than calcite, implies that the solubility product constant of both crystallographic forms is exceeded (aragonite being the higher, as discussed under equilibrium relations).

If evaporation, salinity, and temperature are increased in a solution already supersaturated with respect to $CaCO_3$, precipitation must eventually take place—provided pH is not depressed and other complexing effects do not increase correspondingly. With essentially constant pH, such precipitation will be the result either of evasion or removal of carbon dioxide, bringing about an increase of carbonate ion; or of increasing temperature, lowering the ionic product which must be exceeded in order for precipitation to take place; or of increasing salinity and ionic strength, with resultant decrease in activity coefficients of the participating ions. Carbon dioxide is a mobile component in this system. It is taken up photosynthetically, evades to the atmosphere with increasing temperature and changing partial pressure, and is added to the system by nearly all elements of the biota. Wherever loss of CO_2 exceeds gain at the same pH under supersaturated conditions, precipitation is possible. The effects on the system of increasing salinity, and the anomalies observed in the relation of the ionic product to pH, also indicate kinetic complications in the behavior of calcium carbonate. The results, moreover, are probably magnified by the poverty of the waters studied in lime-secreting plankton or shelly benthos such as tend to keep the surface waters of the ocean or tropical shoal waters elsewhere in a balanced state. Chemical precipitation is visualized as taking place across the entire bank area, with local variations along shore and in and adjacent to the whiting waters. The pertinent chemical equilibria and their significance for the physicochemical mechanism are discussed on pages 111–121.

POSTDEPOSITIONAL EFFECTS

Considering the problems to be solved, disappointingly little information was got on diagenetic effects. That obtained relates mainly to changes of Eh and pH within the sediments, the work of bacteria and pellet makers, and the filling, coating, and interstitial cementation of pellets and porous grains. In experimental consolidation of the sediments, Robertson, Sykes, and Newell produced dense calcite rock (pl. 7*H*) from pelletal aragonite mud only at temperatures normally to be expected at depths of 5,800 meters (19,000 feet) or more and pressures to be found below 1,300 meters (4,200 feet). Consolidation of the sediment was much less complete at lower temperatures and pressures. Although, therefore, work on diagenesis needs to be continued and accelerated more than in any other phase of carbonate studies, by the same token even the present modest findings are of interest.

TRANSITION OF ARAGONITE TO CALCITE

The experimental work of Jamieson (1953) on solutions and of MacDonald (1956) on solids confirms the historic conclusion that aragonite is unstable relative to calcite at the temperature and pressure of the deposits west of Andros Island. Radiocarbon dating (table 13), on the other hand, shows that the basal layer of these preponderantly aragonitic sediments is thousands of years old. In addition, experimental consolidation of the Bahaman sediments by Robertson, Sykes, and Newell seems to confirm the deduction from field relations that immersion in hypersaline sea water gives aragonite a high degree of temporary "stability," up to pressures and temperatures not attained under normal conditions near the earth's surface. The geologic occurrence of calcite and aragonite in Pleistocene and Recent sediments also strongly implies that general inversion to calcite of originally aragonitic marine deposits not deeply buried is evidence of emergence and flushing away of saline interstitial waters.

Because inversion to calcite occurs relatively soon in the geologic sense in aragonite transferred from aragonite-saturated salt water to aragonite-undersaturated fresh water, or to moist atmospheric conditions, it also seems evident that trace-element composition does not have important, long range, stabilizing effects, a conclusion MacDonald and Jamieson reached from thermodynamic considerations. Here is another anomaly. Replicate X-ray diffractometer tests by Blackmon on pure Vesuvian aragonite powdered to dimensions less than 37 microns for laboratory calibration showed 10 to 20 percent inversion to calcite over a 4-year interval. Within the limitations of the method, however, no inversion was found over the same interval for 2 silt-sized fractions and 7 clay-sized fractions of washed and similarly dry-stored aragonite sediments from the Bahama Banks. Semiquantitative spectrographic analyses (by Paul Barnett, U.S. Geol. Survey, Denver) for strontium, barium, lead, and zinc in tested samples show:

	Sr	Ba	Pb	Zn
Vesuvian standard	5×10^{-3}	1.5×10^{-6}	None detected	None detected.
Clay fraction from loc. *B3*	7×10^{-3}	1.5×10^{-6}	Trace	None detected.
Clay fraction from loc. *C26*	7×10^{-3}	1.5×10^{-6}	Trace	None detected.

From the preceding paragraphs, it is suggested as a general condition that calcium carbonate originally laid down as aragonite remains aragonite as long as it is surrounded by fluid in which the effective ionic product $Ca^{++} \times CO_3^{--}$ exceeds the solubility product constant for aragonite under local conditions. Available evidence (p. 123) indicates that such concentrations are rare in fresh-water bodies, but usual in warm marine surface waters and the internal fluids of many organisms. It may also be that inclusion of even traces of calcium-interchangeable cations of large ionic radius can have a long-term retarding effect on inversion of aragonite to calcite, in a dry environment at atmospheric temperature and pressure, but it is hard to see wherein the bank aragonite differs significantly from the Vesuvian standard. The fluid equilibrium relations are discussed in a following section.

IMPLICATIONS OF PRESENT FINDINGS FOR THE DOLOMITE PROBLEM

No dolomite was found in the sediments studied; nor was any magnesium loss detected in the overlying waters, or increase of magnesium to chloride ratios in the interstitial water or basal water in contact with the sediments. This was disappointing, inasmuch as the well-established affinity of dolomitic rocks for toward-shore or shoal waters has long been interpreted as implying greater chance of dolomitization in such areas because of higher temperature, more concentrated solutions, and at least episodically high pH (Dunbar and Rodgers, 1957, p. 244; Fondeur and others, 1954; Cloud and Barnes, 1948, p. 94; Rivière, 1939b).

Under the discussion of interstitial water it was shown that only about 1.2 to 2 percent of the total rock formed from its interspersed sediments could be converted to dolomite by exchange with magnesium ions in that water and in solid solution. Dolomitization of comparable sediments thus requires the addition of magnesium from external sources; and sea water is the logical source of magnesium for most dolomites. Cloud and Barnes (1948, p. 89–95; 1957, p. 182–186) discussed the problem and suggested that a possible dolomitization mechanism might be exchange between calcium carbonate sediments and some magnesium compound within, beneath, or while settling through a basal layer of sea water. They also supposed on empirical grounds that an originally aragonitic composition probably favored dolomitization, as do Dunbar and Rodgers (1957, p. 238) on the basis of experimental work by Rivière and others. However, basal water significantly enriched in magnesium (beyond its normal ratio with chloride) was not found above the bank sediments west of Andros Island, nor did the preponderantly aragonitic sediments show any dolomitization. Indeed southeastern Australia (Alderman and Skinner, 1957; Alderman, 1959) is the only place so far known where dolomite appears to be forming contiguous to a modern marine environment, and that apparently under conditions of drastically restricted circulation, abnormally high pH, and greatly variable salinity.

How then does dolomite happen to prefer shoals and basin margins? Why does it selectively favor aragonitic reefs and avoid the calcitic tests of some organisms, which are later dissolved to leave open spaces? When so much is known geologically about the characteristics and associations of dolomite, why does its origin remain a major chemical mystery? What is the explanation for the apparent absence beneath existing normal marine waters of sediments capable of making a dolomitic rock without addition of magnesium?

These questions cannot yet be answered with any assurance, but the present study suggests some directions of investigation and some limitations on speculation.

Evaluations should be made, in individual and relatively undeformed basins, of the proportions of dolomite to total basin sediments. If in any such sequence dolomite is about 1.2 percent, or higher by this amount above the range of total magnesium derivable from solid solution in original calcite, the dolomitization might be explained by upward and updip migration of squeezed-out connate waters, a diagenetic mechanism emphasized by Emery and Rittenberg (1952). Magnesium ion exchange might thus be concentrated in carbonate sediments updip and upward in the section—along basin margins, where many dolomites are found. It should be added, however, that there seems intuitively no better prospect of this being a quantitatively satisfying general explanation for dolomitization than hydrothermal or other postemergence processes.

As concerns primary precipitation, the salient fact is that no dolomite has as yet been unequivocally synthesized at temperatures and partial pressures of CO_2 comparable with those found in existing sea water. Substitution of Mg^{++} for Ca^{++} apparently occurs in nature (Rivière, 1939a; Dunbar and Rodgers, 1957,

p. 238), but from the time of Sorby (1879, p. 73) it has remained a puzzle to geologists that so common a sedimentary mineral as this double carbonate does not seem to form under ordinary conditions. The dilemma is not alleviated by the fact that Chilingar (1956a, p. 2261–2262) and others before and after him (Dunbar and Rodgers, 1957, p. 238; Kazakov and others, 1957, p. 47, 54–55) have created artificial dolomite at CO_2 partial pressures of 1 to 4 atmospheres or more. Thus, Soviet scientists, who have recently stressed grain orientation as a clue to primary genesis, have had to call on large variations in the CO_2 pressure of the atmosphere as an explanation for supposedly primary dolomites, especially in pre-Mesozoic time (Chilingar, 1956a, 1956b). Kazakov and others (1957, p. 41) summarize the controlling factors for primary precipitation of dolomite in an open sea water system as:

1. alkalinity exceeding 6 me/l at 60°C, or higher for lower temperatures, as compared with 2.43 me/l at 20°C in normal sea water (table 4)
2. Relatively high CO_2 tension, ratio of CO_2 to alkalinity >2.2
3. Low calcium content of water, the order of magnitude being less than 50 mg/l as compared to 420 mg/l in normal sea water (table 4).

The sea and the atmosphere tend to equilibrate with respect to CO_2, however, and Urey (1956) offers reasons for doubting that the atmosphere ever exceeded a partial pressure of about 3×10^{-3}. This corresponds to a partial pressure of CO_2 far below that apparently required for direct precipitation of dolomite unless it be at temperature or pH considerably above that ordinarily found in normal surface waters.

Kazakov and others (1957, p. 36–39) have also shown, though, that coprecipitation of $MgCO_3 \cdot 3H_2O$ (nesquehonite) and $CaCO_3$ is possible in sea water at 15°C and low P_{CO_2} provided alkalinity is greater than 41 me/l (normal 2.4 me/l). They believe nesquehonite to be the stable magnesium carbonate at ordinary temperatures. Magnesite ($MgCO_3$), like dolomite, was not obtained below temperatures of 60°C and in confined or semi-confined systems at elevated P_{CO_2} (Kazakov and others, p. 43–44, 54–55). Brucite, $Mg(OH)_2$, altered rapidly to the basic magnesium carbonates (Kazakov and other, p. 28), not existing concurrently with nesquehonite, as Kline (1929) supposed.

Inasmuch as alkalinity rises to as much as 19 me/l in some Caspian Sea bays (Glazovskaya *in* Kazakov and others, 1957, p. 28) and apparently even 35 me/l in Kooli Lake (Strakhov, 1947, p. 37), the conditions under which sedimentary nesquehonite might form may occur naturally at some places, especially at temperatures above 15°C. Strakhov (1947), however, asserts that the sediments of some high-alkalinity lagoons in such water bodies are predominantly magnesite, formed when $CaSO_4$ starts to precipitate in the presence of $CaCO_3$ by reaction of the latter with $MgSO_4$ (Heidinger's reaction).

Granting, then, at conceivably elevated alkalinity, the likelihood of concurrent or successive precipitation of $CaCO_3$ with $MgCO_3$ or $MgCO_3 \cdot 3H_2O$, the prospects of their recombination to dolomite can be estimated thermodynamically, for the reaction can move only in the direction of decreasing free energy (ΔF) unless energy is added to the system. The contemplated reaction involving nesquehonite is:

$$MgCO_3 \cdot 3H_2O + CaCO_3 = CaMg(CO_3)_2 + 3H_2O$$

From Latimer (1952, p. 39, 318) the standard free energy (ΔF°) of formation for $CaCO_3$ *calcite* is -269.78 and for liquid water -56.69 kilocalories per mole. From R. M. Garrels (oral communication, Nov. 5, 1958) $\Delta F^\circ_{formation}$ for $CaMg(CO_3)_2$ is -520.34 kcal/mol. From data in Latimer (1952, p. 39, 128, 316, 317) $\Delta F^\circ_{formation}$ for $MgCO_3 \cdot 3H_2O$ is computed as -412.10 kcal/mol. Entering these values, -690.41 is on the right side of the equation and -681.88 on the left. This implies that at unit activity, and at 25°C and 1 atmosphere pressure, the reaction will move to the right with an entropy change of roughly 8.53 kilocalories per mole. Thus dolomitization by reaction between calcite and nesquehonite theoretically should take place if the two occur together at surface temperature and pressure.

Similar computations were also made for magnesite and brucite with calcite, using $\Delta F^\circ_{formation}$ for $MgCO_3$ of -246.43 kcal/mol. (Garrels and Siever, 1958) and $\Delta F^\circ_{formation}$ for $Mg(OH)_2$ of -161.65 kcal/mol. (Latimer, 1952, p. 316):

1. $MgCO_3 + CaCO_3 = CaMg(CO_3)_2$
   $-246.43 - 269.78 = -520.34$
   a balance of -4.13 kcal/mol. is shown on the right side of the equation, and the reaction should move to the right (forming dolomite) with that loss of energy at standard conditions, if the ΔF° values are correct.
2. $Mg(OH)_2 + 2CaCO_3 = CaMg(CO_3)_2 + Ca(OH)_2$
   $-199.27 - 539.56 = -520.34 - 214.33$
   a balance of -4.16 kcal/mol. is shown on the left side of the equation; so if the reaction were invoked at standard conditions it would move to the left and dolomite would not form.

The free energy values for calcite are used in all the above estimates, because if a reaction will move to the right for calcite it will do so for aragonite. As each mole of aragonite has 250 to 370 calories more energy to yield to the reaction than an equivalent mole of calcite, aragonite is in a demonstrably more favorable position to be dolomitized than is calcite—by a factor of 6 to 9 percent in the suggested reaction with magnesite or 3 to 4 percent with nesquehonite.

The free energy relations, it is seen, imply that penecontemporaneous or diagenetic dolomitization can take place as a result of recombination of calcite or aragonite either with magnesite or nesquehonite. If, therefore, nesquehonite were precipitated or magnesite were to form as a result of Heidinger's reaction (Strakhov, 1947), these minerals could recombine with either aragonite or calcite to form dolomite, and at normally warm temperatures and atmospheric pressure. Such reactions may help to explain the presence of interbedded dolomite, anhydrite, and limestone in evaporite sequences.

It would be of interest now to investigate further the apparently much larger amount and proportion of dolomite in the sedimentary record before the spread of terrestrial vegetation in Late Silurian time, and again during the arid cycle of late Paleozoic to Triassic time (Steidtmann, 1911; Dunbar and Rodgers, 1957, p. 241–242). From the work of Kazakov and others (1957), and inferentially, it seems that any increase in P_{CO_2} or CO_3^{--} should improve the chances of mixed or successive precipitation of calcium and magnesium carbonates, particularly if Mg^{++} and temperature should increase, and if Ca^{++} should decrease at the same time. Reduced land vegetation, with consequent reduction of total photosynthesis, seems to demand increase of P_{CO_2}, temperature (since CO_2 absorbs reflected heat while transmitting solar radiation, Plass 1956), and perhaps available Mg^{++}.[15] Before so much CO_2 was locked up in carbonate rocks and coal, and when the oceans were smaller (Rubey, 1951), atmospheric CO_2 could have reached perhaps 10 times its present quantity (Urey, 1956). Under conceivable circumstances, also, alkalinity and perhaps eventually total CO_3^{--} content of sea waters might increase under such conditions; so that several trends could be in the right direction for the formation of dolomite. Any increase in pH or salinity might then set a dolomitic cycle in motion. A dolomitic cycle induced by such events might well begin with limestone deposition, whereby calcium depletion would augment the prospects of mixed carbonate precipitation and recombination. A preponderance of the conducive factors would be more likely to prevail or to be enhanced in shallow, restricted waters, or in enclosed basins of favorable chemical composition or physical properties such as high pH, high alkalinity, high temperature, or special ionic composition.

With no illusions that the problem is in any way diminished, but in the hope that its focus may be improved, it is now commended particularly to the further attention of Australian geochemists and ecologists—with advance warning that time of geologic dimensions may be an essential element.

WORK OF BACTERIA AND BURROWING ORGANISMS

From the moment the aragonite needle originates, it may undergo diagenetic effects. When it settles past the depositional interface it truly enters the diagenetic realm. Within the area of low oxidation-reduction potential (fig. 9) that is so nearly coincident with accelerated $CaCO_3$ precipitation west of Andros Island, this realm is drastically different from the water above. The aqueous environment has an average pH of 8.1, Eh of +0.32 volts, and relatively low alkalinity and calcium concentration for its salinity. From free suspension in such waters, the aragonite needle settles into an environment of restricted motion, with average pH about 7.1 and Eh zero, and with relatively high alkalinity and high calcium even for its elevated salinity.

Outside the area of low Eh, however, sediment pH rises to 7.5 and eventually to 7.8 or 7.9 at the bank margins, with Eh generally +0.30 to +0.35 volts, or about that of the overlying water.

These changes appear to be a concurrent function of grain size and bacterial flora. Fine grain size without compaction provides a larger total interstitial area and more numerous contacts for the contact-loving bacteria. It also insures a more viscous medium; which, in turn, retards diffusion effects such as accelerate exchange with more normal water from overhead in coarser grained sediments. By producing carbon dioxide, and perhaps by other effects, the bacteria bring about an increase of hydrogen ion, expressed as a decrease in pH. Together with the addition of HCO_3^- from the reactions $CO_2+H_2O \rightarrow H_2CO_3 \rightarrow H^+ + HCO_3^-$, the combination of new H^+ with CO_3^{--} to make still more HCO_3^- causes a reduction in the CO_3^{--} component of alkalinity and allows both Ca^{++} and alkalinity to reach high values without precipitation.

As a result the fluids in the internal spaces of pellets or skeletal fragments are in a condition favoring precipitation and induration whenever they may be introduced to an environment of higher pH and CO_3^{--} fraction, as by being transferred to the sea floor by burrowing organisms, by stirring up of bottom sedi-

---

[15] From available data, the amount of magnesium actually tied up in chlorophyll appears to be infinitesimal in comparison with that in the sea. Revelle and Fairbridge (1957, p. 241) estimate 3.4×10^{11} metric tons of living and 26×10^{11} of dead organic matter on earth. Willstätter and Stoll (1928, p. 14, 16) indicate that fresh leaves contain about 2 g per kg of chlorophyll and that 4.5 percent of this is MgO. To get some impression of the possible order of magnitude for the magnesium tied up in plant matter on earth, take these estimates, assume that two-thirds of the organic matter is plant, and suppose that there might be 1 part per thousand chlorophyll in living, 1 part per ten thousand in dead plant matter. This gives 240×10^6 metric tons of magnesium, which is 2 to 3 times the annual addition of magnesium to the sea but only about 6 to 9 millionths of the total magnesium in the sea. However, at a state near saturation, a very slight total increase in one component could be significant for the reactions involved, especially allowing for nonuniform introduction.

ments, or by creation of local and temporary microenvironments of high pH by bacterial evolution of ammonia.

Any lateral movement of interstitial waters toward the bank margins would also carry the components of $CaCO_3$ with it. Where waters of such high calcium and alkalinity migrate into higher pH levels, the increase in the CO_3^{--} fraction of the alkalinity as a result of loss of H^+ by HCO_3^- ions would favor precipitation. Increase toward the bank margin of aragonitic induration of the solidified and shiny-surfaced pellets and algal fragments, and aragonitic cementation of grapestone clusters of pellets and other grains, indicates that some $CaCO_3$ precipitation does take place within the sediments there. Probably some of this is simple local transfer, or loss from more normal calcium-saturated interstitial waters, but some also may be due to lateral movement within the sediments.

Regardless of details, bacteria evidently do play a significant part in the mobilization and internal transfer of $CaCO_3$ within the sediments, and possibly, under propitious conditions, in sediment consolidation.

By generation of gas, bacteria may also help to explain some of the unusual patterns of clear calcite, false "algal," or birdseye structures and burrowlike markings that have puzzled students of carbonate rocks (Cloud, 1960). Figure 42 shows a common pattern in the making. Gas bubbles began to grow through accretion in the sediment and against the side of the transparent plastic liner shortly after the core was collected and stoppered. Within 2 weeks a pattern of tracks like that illustrated had been produced, with water-filled spaces where the gas congregated and then moved up. After a month, tracing paper was wrapped around the core barrel and the approximate pattern copied directly. The presence in rocks of crystalline-calcite fillings of former fluid- or gas-filled spaces of this nature, compaction distorted or otherwise, is to be expected. Diagenetic effects of gas trackways made without creating open spaces include flushing of organic fines and chemical reduction. Lack of textural variation or textural variation of a secondary nature, their irregularity, and the concentration in them of pyrite or other minerals indicative of reaction with gases, should help in distinguishing gas passageways from simple animal burrows; but preexisting burrows may also tend to channel sediment gases.

The tendency of bacteria to adhere to surfaces (thigmotaxy) may also provide a means of building some types of ooids, through accretion of successive layers by aggregation of sedimentary particles around successive slimy or gelatinous bacterial sheaths surrounding the initial nucleus. This possibility needs further study.

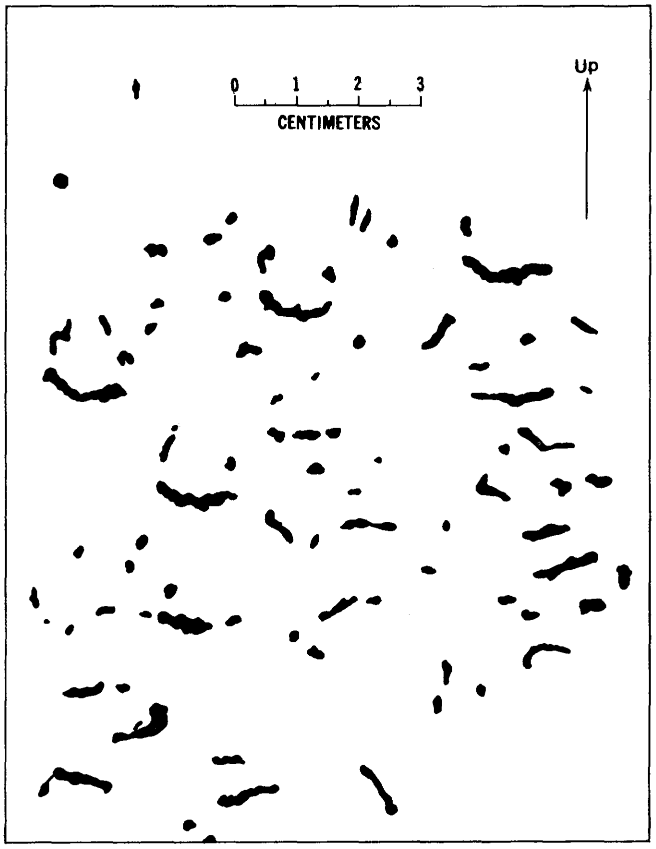


FIGURE 42.—Vertical section of spaces formed by gas generation in aragonite mud from station *It'* during first month after collecting.

The work of the pellet makers themselves hardly needs further elaboration. The discovery and identification of an important producer of ovoid pellets—*Armandia maculata* (Webster)—has already been described. These little polychaetes, with assistance from others, account for the present appearance and partial grain induration of about 22 percent of the total sediment, by the simple process of constantly ingesting and passing mud, while another 10 percent or more of the sediment represents other forms or fragments of fecal pellets of polychaetes, crustaceans, tunicates, mollusks, and other organisms. In such manner, an aragonite mud that would have eventually become an aphanitic limestone (if not first dolomitized or recrystallized) becomes instead a pelletal limestone. The intestinal juices of the armandias seem to have no special effect on the sediment ingested. The creature is also obviously adapted to life under oxygen-poor conditions.

Movement of soft-bodied organisms through the sediment probably also leaves indefinite-bordered disturbed zones which may get preserved as mottles, borings, or false algal structures in the rock. Vertical downward penetration by shrimp and other crustaceans produces sharp-margined burrows that are particularly susceptible to infilling, preservation, and chemical change of filling sediment. They also leave piles of mixed transferred sediment and their own stringlike to cylindrical, generally incoherent fecal pellets. These if buried without disruption, should produce nests or humps of disorganized material on former burrowed surfaces.

LOSS OF BANK SEDIMENT TO DEEPER WATER, AND RECOGNITION OF DEEP- AND SHALLOW-WATER CARBONATE DEPOSITS

Some loss of bank sediment to deeper water seems inevitable. Indeed the finding of a few grapestone clusters of pellets in the Straits of Florida would be proof that this happens could they not as well have dropped from the former holdfasts of floating sargassum. No individual pellets were found in the straits, and their apparent rarity, together with the extreme rarity of recognizable algal debris there, opens the possibility that some or much of the 30 percent clay-size fraction of the straits sediment was precipitated from overhead. The tiny burrlike spicules of didemnid tunicates such as characterize the silt fraction of the bank muds are also abundant in the silt fraction of some straits samples. Although, however, this might suggest transport of spicules from the normally shallow-water didemnids, Van Name (1930, p. 438) records the bank species *Didemnum candidum* Savigny from "fairly deep water." Miliolid Foraminifera found in some of the straits samples are also of species believed to have a wide depth range (Ruth Todd, oral communication, 1956).

On the other hand, the ratio to chloride of calcium given by a precise analysis from bank-edge station *A1'* is that of ocean waters generally, which in its turn suggests no appreciable calcium loss from the straits water beyond normal withdrawal by the planktonic Foraminifera and algae. If, also, there is any validity to the difference between the radiocarbon value of 0.8 mm per year of wet sediment being accumulated and the estimated 1.1 mm per year precipitated, a considerable volume of aragonite needles is winnowed from bank to straits, and this could be the source of the aragonite needles in the straits sediments.

In any case, the abundant planktonic organisms leave no question that this is an open-sea ooze. The attentive microscopist would have no difficulty in separating its ancient counterparts from bank sediments except for something like a recrystallized coccolith or discoaster ooze (Bramlette, 1958), which should give warning by its associations. The striking apparent absence of planktonic elements from the bank deposits is discussed elsewhere.

SIMILAR DEPOSITS OF THE PAST AND PROBABLE FUTURE OF THE BANK DEPOSITS

To study geologically a modern sediment without considering its possible ancient counterparts and probable geologic future would be unthinkable. In fact, the present work has both strengthened analogies earlier drawn between the deposits investigated and certain aphanitic and pelletal limestones of the past (Cloud and Barnes, 1948, p. 89; 1957, p. 170–172) and emphasized some reservations and probably significant anomalies. Such limestones, wherever found in the past, are suspect of bank, lagoon, or restricted shelf origin under semi-stagnant hypersaline conditions approximating those here described. One obvious exception includes thin limestone interbeds or lenses in associations or with microstructures that suggest pelagic deposition, such as the aphanitic limestones that are locally associated with alternating shale and redeposited graywacke in the Alpine flysch. A more troublesome source of prospective confusion includes the coccolith and discoaster chalks and similar organic "ooze" deposits (Bramlette, 1958). Neither of these, however, should be richly pelletal. In any case, independent evidence of depth and type of deposition should be sought; such as dasycladacean algae or polygonal dessication cracks, indicating very shallow depths and restricted circulation, or pelagic organisms and chemical evidence implying open-sea or relatively deep deposition.

It is probably no accident that aphanitic and pelletal limestones are common among the most ancient rocks, whereas their modern counterparts are hard to find. Rubey (1951) has made a very persuasive case for the essential similarity of sea water through time, yet the arrival of important and persistent calcareous reef-builders did not occur until the Paleozoic era was well under way, and abundant planktonic lime secreting organisms come still later. Until these biologic factors came into play, the primary marine mechanism for dumping excess calcium (from terrestrial erosion) would necessarily have been by direct or biologically induced chemical processes, as earlier suggested by Rodgers (1957, p. 2, 9, 10–11; also in Dunbar and Rodgers, 1957, p. 236). The rarity or absence of silica concentrations in the modern carbonate sediments is probably also related to biological effects.

Another factor limiting the analogy between the deposits west of Andros Island and their supposed ancient counterparts is the thinness of the present deposits. Upon expulsion of its 40 to 70 percent water content the thickest sediment of the present cycle west of Andros Island would be only one or two meters thick, allowing for precipitation from the expelled water. Clearly the site of sedimentation must continue to sink, and to sink at a rate no faster than sedimentation (0.8 mm a year with water, 0.38 without) if a thick deposit of comparable nature is to be formed. The present sediments, if they continue to accumulate on a subsiding platform and are compacted into dense rock (pl. 7*E*, *H*, *I*) should ultimately resemble the limestones of the Ellenburger group (pl. 7*J*, *K*) except for their different fossils and low silica content. If, through cation exchange, all the magnesium contained in their interstitial waters and in solid solution could be combined with calcium as the double carbonate, only about 2 percent of the resulting rock could be dolomitized without further enrichment from circulating sea water, upward expulsion of magnesium-containing waters from older deposits beneath, or recombination with coprecipitated magnesium carbonate. A source of chert is not apparent except in trivial quantities from sponge spicules. The sea water is too impoverished in silica to supply it directly; so it too would have to come by migration from unknown sources below, if at all.

SIGNIFICANCE OF THE DATA FOR CALCIUM CARBONATE EQUILIBRIUM RELATIONS

Calcium carbonate is known to be at stable equilibrium at atmospheric temperature and pressure only in the form of calcite (Jamieson, 1953; MacDonald, 1956). At these same conditions aragonite is unstable, or metastable. Yet the precipitation and persistence of aragonite in sea water responds as if to an equilibrium system.

Thus, to confront the problem of aragonite muds is to confront the problems of the solubility relations of calcium carbonate and of its polymorphism in the solid state; and to consider these together is to realize that, with all their complexities, there are regular and measurable connections between them. The seeming conflict between published values of the apparent solubility product constant for calcium carbonate in sea water essentially disappears when recent estimates are considered separately as they apply to aragonite or to calcite. Qualitatively comparable and quantitatively more meaningful values can be computed in terms of activity product and activity product constant. It becomes evident that there is a regular relation between the mineral species precipitated, its persistence, the apparent solubility and activity product constants for aragonite and for calcite, and the ionic strength and ionic product $Ca^{++} \times CO_3^{--}$ in the parent fluid.

In brief, it appears that precipitation of calcium carbonate from sufficiently highly supersaturated solutions favors the higher free-energy polymorph aragonite; that such supersaturation is more easily attained and more slowly discharged in mixed solutions of increasing concentration up to an ionic strength of about one; and that, in such solutions, a condition of metastable equilibrium with regard to aragonite tends to be approached, beyond which further reaction is infinitely slow. These relations can be and are expressed in thermodynamic terms; but complex-formation and rate-determining factors may be critical, and the balance of processes involved is not conducive to simple all-or-none summation as either thermodynamic or kinetic.

The familiar basic equilibria of the cycle studied are:

$$CO_2 + H_2O \rightleftharpoons H_2CO_3$$

$$H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$$

$$HCO_3^- \rightleftharpoons H^+ + CO_3^{--}$$

$$2HCO_3^- \rightleftharpoons CO_2 + H_2O + CO_3^{--}$$

$$Ca^{++} + CO_3^{--} \rightleftharpoons CaCO_3$$

The values which it is sought eventually to quantify are the activity products $aCa^{++} \times aCO_3^{--}$ calcite and $aCa^{++} \times aCO_3^{--}$ aragonite, and the activity product constants $K_{calcite}$ and $K_{aragonite}$. Methods and data for attempting even roughly to approximate such values, however, have only recently become available, and standard oceanographic procedure employs a different technique to compute an empirical concentration product $cCa^{++} \times cCO_3^{--}$ and apparent solubility product constant K'_{CaCO_3}.

In the immediately following pages the empirical parameters are summarized; illustration is given of the computation of the apparent solubility product constant and some other values of interest according to conventional oceanographic procedures; and the results of the empirical method are interpreted. Then the estimation of the activity product is discussed; the results of the two methods are compared and evaluated; and questions of solubility relations and solid state polymorphism are considered. Where comparison is made between the different products computed, *c* indicates empirical concentration (oceanographic method), *m* indicates stoichiometric mass (comparable to *c* but involving an intermediate step toward *a*), and *a* indicates activity. It will become evident as the discussion proceeds that the empirical values take account of some activity factors in their own way.

ESTIMATION OF THE EMPIRICAL PARAMETERS

The objective here is to compute the ionic product $Ca^{++} \times CO_3^{--}$ for particular water samples, to estimate the apparent solubility product constant K'_{CaCO_3}, and to interpret the results. The apparent solubility

TABLE 35.—*Main steps in computation of empirical solubility relations*

Station	T° C* Field above (analytical below)	Cl^-† (g/l)	Chlorinity (°/₀₀ at 20° C)	Salinity (°/₀₀ at 20° C)	Ionic strength in moles/l ($\sqrt{\mu}$ beneath)	ΣB^{+++} (mg-atom/l)	K'_B $\times 10^9$	A_t‡ Titration alkalinity (me/l)	A_c Carbonate alkalinity (me/l)	A_t' Theoretical alkalinity (me/l)	pH§ Field above (analytical below)	$a\mathrm{H}^+$ $\times 10^9$	$\alpha 0$ (mole/l)
A1' (1956 surface sample)	28.00 (26.60)	20.41	19.93	36.00	0.739 (0.860)	0.42	2.40	2.44	2.32	2.45	8.20 (8.22)	6.31	0.0314
It' marginal to whiting (1956 surface sample)	29.50 (26.60)	23.77	23.12	41.76	0.858 (0.926)	.51	2.79	2.44	2.32	2.85	8.04 (8.15)	9.12	.0303
It' whiting (1956 surface sample)	29.50 (26.60)	23.80	23.15	41.82	0.863 (0.929)	.51	2.80	2.02	1.89	2.86	8.10 (8.05)	7.94	.0303
B3 (1955 sample, Ca det. 1956)	28.00 (31.00)	26.00	25.25	45.61	0.927 (0.963)	.55	2.78	1.78	1.66	3.12	8.00	10.0	.0310
B4 (1955 sample, Ca det. 1956)	28.00 (27.00)	24.30	23.63	42.68	0.874 (0.935)	.51	2.69	1.84	1.73	2.92	8.00	10.0	.0310
C7 (1955 sample, Ca det. 1956)	29.25 (31.00)	26.60	25.80	46.60	0.977 (0.988)	.58	3.02	1.78	1.65	3.19	8.00	10.0	.0305

*Field values are used in computing apparent dissociation constants and in converting product $Ca^{++} \times CO_3^{--}$ to standard temperatures. Laboratory values affect only conversion from volume to weight basis, and pH and ionic strength insignificantly. All computations are made on volume basis and conversion to weight is made at the last from specific gravity. Variations in intermediate steps as well as the final conversion are within experimental error.

†Cl^-g/l is at analytical temperature. It is *not* chlorosity which is mg/l at 20° C.

‡*B3*, *B4*, and *C7* are average of field and laboratory values, which agree within 2 percent, others are laboratory values (no field values having been read). It is assumed, as explained in the text, that pH changes from field to laboratory represent movement of carbonate equilibria to the left, without appreciable change in total alkalinity. This would not affect Ca, except to suggest some postsampling precipitation at *It'* only, which would not affect the validity of the computed ionic product.

product constant empirically identifies the approximate ionic concentrations of analytical calcium and computed carbonate above which precipitation is likely and below which solution of the mineral species involved will occur at particular conditions of temperature, salinity, and pressure.

Procedures employed assume atmospheric pressure and utilize as basic data field determinations of temperature, pH, chloride, and alkalinity, supplemented by laboratory analyses of calcium and boron. Other analytical data supplement and check the field values, and boric acid correction is feasible without analysis, but this framework is otherwise essential to the method.

The rather tedious computations have been discussed at length by a series of authors from the 1930's onward (Buch and others, 1932; Moberg and others, 1934), but most recently in an as yet unpublished Scripps Institution thesis by James C. Hindman (1943). The usual procedures are also summarized by Harvey (1955, p. 153–182) and by Sverdrup and others (1942, p. 192–210).

It is necessary here, therefore, only to present the results of the computations (table 35) and to state what they signify and how they were obtained.

DEFINITIONS AND PROCEDURES

The definitions and procedures, in the order in which the values appear in table 35, are as follows:

T Centigrade temperature; measured in duplicate with standard mercury thermometers calibrated to degrees and read to nearest 0.5° before averaging.

Cl^- mg/l Titration chlorosity; determined with $AgNO_3$, using K_2CrO_4 indicator.

Cl^- °/₀₀ Chlorinity=Cl^- mg/l÷specific gravity at 20°C (Sverdrup and others, 1942, p. 52).

S°/₀₀ Salinity=Cl^- °/₀₀×1.805+0.03 (Sverdrup and others, 1942, p. 51).

μ Ionic strength in moles/l; computed from the relation $\mu = \Sigma 1/2 c_i z_i^2$, where c_i is the concentration of each ion in moles/l and z_i its valence. In fact it was found that these figures check to the second decimal place with those based on chloride ratio (Sverdrup and others, 1942, p. 205) except at station *B3*. where the latter gave a value 0.022 above that listed here. As $\sqrt{\mu}$ is used in computation, it is listed parenthetically below the μ values in table 35.

ΣB Total boron; determined colorimetrically by Kramer, using carminic acid, as described on p. 73.

K'_B* Apparent boric acid dissociation constant. Computed from relation $pK'_B = 9.28 - 0.639\sqrt{\mu}$ at 20°C, corrected by −0.014 per °T increase from 20° to 30°C (Hindman, 1943, p. 82, 129; as modified from Buch, 1933).

A_t Titration alkalinity (the sum of HCO_3^-, CO_3^{--}, and other Brønsted bases, expressed in milliequivalents per liter); determined by potentiometric titration to pH 4.5 with 0.02N H_2SO_4 or HCl.

A_c Carbonate alkalinity as computed from—

$$A_c = A_t - \frac{K'_B \cdot \Sigma B}{a\mathrm{H}^+ + K'_B}$$ (C. L. Smith, 1941, p. 236; Harvey, 1955, p. 165–166).

---

*See footnote on page 114.

of calcium carbonate in selected water samples ||

$a\,H_2O$	P_{CO_2} $X10^3$	ΣCO_2 (mmole/l)	cCO_3^{--} (mmole/l)	cCa^{++} (mg-atom/l)	$Ca^{++}\times CO_3^{--}\times 10^6$					ΔCO_2 mmole/l	Apparent precipitation of $CaCO_3$ at field salinity (mg/l)—		$K_1'\times 10^6$ $\frac{aH^+\times cHCO_3^-}{cH_2CO_3}$	$K_2'\times 10^9$ $\frac{aH^+\times cCO_3^{--}}{cHCO_3^-}$
					At computed T and S (per liter)	At salinity 36 °/₀₀—					From alkalinity	From Ca		
						Per liter		Per kilogram						
						30° C	20° C	30° C	20° C					
0.981	0.34	2.03	0.29	[1] 10.85	3.15	2.97	3.91	2.90	3.81	None	None	None	1.04	1.05
.978	.51	2.06	.26	[1] 11.90	3.09	1.86	2.45	1.81	2.38	0.16	20	59	1.09	1.29
.978	.35	1.66	.23	[1] 12.23	2.81	1.68	2.22	1.63	2.15	.31	42	84	1.09	1.30
.976	.39	1.48	.18	[2] 13.18	2.37	.98	1.28	.95	1.24	.52	67	48	1.10	1.40
.977	.42	1.55	.18	[2] 12.13	2.18	1.16	1.53	1.13	1.48	.43	54	64	1.07	1.29
.975	.37	1.46	.19	[2] 13.30	2.53	.99	1.30	.96	1.26	.54	72	67	1.13	1.52

[1] Ca^{++} gravimetric, triple precipitate with ammonium oxalate corrected for Sr^{++} (Ba^{++} inconsequential); differences from duplicate determinations by the Carpenter method are 0.1 and 0.4 percent.

[2] Ca^{++} by ion-exchange photometric titration using EDTA (method of James Carpenter).

§Field pH is used in all computations.

|| Note that the sign of exponential values of 10 changes from column head to entry: $Ca^{++}\times CO_3^{--}\times 10^6=0.99$ is equivalent to $Ca^{++}\times CO_3^{--}=0.99\times 10^{-6}$

A_t' Theoretical A_t; computed from the ratio $\frac{A_t}{Cl^-\ gm/l}=0.12$, as found in oceanic and in Straits of Florida waters.

pH* Negative logarithm to base 10 of hydrogen ion concentration in g/l. Measured potentiometrically, using glass and calomel 5-inch external electrodes with Beckman pH meter Model G2, calibrated against buffer solutions at U.S. Bureau of Standards scale.

aH^{+*} Hydrogen ion activity; $pH=-\log H^+=-\log aH^+$ (assuming concentration $H^+=$activity H^+).

αo Solubility of CO_2 in moles/l in pure water at temperature of reaction and pressure of one atmosphere; from Bohr's data (*in* Harvey, 1955, p. 168; or Buch, 1951, p. 14).

aH_2O $1-(9.69\times 10^{-4}\times Cl^-\ °/_{oo})$; according to Harvey (1955, p. 169).

P_{CO_2} Partial pressure of CO_2 in °/₀₀

$$=\frac{A_c\cdot aH^+}{K'_1\alpha o\left(1+\frac{2K'_2}{aH^+}\right)aH_2O}$$

The equation is from Harvey (1955, p. 172).

ΣCO_2 "Total CO_2"$=A_c\cdot\frac{aH^++K'_2}{aH^++2K'_2}$ (Moberg and others, 1934, p. 237) and ΣCO_2+cCO_3 must equal A_c.

cCO_3^{--} Computed concentration of CO_3^{--} $=\frac{A_c\cdot K'_2}{aH^++2K'_2}$ (Harvey, 1955, p. 173).

cCa^{++} Analytical concentration of calcium, assumed to be all calcium ion. Determined gravimetrically by triple precipitation with $(NH_4)_2C_2O_4$ as described on page 73, or, for underlined values, by photometric titration with EDTA, after isolation of calcium in distilled water by means of ion exchange resins as described on page 75.

$cCa^{++}\times cCO_3^{--}$ The apparent ionic product at atmospheric pressure, and at temperature and salinity of solution (not the apparent solubility product constant K'_{CaCO_3}), there being a correction to the log of -0.012 per degree increase T (Hindman, 1943, p. 129) and -0.038 for each 1°/₀₀ decrease in salinity (Wattenberg, 1933). Minimal values of the ionic product should approach K'_{CaCO_3}.

ΔCO_2 Evaded free $CO_2=\Sigma CO'_2-\left(\frac{A'-A}{2}+\Sigma CO_2\right)$, where $\Sigma CO'_2$ is theoretical ΣCO_2 computed from theoretical alkalinity reduced to the carbonate equivalent A'_c (C. L. Smith, 1940, p. 177). The symbols A' and A in the parenthetical term, for theoretical and actual alkalinity, can represent either titration or carbonate alkalinities; but here they are carbonate alkalinity.

Apparent precipitation $CaCO_3$—

From alkalinity, $\frac{A'-A}{2}\times$mol. wt $CaCO_3=$ $CaCO_3$ mg/l

---

*See footnote on page 114.

From calcium, 2.5 $\left[0.02106 \text{ Cl}^- \text{ mg/l} - \text{at. wt Ca} \left(\frac{A_t}{2} + 0.465 \text{ Cl}^- \text{ mg/l}\right)\right]$, 2.5 being the ratio mol. wt $CaCO_3$÷at. wt Ca

K'_1* Apparent first dissociation constant of carbonic acid. Computed from the relation $pK'_1 = 6.380 - 0.392\sqrt{\mu}$ at 20°C, corrected by −0.006 per °*T* increase from 20° to 25°C and −0.005 from 25° to 30°C (as modified from Buch and others, 1932, by Hindman, 1943, p. 27, 129).

K'_2* Apparent second dissociation constant of carbonic acid. Computed from the relation $pK'_2 = 10.048 - 1.189\sqrt{\mu}$ at 20°C, corrected by −0.006 per °*T* increase 20° to 30°C (as modified from Buch, 1938, by Hindman, 1943, p. 27, 129).

ILLUSTRATION OF THE METHOD

To illustrate the method by which a particular ionic product is estimated, the computation of values for station *C7* follows.

1. Temperature, titration chlorosity, chlorinity, salinity, ΣB, A_t, pH, and Ca^{++} are determined instrumentally, analytically, or by simple conversions as indicated above.
2. $\mu = 0.977$ and $\sqrt{\mu} = 0.988$

   $\mu = \Sigma 1/2 c_i z_i^2$; take calcium value determined by ion-exchange photometric titration and other analytical data from table 25, divide grams per liter by atomic or molecular weight to get moles per liter, multiply each mole/l value by the square of the valence, sum up, divide by 2, and extract square root to get values above.

3. $$K'_B = \frac{1}{pK'_B}$$

   $pK'_B = 9.28 - 0.639\sqrt{\mu}$ at 20°C

   $= 9.28 - (0.639 \times 0.988) = 9.28 - 0.63 = 8.65$ at 20°C

   Subtracting for *T* coefficient $0.014 \times 9.25 = 0.13$

   $8.65 - 0.13 = 8.52$ at 29.25°C

   $$K'_B = \frac{1}{10^{8.52}} = 10^{-8.52} = \text{antilog } 0.48 \times 10^{-9} = 3.02 \times 10^{-9}$$

4. pH=8.0

   $$aH^+ = \frac{1}{10^8} = 10^{-8} = 10 \times 10^{-9}$$

5. $$A_c = A_t - \frac{K'_B \cdot \Sigma B}{aH^+ + K'_B}$$

   $$= 1.78 - \frac{3.02 \times 10^{-9} \times 0.58}{(10 \times 10^{9}) + (3.02 \times 10^{-9})}$$

   $$= 1.78 - \frac{1.75 \times 10^{-9}}{13.02 \times 10^{-9}}$$

   $= 1.78 - 0.13 = 1.65$

6. $\alpha o = 0.0305$ at *T* 29.25°C, from Bohr's data in Harvey (1955, p. 168).
7. $aH_2O = 1 - (9.69 \times 10^{-4} \times Cl^- ‰)$

   $= 1 - (9.69 \times 10^{-4} \times 25.8) = 1 - 0.025 = 0.975$

8. $$K'_1 = \frac{1}{pK'_1}$$

   $pK'_1 = 6.380 - 0.392\sqrt{\mu}$ at 20°C

   $= 6.380 - (0.392 \times 0.988) = 6.380 - 0.383 = 5.997$ at 20°C

   Subtracting for *T* coefficient $(0.006 \times 5) + (0.005 \times 4.25) = 0.051$

   $5.997 - 0.051 = 5.946$ at 29.25°C

   $$K'_1 = \frac{1}{10^{5.946}} = 10^{-5.946} = \text{antilog } 0.054 \times 10^{-6} = 1.13 \times 10^{-6}$$

9. $$K'_2 = \frac{1}{pK'_2}$$

   $pK'_2 = 10.048 - 1.189\sqrt{\mu}$ at 20°C

   $= 10.048 - (1.189 \times 0.988) = 10.048 - 1.175 = 8.873$

   Subtracting for *T* coefficient $0.006 \times 9.25 = 0.056$

   $8.873 - 0.056 = 8.817$ at 29.25°C

   $$K'_2 = \frac{1}{10^{8.817}} = 10^{-8.817} = \text{antilog } 0.183 \times 10^{-9} = 1.52 \times 10^{-9}$$

10. $$P_{CO_2} \times 10^{-3} = \frac{A_c \cdot aH^+}{K'_1 \alpha o \left(1 + \frac{2K'_2}{aH^+}\right) a\,H_2O}$$

    $$= \frac{1.65 \times 10 \times 10^{-9}}{1.13 \times 10^{-6} \times 0.0305 \times \left(1 + \frac{2 \times 1.52 \times 10^{-9}}{10 \times 10^{-9}}\right) \times 0.975}$$

    $$= \frac{16.5 \times 10^{-9}}{0.0345 \times 10^{6} \times (1.304) \times 0.975}$$

    $$= \frac{16.5 \times 10^{-9}}{0.0439 \times 10^{-6}} = \frac{16.5}{43.9} = 0.376$$

11. $$\Sigma CO_2 \text{ mmole/l} = A_c \cdot \frac{aH^+ + K'_2}{aH^+ + 2K'_2}$$

    $$= 1.65 \, \frac{(10 \times 10^{-9}) + (1.52 \times 10^{-9})}{(10 \times 10^{-9}) + (3.04 \times 10^{-9})}$$

    $$= 1.65 \, \frac{11.52}{13.04} = 1.65 \times 0.883 = 1.46$$

---

*Hindman's modifications are to allow for a difference of −0.04 units from U.S. Bur. Standard pH scale used by him (and this report) to the Sørenson scale employed by Buch, C. L. Smith, and others. The symbols pK', pH, and similar factors of p are the negative logarithms of the values K', H^+, and corresponding variables to the base 10. Their use avoids negative numbers and exponents, but it must be remembered (a) that they are exponential to 10 and (b) that they are reciprocal to the true value represented.

12. cCO_3 mmole/l$=\frac{A_c\cdot K'_2}{aH^{+}+2K'_2}$

$$=\frac{1.65\times 1.52\times 10^{-9}}{(10\times 10^{-9})+(3.04\times 10^{-9})}$$

$$=\frac{2.51}{13.04}=0.192$$

And $0.19+1.46=1.65$; so $cCO_3+\Sigma CO_2=A_c$

13. $\Sigma CO'_2$ mmole/l=theoretical carbonate alkalinity
$A'_c\times 0.883$ (from 11 above)
$A'=0.12\times Cl^-$ gm/l
$A't=0.12\times 26.6=3.19$
$A'c=3.19-0.13$ (from 5 above)$=3.06$
$\Sigma CO'_2=3.06\times 0.883=2.70$

14. ΔCO_2 mmole/L$=\Sigma CO'_2-\left(\frac{A'-A}{2}+\Sigma CO_2\right)$

$$=2.70-\left(\frac{3.06-1.65}{2}+1.46\right)$$

$$=2.70-2.16=0.54$$

15. Apparent $CaCO_3$ precipitation—
From alkalinity, $1/2\ A'-A\times 100=50\times(3.19-1.78)=70$ mg/l

From calcium, $2.5\left[0.02106\ Cl^-\ \text{mg/l}-\text{at. wt Ca}\left(\frac{A_t}{2}+0.465\ Cl^-\ \text{mg/l}\right)\right]$

$$2.5\left[(0.02106\times 26{,}600)-40.08\left(\frac{1.78}{2}+12.37\right)\right]$$

$$2.5\ (560.2-531.5)=72\ \text{mg/l}$$

16. cCa^{++} converted to 13.30 mg-atoms/l; from ion-exchange photometric titration by James Carpenter, assuming all analytical calcium as calcium ion.

17. $cCa^{++}\times cCO_3^{--}$ (moles per liter)$=(13.30\times 10^{-3})\cdot(0.19\times 10^{-3})=2.527\times 10^{-6}$ at 29.25°C and 46.6‰ S

Convert to value at 36‰ S by applying a correction to the log of -0.038 for each ‰ salinity decrease.

Log $25.27\times 10^{-5}=1.40261\times 10^{-5}$, and -0.038×10.6‰ $S=-0.4028$.

Applying correction, $1.40261-0.4028=0.99981$.

For values at 30°C, 25°C, and 20°C adjust log above by -0.012 per °C increase.

T correction to log at 30°C is -0.009, at 25°C $+0.051$, and at 20°$+0.111$.

Applying to logs gives 0.99081, 1.05081, and 1.11081×10^{-5}.

Converting to antilogs and values$\times 10^{-6}$ gives:
at 30°C=0.98, at 25°C=1.12, and at 20°C=1.29, all at salinity of 36‰

INTERPRETATION OF THE EMPIRICAL RESULTS

Chemical reactions, once started, tend to move with progressive loss of energy toward a state of equilibrium or metastable equilibrium for the existing conditions of temperature, pressure, and other variables of the system. The sluggish bank water at inshore sites of maximal apparent calcium loss or minimal alkalinity values, therefore, should approach such a state with reference to $CaCO_3$. From this it follows that the computed ionic product $cCa^{++}\times cCO_3^{--}$ at these sites should approach the desired apparent solubility product constant K'_{CaCO_3} for the mineral form being precipitated (at the existing values of the important variables). Assuming this, the computed value of K' at atmospheric pressure can be converted to any reference conditions of temperature and salinity at which it is desired to make comparisons, by applying corrections as illustrated in the preceding section. It is at least certain that this K' cannot be lower than the "equilibrium" K' for the pertinent mineral form. And, from correspondence of field and experimental values, the figure here found probably approaches a minimum and therefore the value sought for $K'_{aragonite}$.

In order to estimate this $K'_{aragonite}$, precise calcium determinations were obtained on 1955 bank stations *B3*, *B4*, and *C7*, where large calcium losses were indicated and where alkalinity values were low. Bank-edge water from 1956 Station *A1'* was computed for reference purposes, and waters from and marginal to the whiting at *It'* out of curiosity.

Sample *C7* shows excellent correlation of theoretical calcium values, which is taken to confirm the significance of the apparent ionic product $Ca^{++}\times CO_3^{--}$. Precise correspondence is observed between the ionic products here and at *B3*, also believed accurate, although without such good confirmation from estimated calcium losses.

These results indicate K'_{CaCO_3} for the solid phase aragonite at a salinity of 36‰ to be 0.98×10^{-6} at 30°C, 1.12×10^{-6} at 25°C, and 1.29×10^{-6} at 20°C, all on a moles-per-liter basis (tables 35, 36). Within the limits of the method, this is the same value as was obtained by Hindman (1943, p. 131) upon recomputing C. L. Smith's 1941 results from sea-water experiments to allow for differences in pH scale and the second dissociation constant of carbonic acid. Hindman's own value for aragonite (table 36) is based on conversion from the identical values for calcite obtained by himself and by Wattenberg and Timmerman (1936, p. 25), using the free-energy difference of −273 calories estimated by Kelley and Anderson (1935, p. 15). At 25°C and atmospheric pressure, which is the conventional reference state, this gives the relation $K'_{aragonite} \div K'_{calcite} = 1.59$, whereas the present results give the relation $K'_{aragonite} \div K'_{calcite} = 1.84$.

Now, from standard physical chemistry (for example, Latimer, 1952, p. 8–9), the standard free energy of reaction at unit concentration is given by the expression $\Delta F^{\circ}_{reaction} = -RT \ln K$, which at atmospheric pressure and T 25°C $= -1.3643 \log K$ in kilocalories per mole. For purposes of approximate quantitive comparison let $K' = K$. From table 36, $K'_{aragonite}$ is 1.12×10^{-6} and $K'_{calcite}$ is 0.61×10^{-6}, figured as moles per liter in sea water of salinity 36°/oo at 25°C. Then $\Delta F^{\circ}_{reaction}$ for aragonite $= -1.3643 \log 1.12 \times 10^{-6} = -1.3643\ (-6\text{-}\log 1.12) = 1.3643\ (6 - 0.04922) = 8.119$ kilocalories per mole; and $\Delta F^{\circ}_{reaction}$ for calcite $= -1.13643 \log 6.1 \times 10^{-7} = -1.3643\ (-7\text{-}\log 6.1) = 1.3643\ (7 - 0.78533) = 8.478$ kilocalories per mole (plus or minus perhaps 20 or 30 calories).

The standard free-energy difference for the transition from aragonite to calcite according to these figures is thus roughly −360 calories per mole. This compares with a range of published values at 25°C from −190 to −414 cal/mole, or, admitting only post-1950 values, −250 to −334.[16] The approximate agreement between the present results and these recent experimental values for free energy difference lends credibility to the estimated values of $K'_{\mathrm{CaCO_3}}$ for aragonite and for calcite.

Present results, therefore, confirm Smith's perceptive work and Hindman's painstaking revision of it. Related findings of other than historic significance are given in table 36, where it is shown that within themselves the best K' values computed from original data for calcite and for aragonite are not discrepant.

TABLE 36.—*Reported values of apparent solubility product constant for calcite and aragonite, converted to 36 parts per thousand salinity (equivalent to 19.9 parts per thousand chloride ion or ionic strength of 0.74) at atmospheric pressure.*

Reference [1]	Value × 10^{-6}					
	Moles per kilogram			Moles per liter		
	30°C	25°C	20°C	30°C	25°C	20°C
Calcite:						
Wattenberg and Timmerman (1936, p. 25	0.52	0.60	0.69	0.53	0.61	0.71
Hindman (1943, p. 131)	.52	.60	.69	.53	.61	.71
Aragonite						
C. L. Smith (1941, p. 240)	1.13	1.30	1.49	1.16	1.33	1.53
Hindman's revision (1943, p. 131) of Smith's 1941 value to correct for difference in pH scale and pK'_2	.96	1.10	1.27	.99	1.13	1.30
Hindman, 1943, p. 132 (by conversion from his value for calcite, using ΔF° difference of −273 calories)	.83	.95	1.09	.85	.97	1.12
Present paper	.95	1.09	1.26	.98	1.12	1.29

[1] Conversion to 20°C and 25°C from published values at 30°C based on T correction to the log of +0.012 per °C decrease.

It is of interest now to inspect the relation to increasing chloride of the empirical product $c\mathrm{Ca}^{++} \times c\mathrm{CO_3}^{--}$ and its ratio to chloride. Figure 43 shows the computed ionic product before adjustment to standard temperature and salinity. Both the ion product and its ratio to chloride show a general and nearly parallel, but strongly asymmetrical, decrease with increasing chloride. When the same data are converted to their apparent values at 25°C and 36°/oo salinity (μ0.74), their distribution becomes more symmetrical (fig. 44). Indeed, strikingly regular curves can be drawn between the four samples which from their chemistry and field relations might be expected to approach a state of balance. Slightly above these curves are the two samples which chemical and field evidence suggests could be out of phase with the general reaction cycle, or which could mark a flexure in it. If the curves in figure 44 approximate the precipitation curve, they mean either that it proceeded from about 200 percent supersaturation for aragonite (450 percent for calcite) at Station *A1* to near metastable equilibrium at *B3* and *B7*, or that there is some still obscure relation between the reaction and chloride or ionic strength.

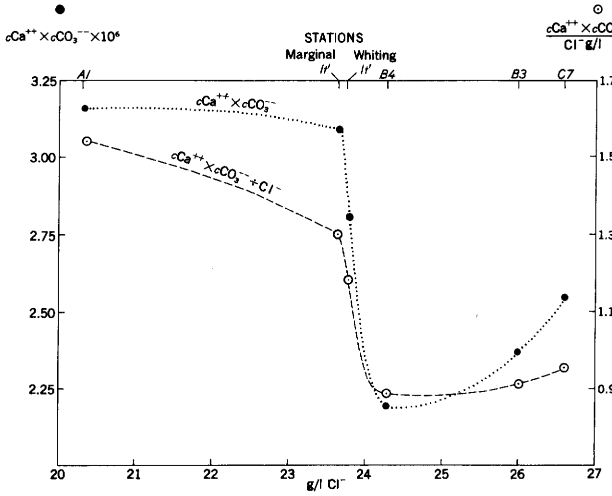


FIGURE 43.—Relation to changing chloride of unadjusted empirical $c\mathrm{Ca}^{++} \times c\mathrm{CO_3}^{--}$, and its ratio to chloride, for water samples with presumably accurate calcium determination.

---

[16] Bäckström (1925, p. 2442) found −190 from heat-capacity studies; Buchan (1927a, p. 671) got −414 from electrometric cell measurements (and, 1927b, p. 675, −380 cal/mole at 18°C from lattice energy considerations); Kelley and Anderson (1935, p. 15) calculated −273 from entropy and specific-heat differences; Kobayashi (1951, p. 116–118) found −311 ±23 from heat capacity studies; Latimer (1952, p. 320) calculated −250; and Jamieson (1953, p. 1389) confirmed the results of Kelley and Anderson with a figure of −272.5 ±3 from electrical conductivity studies.

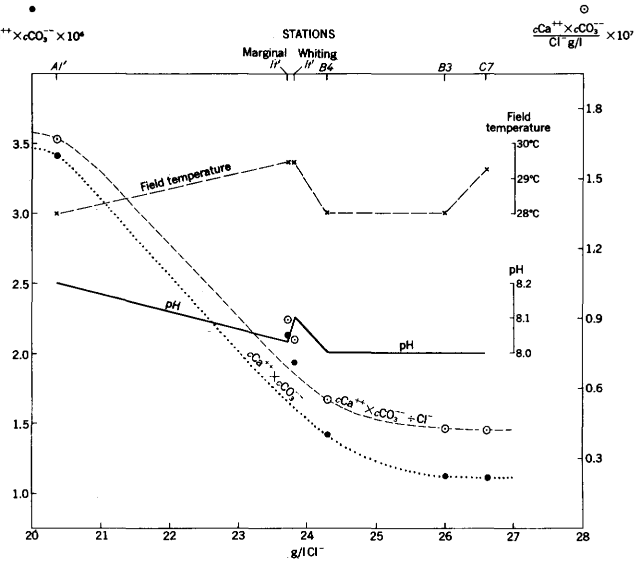


FIGURE 44.—Relation to changing chloride of empirical $c\mathrm{Ca}^{++} \times c\mathrm{CO}_3^{--}$, and its ratio to chloride, for same samples as in figure 43; but with ionic products converted to apparent values at 25°C and 36°/₀₀ salinity (at atmospheric pressure).

ESTIMATION OF THE ACTIVITY PRODUCT

THE PROBLEM

It is shown above that computed values for the empirical ionic product $c\mathrm{Ca}^{++} \times c\mathrm{CO}_3^{--}$ and for K'_{CaCO_3} are consistent among themselves. This is useful enough, as long as we are interested only in relative conditions, but K'_{CaCO_3} for sea water changes with salinity and is several orders of magnitude larger than the activity product constant K_{CaCO_3} for the pertinent mineralogical species in simple solutions.

If, as is often stated, the reactions involved really obey the law of mass action, then, at a particular temperature and pressure, solubility relations should be expressible by a true numerical constant K, which will not vary with ionic strength (and, in effect, pH) as does K', provided the determining variables are properly accounted for. Except at infinite dilution, moreover, the analytical or stoichiometric concentrations of an ionized compound are not a suitable measure of its effective concentration. To estimate this, it is necessary to know also the activity coefficients (γ), which decrease with increasing ionic strength in the range and for the ions here considered.

When the stoichiometric product $m\mathrm{Ca}^{++} \times m\mathrm{CO}_3^{--}$ is multiplied by the appropriate activity coefficients ($\gamma\ \mathrm{Ca}^{++} \cdot m\mathrm{Ca}^{++}) \times (\gamma\ \mathrm{CO}_3^{--} \cdot m\mathrm{CO}_3^{--}$), the activity product $a\mathrm{Ca}^{++} \times a\mathrm{CO}_3^{--}$ is obtained. Assuming, then, that the natural system west of Andros Island at some times and places approaches something resembling equilibrium with regard to CaCO_3, minimal values there found for the activity product should approach $K_{aragonite}$. Inasmuch, also, as the stoichiometric concentration of calcium is given by analysis, and carbonate can be estimated in alternative ways that give closely comparable results (p. 113), the problem revolves around the estimation of activity coefficients—a yet unsatisfactorily resolved matter. Activity relations in electrolytic solutions cannot at present be computed with confidence above the very low ionic strengths to which Debye-Hückel theory applies (Garrels, 1960, p. 27–30, 39–40; Klotz, 1950, p. 328–336). The absence of a rigorous method, however, does not eliminate the geological and oceanographic problem. Therefore, with advance apologies to the pure solution chemists for the unwarranted assumptions and inelegant methods employed, let us see what results can be obtained at the salinity of sea water. Whether they be credible or not, estimates for $\gamma\ \mathrm{Ca}^{++}$ and $\gamma\ \mathrm{CO}_3^{--}$ can be made either by assuming applicability of the Debye-Hückel approximations or by the mean-salt method (Garrels, 1960, p. 25–27), and for $\gamma\ \mathrm{CO}_3^{--}$ also by the empirical method outlined by Sverdrup and others (1942, p. 204–205).

It happens, when this is done, that the mean-salt values and Debye-Hückel second approximation values for $\gamma\ \mathrm{Ca}^{++}$ at the ionic strengths involved are roughly comparable (0.26 compared with 0.21 at station *C7*, for instance). On the other hand, the mean-salt value for $\gamma\ \mathrm{CO}_3^{--}$ is about three times that obtained from the Debye-Hückel first approximation and gives an activity product CaCO_3 correspondingly larger than the values listed in table 37. The mean-salt method for $\gamma\ \mathrm{CO}_3^{--}$ is therefore rejected because suitable data are lacking at the salinities in question, and because a back computation assuming partial pressure of CO_2 in equilibrium with the atmosphere supports the essential validity of $\gamma\ \mathrm{CO}_3^{--}$ obtained from the Debye-Hückel first approximation. Why the latter computation should give such reasonable results for so easily complexed an ion (Garrels and others, 1959) is not clear.

The product $(\gamma\ \mathrm{Ca}^{++}\ .\ m\mathrm{Ca}^{++}) \times (\gamma\ \mathrm{CO}_3^{--}\ .\ m\mathrm{CO}_3^{--})$ obtained using either Debye-Hückel values for $\gamma\ \mathrm{Ca}^{++}$ and $\gamma\ \mathrm{CO}_3^{--}$ or mean-salt $\gamma\ \mathrm{Ca}^{++}$ in combination with Debye-Hückel $\gamma\ \mathrm{CO}_3^{--}$ reaches a minimal value at station *C7*, and this value closely approaches K_{CaCO_3} for the solid phase aragonite as given by Latimer (1952, p. 319). Thus Latimer gives 6.9×10^{-9} at 25°C, Debye-Hückel results at *C7* are 6.2×10^{-9}, and Debye-Hückel $\gamma\ \mathrm{CO}_3^{--}$ combined with mean-salt $\gamma\ \mathrm{Ca}^{++}$ gives 7.8×10^{-9}. Considering the nature of the data and the presumed inapplicability of the method, it is remarkable and quite possibly fortuitous that these values compare favorably. The fact that they do is sufficient reason for presenting the results and a more detailed exposition of the method. It can be abandoned when a better method becomes available.

Since, however, it is improbable that the value $K_{aragonite}$ in sea water would be lower than its experimental value, or even that field precipitation of aragonite would be detected at exhaustion, the results obtained from Debye-Hückel γ CO_3^{--} and mean-salt γ Ca^{++} are taken as more probable values than the straight Debye-Hückel results, which are not examined in detail here. Actually a value of γ Ca^{++} midway between Debye-Hückel and mean-salt values here calculated would give $K_{aragonite}$ precisely that of Latimer; so either variation gives thermodynamically more congruent results than have previously been available for sea water (despite their dubious theoretical basis).

Station *C7* is chosen to illustrate the application of the outlined method for estimating the activity product, because it can then be compared directly with the empirical method for the simple concentration product employing the same data.

THE METHOD AND ITS RESULTS

The Debye-Hückel theory as it applies at different ionic strengths, the equations, and the standard values needed to approximate the activity product $a\text{Ca}^{++} \times a\text{CO}_3^{--}$ are given by Robinson and Stokes (1949, 1955), Klotz (1950, p. 328–336), Garrels and Dreyer (1952, p. 332–336), Latimer (1951, p. 349–351), Harned and Owen (1958, p. 489–490, 731, 758), and Garrels (1960, p. 27–30, 39–40, 43–60). At station *C7*, where minimal alkalinity and ionic product values are found, the computation of $a\text{Ca}^{++} \times a\text{CO}_3^{--}$ should give a value approximating $K_{aragonite}$. To get the activities a, the activity coefficients γ are needed. To get γ values, various manipulations are possible if the molality and ionic strengths of the solutions are first obtained. The basic computations for the hydrated salts require data also on diameter of the hydrated ions, $\mathring{a}$; molecules of bound water per unit, or hydration number, n; and water activities at molal concentration a_w—but this operation can be bypassed by means of tables and graphs. The computations below are at atmospheric pressure, and they assume T 25°C throughout, neglecting the 4.25°C by which field temperature at station *C7* exceeds this amount.

The fact that rational numbers emerge from this theoretically outrageous application of course does not prove that the procedure is valid. It encourages hope that accurate figures may yet be placed on the solubility of calcium carbonate in the sea; but it would be grossly unwarranted to accept this as basis for general extension of the Debye-Hückel limiting law beyond ionic strengths of 0.1 (and for parts of it beyond 0.01).

1. μ, the ionic strength, is known from table 29 to be 0.977, $\sqrt{\mu}=0.988$.
2. From the Debye-Hückel theory (Latimer, 1952, p. 351):

$$\log \gamma\text{HCO}_3^- = -0.505\ Z^2\sqrt{\mu}\ \text{(where } Z=\text{valence)}$$
$$= -0.505 \times 0.988 = -0.4989$$
$$\gamma\text{HCO}_3^- = \text{antilog } 0.5011 \times 10^{-1} = 0.317$$

3. Log $\gamma\text{CO}_3^{--} = -0.505\ Z^2\sqrt{\mu}$

$$= -0.505 \times 4 \times 0.988 = -1.9958$$
$$\gamma\text{CO}_3^{--} = \text{antilog } 0.0042 \times 10^{-2} = 0.0101$$

(From computation No. 7 $m\text{CO}_3^{--}=0.00022$ e/l; and, since $\gamma\text{CO}_3^{--} \times m\text{CO}_3^{--} = a\text{CO}_3^{--}$, $a\text{CO}_3^{--} = 2.22 \times 10^{-6}$. So the above computation can be checked by obtaining $a\text{CO}_3^{--}$ from the relation $CO_2+H_2O=2H^++CO_3^{--}$, if we assume P_{CO_2} in equilibrium with atmosphere at 3×10^{-4}. This computes to be 2.22×10^{-6}, which is a satisfactory verification of the above.)

4. γCa is obtained indirectly, from data on $CaCl_2$ and KCl, by the mean-salt method (Garrels and Dreyer, 1952, p. 334), starting with computation of molality for these compounds using the Lewis equation (Latimer, 1952, p. 350):

$$\text{For KCl, } \mu = \frac{Z_+^2 m_+ + Z_-^2 m_-}{2} = \frac{1^2 m_+ + 1^2 m_-}{2} = m$$

and molality KCl=0.977

$$\text{For CaCl}_2,\ \mu = \frac{Z_+^2 m_+ + Z_-^2 m_-}{2} = \frac{2^2 m_+ + 1^2 2m_-}{2} = 3m$$

and molality $CaCl_2 = 1/3\mu = 0.326$

γCaCl_2 and γKCl may be read by interpolation to the appropriate molality from tables in Harned and Owen (1958, p. 731, 738) or Latimer (1952, p. 354–355); or they may be calculated using equation No. 3 of Robinson and Stokes (1949, p. 594). Calculations were done using values for $CaCl_2$ of $\mathring{a}=4.7$, $n=12$, $a_w=0.984$, and for KCl of $\mathring{a}=4$, $n=2$, $a_w=0.968$. The results of such computations were not far from those given by Robinson and Stokes (1955, p. 479–482), but they departed so widely from the later tabulated values of Harned and Owen for $CaCl_2$ at the ionic strength of sea water that the Harned and Owen tables were used in preference to computation.[17]

From Harned and Owen, then

γCaCl_2 at m 0.326=0.460
and γKCl at m 0.977=0.607

---

[17] Final values for $a\text{Ca}^{++} \times a\text{CO}_3^{--}$ using computed γCaCl_2 and γKCl are about 60 percent of those found when the Harned and Owen tables are used; in the present instance 4.8×10^{-9} instead of 7.8×10^{-9}.

Now, from Latimer (1952, p. 350)

$\gamma = (\gamma_+^{v+} \cdot \gamma_-^{v-})^{1/v_+ + v_-}$, where v is the number of positive or negative ions

So $\gamma KCl = (\gamma K^+ \cdot \gamma Cl^-)^{1/1+1}$

Then, since (from activity relations) γK^+ and γCl^- are nearly equal

$$\gamma \pm CaCl_2 = (\gamma Ca^{++} \cdot \gamma KCl^{-2})^{1/1+2}$$

$$\gamma \pm Ca^{++1/3} = \frac{\gamma CaCl_2}{\gamma KCl^{2/3}}$$

$$\gamma \pm Ca^{++} = \frac{\gamma CaCl_2{}^3}{\gamma KCl^2} = \frac{0.460^3}{0.607^2} = \frac{0.09734}{0.3684} = 0.264$$

5. Next, from table 29, $mCO_3^{--} + mHCO_3^- =$ carbonate alkalinity $= 0.00165$ e/l

6. Then, from Latimer (1952, p. 135), or by calculation, $\frac{aH^+ \cdot aCO_3^{--}}{aHCO_3^-} = 10^{-10.32}$ at 25°C and atmospheric pressure

While pH=8, and $a = \gamma \cdot m$

$$\text{So } \frac{10^{-8} \times 0.0101\ mCO_3^{--}}{0.3171\ mHCO_3^-} = 4.79 \times 10^{-11}$$

$$\frac{10.10 \times 10^{-11}\ mCO_3^{--}}{4.79 \times 10^{-11}} = 0.3171\ mHCO_3^-$$

$$2.109\ mCO_3^{--} = 0.3171\ mHCO_3^-$$

$$mCO_3^{--} = 0.150\ mHCO_3^-$$

7. So $1.150\ mHCO_3^- =$ carbonate alkalinity $= 0.00165$ e/l (from computation No. 8)

and $mHCO_3^- = 0.00143$ e/l

while $mCO_3^{--} = 0.00022$ e/l

8. From analysis $mCa^{++} = 0.0133$ e/l

9. $aCa^{++} \cdot aCO_2^{--} = (\gamma Ca^{++} \cdot mCa^{++}) \times (\gamma CO_3^{--} \cdot mCO_3^{--})$
$= 0.264 \times 0.0133 \times 0.0101 \times 0.00022$
$= 7.8 \times 10^{-9}$

Activity product values computed by the same method for selected stations and groups of stations are given in table 37, together with the main steps by which reached. Activity product values trend generally downward across the bank, and the minimal values cluster around 7.8 to 7.9×10^{-9}, that for station *C7*, being lowest, as the field data indicated it should be.

TABLE 37.—*Main steps in computation of activity product $aCa^{++} \times aCO_3^{--}$ for selected stations and groups of stations*

Station or composite	Cl^-‰	μ	$\sqrt{\mu}$	$\gamma \pm HCO_3^-$	$\gamma \pm CO_3^{--}$	KCl*m*	γKCl	$CaCl_2m$	$\gamma CaCl_2$	$\gamma \pm Ca^{++}$	A_te/l
Averaged data for groups of stations											
Straits bottom, 5 stations	19.61	0.733	0.855	0.370	0.0187	0.733	0.623	0.244	0.473	0.273	0.00262
Straits surface, 5 stations	19.89	.742	.862	.367	.0182	.742	.622	.247	.472	.272	.00243
Bank edge, 6 stations	21.02	.787	.887	.357	.0162	.787	.619	.262	.471	.273	.00239
Outer bank, 11 stations	21.15	.791	.890	.355	.0159	.791	.618	.264	.470	.272	.00228
Midbank, 26 stations	22.34	.837	.915	.345	.0142	.837	.614	.276	.467	.271	.00210
Inner bank, 19 stations	23.50	.894	.945	.333	.0123	.894	.611	.298	.462	.264	.00191
Selected individual stations											
A1	19.93	0.739	0.860	0.368	0.0183	0.739	0.622	0.246	0.473	0.274	0.00244
It' marginal	23.12	.858	.926	.341	.0135	.858	.613	.286	.466	.271	.00244
It' whiting	23.15	.863	.929	.340	.0133	.863	.613	.288	.465	.268	.00202
B4	23.63	.874	.935	.337	.0129	.874	.612	.291	.463	.265	.00184
B3	25.25	.927	.963	.326	.0113	.927	.607	.309	.461	.266	.00178
C7	25.80	.977	.988	.317	.0101	.977	.604	.326	.460	.264	.00178

Station or composite	ΣB g-atom/l	K'_B	pH	Boron correction	A_c e/l	$mHCO_3^-$e/l	mCO_3^{--}e/l	mCa^{++} e/l	$aCa^{++} \times aCO_3^{--}$
Averaged data for groups of stations—Continued									
Straits bottom, 5 stations	0.00041	2.17×10^{-9}	7.83	0.00007	0.00255	0.00234	0.00021	0.01080	11.58×10^{-9}
Straits surface, 5 stations	.00036	2.19×10^{-9}	8.04	.00007	.00236	.00213	.00023	.01065	12.13×10^{-9}
Bank edge, 6 stations	.00042	2.28×10^{-9}	8.14	.00010	.00229	.00200	.00029	.01137	14.58×10^{-9}
Outer bank, 11 stations	.00042	2.28×10^{-9}	8.16	.00010	.00218	.00189	.00029	.01142	14.32×10^{-9}
Midbank, 26 stations	.00043	2.37×10^{-9}	8.10	.00010	.00200	.00174	.00026	.01172	11.73×10^{-9}
Inner bank, 19 stations	.00048	2.48×10^{-9}	8.02	.00010	.00181	.00159	.00022	.01214	8.67×10^{-9}
Selected individual stations—Continued									
A1	0.00042	2.40×10^{-9}	8.20	0.00012	0.00232	0.00201	0.00031	0.01085	16.87×10^{-9}
It' marginal	.00051	2.79×10^{-9}	8.04	.00012	.00232	.00205	.00027	.01190	11.75×10^{-9}
It' whiting	.00051	2.80×10^{-9}	8.10	.00014	.00189	.00164	.00025	.01223	10.90×10^{-9}
B4	.00051	1.73×10^{-9}	8.00	.00010	.00173	.00154	.00019	.01213	7.88×10^{-9}
B3	.00055	1.66×10^{-9}	8.00	.00012	.00166	.00146	.00020	.01318	7.92×10^{-9}
C7	.00058	1.65×10^{-9}	8.00	.00013	.00165	.00143	.00022	.01330	7.80×10^{-9}

The *C7* figure of 7.8×10^{-9} is so close to $K_{aragonite} = 6.9 \times 10^{-9}$ given by Latimer (1952, p. 319) that it strengthens the inference of approaching metastable equilibrium for aragonite at station *C7*, and encourages the provisional use of the method in estimating the thermodynamic relations of $CaCO_3$ in the range of ionic strength considered. Considering the roundabout and nonrigorous approach, as well as the temperature difference, it is not suggested, to be sure, that the present approximation $K_{aragonite} = 7.8 \times 10^{-9}$ is an accurate value of that constant. Its close approach to Latimer's value, however, favors the inference that a similar estimate for calcite would come similarly close; and when comparison of the here computed aragonite value is made with $K_{calcite} = 4.7 \times 10^{-9}$ (Latimer, 1952, p. 319), this gives aragonite÷calcite=1.66 and a standard free-energy difference aragonite→calcite of −300 calories. This compares with the −273 calories estimated by Jamieson (1953, p. 1389) and by Kelley and Anderson (1935, p. 15) and the −230 calories indicated by Latimer's $K_{aragonite}$ value.

INTERPRETATION OF THE RESULTS AND COMPARISON WITH THOSE OBTAINED BY THE EMPIRICAL METHOD

The systematic variation of the activity product $aCa^{++} \times aCO_3^{--}$ is clear from figures 45 and 46. Comparison between figures 44 and 45 brings out that both the concentration and the activity products slope toward a metastable state at the selected low-alkalinity stations, but figure 45 suggests incomplete approach to the final level. The minimal value of 7.8×10^{-9} found for the activity product at Station *C7* thus may imply still lower (but not much lower) final values for both $K_{aragonite}$ and $K'_{aragonite}$. It also weakens the likelihood of calcite precipitation under normal bank conditions.

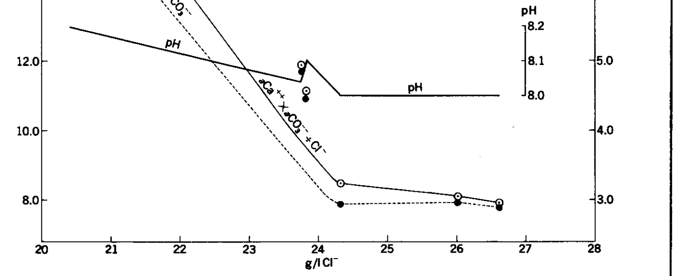


FIGURE 45.—Relation to changing chloride of activity product $aC_a^{++} \times aCO_3^{--}$ (aragonite), and its ratio to chloride, for same water samples as in figures 43 and 44 (assuming *T* 25°C and atmospheric pressure).

The cycle of warm weather changes from ocean water across the bank is indicated in figure 46. Qualitatively the stoichiometric and the activity data, and their ratios to chloride indicate much the same thing. Discounting details of parentage: bottom water, which under pressure existing at depth may be barely saturated with $CaCO_3$, rises and becomes ostensibly supersaturated because of increasing temperature, pH, and salinity, and decreasing pressure. The activity product reaches a maximal value along the bank edge. In this apparent disequilibrium state, the slight increase in temperature accompanying movement onto the bank, and perhaps the presence of seed crystals, is enough to trigger the reaction, and precipitation begins over the outer banks (the apparent pH increase from straits surface waters bankward as shown in fig. 46 is due to nighttime readings at straits stations and daytime readings over the banks, and the drop in temperature from station *It′* to station *B4* is due to the primed stations being occupied 13 months later than the others). Equilibration of the system thereafter proceeds more or less continuously, conditioned by steadily though slightly increasing temperature and strongly increasing salinity. The slight decline in pH across the banks is possibly attributable to CO_2 increment from the sediments beneath or to a lag in CO_2 equilibration in the reaction itself. Local approach to a quasi-equilibrium state over the inner banks is suggested by minimal alkalinity values at individual stations (fig. 45). The average value for $aCa^{++} \times aCO_3^{--}$ of the inner bank stations of figure 46 is naturally greater than at such sites of minimal alkalinity.

The activity computations substantiate the qualitative significance of the previously outlined empirical method for estimating the apparent solubility relations of calcium carbonate in sea water. The empirical results also indicate that certain waters are supersaturated in calcium carbonate with reference to others, but the computed values of about 200 percent supersaturation for aragonite and 450 percent for calcite in the range of figures 44 and 45 are higher than the 115 percent for aragonite and 250 percent for calcite suggested by the activity data. In this and other respects, the results of the empirical method are quantitatively less satisfactory than even the crude thermodynamic approximations made, and the computations involved are also more tedious than those employed to estimate the activity figures.

In contrast to the empirical estimation of ionic products, the outlined method for estimating the activity product of calcium carbonate is simpler and more direct, provides closer comparison with data from other fields,

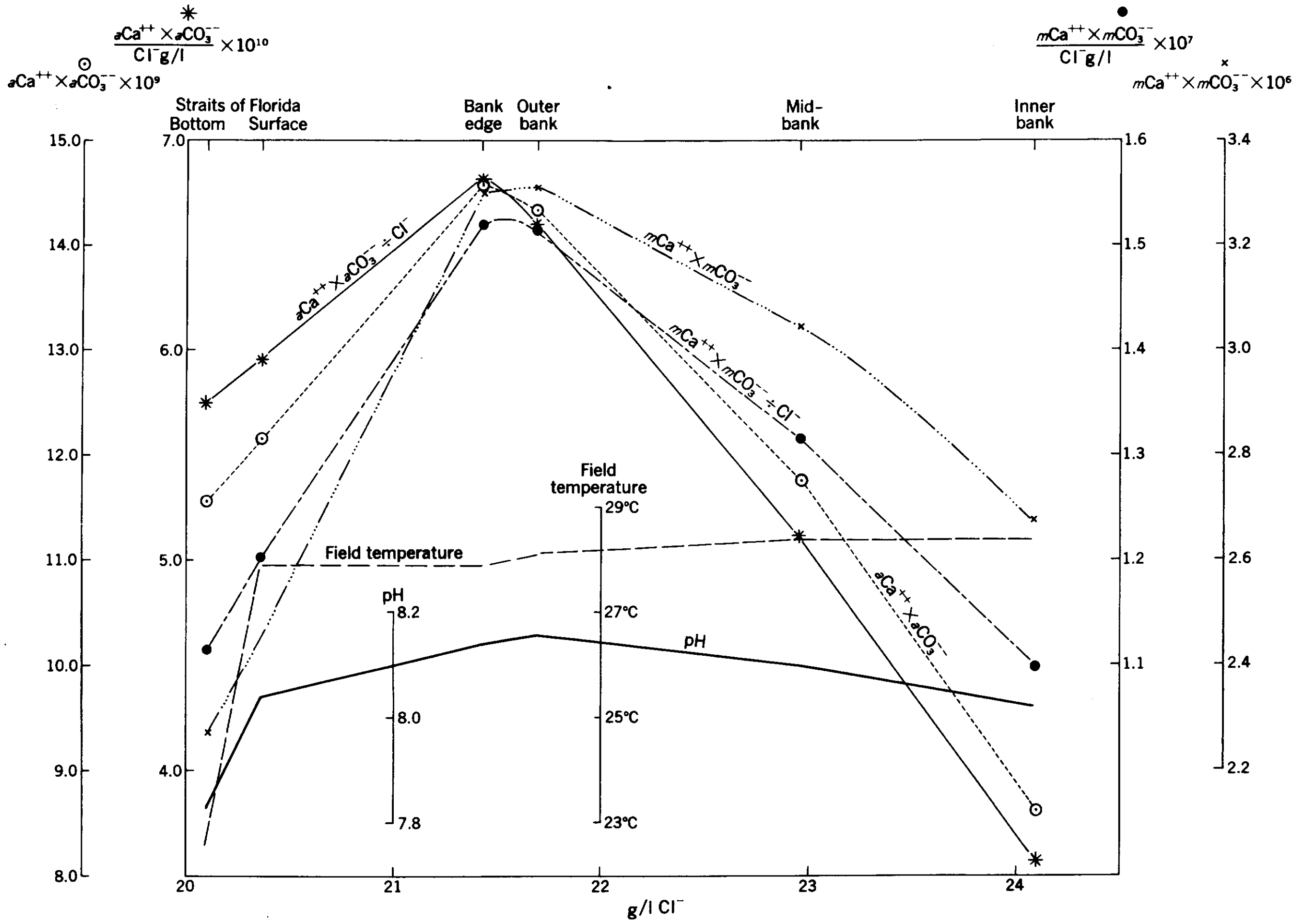


FIGURE 46.—Relation to changing chloride of $aCa^{++} \times aCO_3^{--}$, of $mCa^{++} \times mCO_3^{--}$, and of ratio to chloride of each, averaged for water samples from groups of stations over the banks west of Andros Island and in the Straits of Florida. (The apparent increase in pH of the surface waters as they move bankward from the straits is due to the fact that the straits readings were made at night, and the drop in temperature from station *It*[1] to station *B4* is due to the primed stations being occupied 13 months later than the others.)

and gives more congruous supersaturation figures. Considering its unverified assumptions, plus the fact that "no method is at present available for the experimental determination of the activity coefficient of a single ionic species" (Glasstone, 1947, p. 410), its results also are only approximations. The close approach to the results of other investigations, however, inspires cautious optimism with regard to the general procedure and the prospect of eventually refining it to one that will give acceptable consistency for acceptable reasons.

SOLUBILITY RELATIONS AND SOLID STATE POLYMORPHISM OF CALCIUM CARBONATE

It has long been recognized that the high supersaturations indicated by the apparent solubility product constants for aragonite and for calcite in sea water are anomalous. The need is also clear to explain why $CaCO_3$ in some circumstances precipitates, and persists, as metastable aragonite instead of as stable calcite.

The present results bear on both of these questions.

ANOMALY OF SUPERSATURATION AND ITS FIELD DETECTION

Assuming that the minimal computed activity product of 7.8×10^{-9} does approximate $K_{aragonite}$ (at 29°C), the maximal bank-edge value of 16.9×10^{-9} implies a supersaturation of about 115 percent for aragonite instead of the 200 percent given by $K'_{aragonite}$ for the same sites. Comparable figures for calcite are 250 percent from K and 450 percent from K'.

To be sure, both sets of figures denote a high percentage supersaturation, but, in fact, total computed loss of calcium carbonate from bank edge to quasi-equilibrium at island margin is only about 5 percent of original total in solution (allowing for loss of water by evaporation). Taken together with the fact that the activity results cut apparent supersaturation in half and reduce the product of the combining ions from absolute values in the range of 10^{-6} to the range of 10^{-9}, it seems reasonable to attribute the apparent supersaturation observed to ordinary kinetic factors, amplified by the formation of complexes: of calcium, for example, with chloride, bicarbonate, sulfates, or chelate organic substances, and of carbonate not only with hydrogen but also with sodium and magnesium (Garrels and others, 1959; Cloud, 1959, p. 402, Alekin and Moricheva, 1957; Eyster 1958).

Discussion to the latter point as concerns sea water has focussed on the facts that both the amount of CO_3^{--} in the alkalinity complex (fig. 7) and the product $Ca^{++} \times CO_3^{--}$ (Sverdrup and others, 1942, fig. 42) increase with rising pH. Inasmuch as one member of the couple increases, it is obvious that the product must also increase if no precipitation takes place. The anomaly is that the calculated product does increase greatly without precipitation, and at constant temperature and salinity. It was recognized by Sverdrup and others (1942, p. 207), and has been repeatedly since, that this suggested complexing. Garrels and Dreyer (1952, p. 333–336),[18] therefore, worked out a method for computing amounts of calcium carbonate theoretically present in both ionic and nonionic states under specified conditions, the nonionic phase being taken as dissolved $CaCO^3$. Similar computations, however, indicate only trivial nonionic calcium for the present data, and experiments with ammonium oxalate suggest no nonionic calcium (Leonard Shapiro, written communication, July 18, 1956). Thus it looks as if complexing of calcium may not be very important after all, and the lesser supersaturations indicated by the activity products may in large degree be real. The degree of supersaturation cannot be conclusively evaluated until the degree of complexing of carbonate with ions other than hydrogen (in the marine environment) is better understood.*

In this same connection, it is of interest that the few accurate calcium values for bank waters nearly coincide with those predicted from the ratio of Wattenberg (1936): Ca mg atom/l = ½ alkalinity me/l × 0.465 Cl^- mg/l. This emphasizes that departures from aragonite equilibrium in the surface waters of the sea cannot be as large as indicated by K'_{CaCO_3}. It also implies a broad extension of the field survey of calcium anomalies in the sea, based on simple shipboard analyses for chloride and alkalinity, and considering that the simple Dittmar and Wattenberg ratios of calcium and alkalinity to chloride (Sverdrup and others, 1942, p. 173, 196) apply to Straits of Florida water but not to bank water. Inasmuch as Wattenberg's ratio using alkalinity and chloride for computation of calcium works in both straits and bank water, it seems to be valid as a means of estimating approximate calcium present even after precipitation (or, presumably, solution) has taken place. Difference between calcium estimated from the simple chloride ratio and that from the mixed ratio to chloride plus alkalinity should, then, give an approximate measure of ionic calcium lost or added to the sea, without reference to solubility product, real or apparent, and without calcium analyses. Nearly comparable results as far as loss or gain of $CaCO_3$ is concerned, can, of course, be obtained from difference between titration alkalinity and theoretical alkalinity based on chloride ratio.

CAUSES OF THE PARTICULAR MINERALOGICAL STATE

At 25°C and atmospheric pressure calcium carbonate may crystallize from solution as calcite, aragonite, or vaterite, respectively its stable, metastable, and highly unstable forms. These different forms appear in different solutions or in the same solution under varying conditions. The controlling factors, however, are not agreed upon, despite many thoughtful studies of the problem (for example, Johnston, Merwin, and Williamson, 1916; Lowenstam, 1954a, 1954b; Pobeguin, 1954; Togari and Togari, 1955; Monaghan and Lytle, 1956; Zeller and Wray, 1956; Wray and Daniels, 1957).

The investigations here reported have led to the thesis that the agreed upon facts and most of the apparent anomalies can be harmonized by regarding the mineralogical state of the precipitate as primarily a function of degree of supersaturation of the parent solution. This view was anticipated by Pobeguin (1954, especially p. 95–99, 107) from her painstaking work with pure water solutions, and it was approached by Zeller and Wray (1956, p. 149) and by Wray and Daniels (1957). It accepts the now generally recognized facts that, other factors being equal, the formation of aragonite is favored by increasing temperature and pH. But it incorporates these in the broader concept that all factors favoring the attainment of high apparent supersaturation favor initial precipitation of the more soluble, higher energy polymorphs. Among such factors are increasing temperature, increasing concentration, increasing alkalinity at fixed pH, increasing pH, accelerated photosynthesis, variations in rate of diffusion, decreasing pressure, and carbon dioxide evasion for other reasons—any or all of which may cause or contribute to increasing saturation. Any of these several factors also can be controlling, subordinate, or outweighed in given circumstances. Decreasing activ-

---

[18] Garrels and Dreyer write of the ionic product in fig. 42 of Sverdrup and others as *K'*, whereas in fact Sverdrup and others correctly differentiated between *K'* and the product $C_a^{++} \times CO_3^{--}$. In fact, this does not affect the arguments of Garrels and Dreyer.

*This problem is discussed by R. M. Garrels, M. E. Thompson and R. Siever (1961, Am. Jour. Sci., v. 259, p. 24–45).

ity of the combining ions with increasing ionic strength of the solute up to the range of sea water and the body fluids of organisms may play a governing role.

Drawing now mostly on evidence detailed on preceding pages, the route by which this interpretation was reached may be summarized as follows:

1. Supposedly conflicting values for the apparent solubility product constant K'_{CaCO_3} in sea water become compatible when crystallography and free-energy relations are considered. The computed ionic concentration products show a parallel relationship to computed activity products, and the saturation values of both indicate standard free-energy differences for the transition from aragonite to calcite that compare favorably with those derived from experimental work.
2. Ratios to chloride of the concentration products and activity products of calcium carbonate across the banks west of Andros Island (figs. 44, 45) curve regularly downward with increasing salinity from a minimum of perhaps 100 percent supersaturation toward the apparent level of metastable equilibrium for aragonite. The system is thus regular, predictable, and measurable, and it says that the sea is supersaturated with respect to both aragonite and calcite in the areas where aragonite is precipitating.
3. Upon precipitating $CaCO_3$ from Bahaman sea water (sta. *A1'*) by slow washing out of CO_2 during 9 months at laboratory temperature, first aragonite and then calcite (with subordinate aragonite) was obtained.
4. Experimental precipitation with simple solutions showed correlation of mineralogy with temperature, but not with barium, strontium, or other impurities.
5. Artificial stalactites made by Pobeguin (1955) from pure water solutions, however, showed no correlation between mineralogy and temperature. She obtained either calcite or aragonite at 9° to 13°C, depending on rate of evaporation or diffusion of the solutions. If the solution was allowed to drip slowly, calcite was precipitated; if it was retarded to a slow ooze, aragonite formed. Ellis (1959) also found diffusion or desorption to be a rate-determining (saturation controlling) process.
6. Determinations of the mineralogy of calcium carbonate sediments precipitated in open-water bodies of low ionic strength seem to be primarily calcite without respect to temperature. Aragonite reported in sediments of fresh-water lakes (Twenhofel and McKelvey, 1941, p. 840) is perhaps mainly or wholly skeletal detritus. Sediments from a fresh-water lake on Andros Island itself proved to be calcite (Newell and Rigby, 1957, p. 61, pl. 16, fig. 2). X-ray analysis shows a calcite mineralogy for deposits from Unter Lunzer See in Austria. (See also Gotzinger, 1912.)
7. Naturally precipitated aragonite in the range of atmospheric pressure and temperature appears to be restricted to solutions of relatively high ionic strength such as the sea, some salt lakes, and the internal fluids of organisms; or to form as cave and other dripstone deposits where (Pobeguin, 1955) rates of diffusion may become a controlling factor (not necessarily as a function of temperature, contrary to Moore, 1956).
8. The irregularities observed diminish, and the regularities become part of a consistent whole if viewed as an expression of Ostwald's rule of successive reactions (Ostwald, 1900, p. 447–448; Findlay and Campbell, 1938, p. 49–50; Glasstone and others, 1941, p. 99–100, 199–201; Goldsmith, 1953; Eitel, 1954, p. 589–590, 628). Ostwald held that the release of solid polymorphs from an unstable solution takes place stepwise, from the least to the most stable solid form that can precipitate from a given initial concentration. Stated differently, this is to say that equilibration of a solution that is supersaturated with respect to polymorphs of the same substance tends to take place (assuming no extraneous effects) by the smallest possible successive energy losses, or through successively lower energy phases. The existence of entropy barriers (Glasstone and others, 1941, p. 99–100; Goldsmith, 1953) can create gaps in the sequence and retard the reaction at metastable levels. In nature, the kinetic factors that permit attainment of apparent supersaturation for aragonite seem to be strongly influenced by increasing ionic strength of the solution (up to about 1μ, at least) and by variations in rate of diffusion.

Reduced to its simplest terms the generalization here proposed is that aragonite is the expectable precipitate from solutions that compute to be supersaturated for both calcite and aragonite; only calcite should form between the saturation levels for the two mineral species. Trace elements of suitable ionic radius are presumably trapped in the crystal structure of the host mineral as traditionally supposed and do not exercise a control over primary mineralogy.

It remains to be explained why Zeller and Wray (1956), and Wray and Daniels (1957), found the sequence of formation in some of their experiments to be vaterite-calcite-aragonite, why aragonite and calcite form successive layers of shell in the same mollusks, and why some aragonite sediments persist unaltered for long periods of time.

It is instructive that apparently neither aragonite nor calcite have ever appeared before vaterite in any experiments. In those tabulated by Wray and Daniels, either vaterite or aragonite appears with or before calcite, with one exception where calcite preceded aragonite. Thereafter calcite increases at the expense of the accompanying species with aging up to 18 hours. These results could be reconciled with the foregoing if the calcite accompanying vaterite in the absence of aragonite, or preceding aragonite, in the apparent absence of vaterite, were being formed by rapid direct changeover from vaterite (table 38). The great instability of vaterite and its crystallographic relations to calcite might cause bypassing of the aragonite step if the unknown but presumably small free-energy loss from vaterite to aragonite were overweighed by crystal kinetics. As for the rest of this experimental system, if the instability of aragonite were increased by the high temperatures and simple solutions, much of the calcite might be due to changeover from aragonite itself. Variant diffusion rates and crystal seeding are other possibly complicating factors.

TABLE 38.—*Possible crystallographic sequences of calcium carbonate polymorphs precipitated from solution at maximal supersaturation*

$$\begin{tikzcd}
\textit{Complete theoretical sequence} & \textit{Apparent sequence with rapid inversion of vaterite to calcite} & \textit{Final result after aging} \\
\text{Vaterite} \arrow[r] \arrow[d] & \text{Calcite} \arrow[r] \arrow[d] & \text{Calcite} \\
\text{Aragonite} \arrow[r] \arrow[d] & \text{Aragonite} \arrow[r] \arrow[d] & \text{Calcite} \\
\text{Calcite} \arrow[r] & \text{Calcite} \arrow[r] & \text{Calcite}
\end{tikzcd}$$

The influence of biologic factors on crystallography especially needs more study. The work of Pobeguin (1954, p. 90–91, 97, 101) indicates that it is primarily a metabolic, and, above all, an enzymatic function, but that there may also be some relation between degree of saturation of the body fluids and calcium carbonate crystallography. Even shells that secrete both aragonite and calcite layers presumably do so in different internal chemical environments, according to studies which show higher concentrations of glycine and tyrosine in the calcite layers than are found in the aragonite layers of the same three pelecypods (Roche, Ranson, and Eysseric-Lafon, 1951). Togari and Togari (1959) found a relation between shell mineralogy and chemistry of the ambient waters.

The fact that submerged aragonite sediments thousands of years old are still aragonite, whereas in other circumstances alteration to calcite takes place in a few hours, days, or months indicates marked differences in degree of stability of aragonite under different circumstances. Present and other geological evidence implies that aragonite at relatively low temperature and pressure will remain aragonite indefinitely in contact with solutions similar to those from which precipitated (or dry-sealed), and that alteration to calcite of submerged marine sediments indicates former exposure to fresh water or the moist atmosphere. Included trace components may have a retarding effect on the inversion of aragonite to calcite in a dry atmosphere (at atmospheric temperature and pressure). Replicate X-ray determinations by Blackmon on finely ground pure vesuvian aragonite used for instrumental calibration showed 10 to 20 percent inversion to calcite over a four-year interval (p. 105). In contrast, washed and similarly dry-stored aragonitic sediments from the banks west of Andros Island showed no inversion over the same interval. The slightly higher strontium and lead content (p. 106) and relatively high magnesium content (table 26) of the Bahaman sediments may bear on their slowness to invert. It is contradictory but not necessarily fatal to such a possible long term retarding effect that MacDonald (1956) found no stabilization of aragonite from included isomorphous carbonates below 30 mole percent under experimental conditions.

NEEDED RESEARCH ON THE GENESIS AND DIAGENESIS OF CARBONATE SEDIMENTS

Carbonate research is now so active that it may be fruitful to summarize the principal needs that come to mind as a result of the present study, even though some are mentioned elsewhere in this report and all may change shortly. Naturally these suggestions emphasize the province studied, but even those of a strictly local nature bear on the whole problem through their application to this region.

Regional analysis

As a proper setting for future research in the Bahaman-Floridian carbonate province, it is desirable to know how this particular distribution of land and water came about and why parts of it have apparently persisted in a shoal state since Early Cretaceous. Dredgings should be made up along the walls of the deep channels for datable rock samples of recognizable ecologic facies that would answer the question as to whether the channel margins are cut, slumped, or built. Deep cores should be obtained for lithologic study, to determine what systematic changes might be found in the chemistry of the connate waters and to see whether the porosity and permeability of the system is such as to facilitate movement through it of water from the surrounding ocean. In the latter event, evidence should be sought for possible correlation with diagenetic effects such as dolomitization. Additional ecologic, sedimentary, and chemical surveys, preferably from long-term field laboratories, are also needed of other selected parts of the Great and Little Bahama Banks, the Bay of Florida, and the inland lakes and mangrove swamps of the larger islands. More field surveys are also needed of other modern sites and types of carbonate sedimentation in both deep and shallow waters. In addition, possible ancient counterparts of a variety of ages and settings should be systematically studied or restudied from paleoecological, sedimentological, geochemical, and genetic points of view.

Nutrient budget, water circulation, and whitings

More serial and seasonal analyses of mineral nutrients are needed from shoals to depths, on all sides of and over the Bahama Banks and Florida Bay (and in other areas of modern carbonate sedimentation). In particular, more nutrient analyses are needed of waters in and adjacent to whiting areas. If it is found that the whiting waters are generally higher in mineral nutrients than surrounding waters, effort should be made to learn why and how. Repeated reconnaissance surveys should be made to determine whether or not whitings are more prevalent at particular areas or seasons. It is desirable also to know in detail what countercurrent systems operate within the straits and channels, how their nutrient and calcium content compares with the main currents, and which introduce the most water to the banks.

Microbiology and biochemistry

The nannoplankton responsible for the high photosynthetic rate at station *It'* should be indentified and a bankwide survey made of their activities. We need to know whether they work at about the same or different rates at different places, and to what extent total CO_2 uptake may exceed respiratory and bacterial production.

The attempt should be repeated, and at different places, to find out what gases or solutions, if any, are transferred to the overlying water from the sediment below. It is especially important to find out, if possible, what is the relation between bacterially generated CO_2 and the CO_3^{--} budget. It would of course be interesting too, and perhaps important for hydrocarbon theory and nuclear energy, to know how, from what, where and to what extent bacteria extract and fractionate hydrogen, and where the various isotopes go after fractionation. Further suggestions for microbiological study are given at the end of Sisler's section on "Microbiology and biochemistry of the sediments and overlying water."

Chemical oceanography and solubility relations

Calcium determinations need to be refined and standardized to the point where they will give consistent results from one laboratory and analyst to another. If possible they should separate ionic and different forms of non-ionic calcium. Work also should be continued on the various equilibrium constants leading toward more accurate estimates of the activity product $a\mathrm{Ca}^{++} \times a\mathrm{CO}_3^{--}$. The suggestion that calcium carbonate crystallography is a general function of effective saturation state and the kinetic factors affecting it calls for more experiments at fluid concentrations across the vaterite-aragonite-calcite range and at different ionic strengths and rates. More analyses of the internal fluids of calcite- and aragonite-secreting organisms at the specific sites of secretion would also be of interest.

Distribution and petrography of aphanitic limestone in time and space

Different types of aphanitic limestone should be discriminated and correlated with their environment and in time, even though some be only of trivial bulk. To be able to distinguish petrographically and consistently between chemical precipitates, microplanktonic oozes, and detrital limemuds, and consistently to correlate these with particular genetic associations would help the interpretation of a very widespread rock suite. The possibility of using different primary trace-element and isotopic compositions of calcite and aragonite as paleoecological tools needs continuing study.

Diagenesis

Experimental rock formation should be continued, using a variety of calcareous sediments of different types with original interstitial water, with fresh water, and dry. We should try to find out how or if a calcareous sediment never exposed to the atmosphere or deep burial becomes a rock. The diagenetic effects of migrating interstitial waters should also be studied, with and without bacteria. Microbiological and biochemical effects on ooid formation and other diagenetic processes should be investigated with the most precise available techniques.

Dolomitization is the salient diagenetic problem, and suggestions for future work are briefly discussed on pages 106-108. Trace-element and isotope analysis deserves investigation for possible clues to whether a particular dolomite might most likely have been formed by diagenetic or hydrothermal alteration of aragonite or calcite, or primarily precipitated.

Under diagenesis also, comes the interesting affinity of oil and ore deposits for carbonate rocks. This in part relates to porosity and permeability, the nature and origin of which deserves still further study. It is quite evidently also geographic and in part paleoecologic. In certain lead, zinc, and manganese deposits the location of ore may well reflect some intrinsic chemical, biological, earlier diagenetic, or textural property of the rock. The low strontium and barium content of virtually all analyzed calcite limestones suggests that alteration of aragonite to calcite is ordinarily accompanied by expulsion of trace elements to the pore waters. Strontium, barium, lead, and zinc deposits associated with carbonate rocks, can probably in many instances be explained by ground water leaching, transport, and concentration of disseminated cations and are likely to be associated with cavern fillings, solution structures, dripstone, and collapse breccias at the more soluble stratigraphic levels in an ore-bearing sequence. It would be a tedious but possibly rewarding activity, therefore, to measure, analyze, tabulate, and compare the physical properties, trace-element compositions, fluid contents, and biotal composition and structure of a large number of different kinds of limestones, near and far from ore bodies and oil fields.[†]

REFERENCES CITED

Agassiz, Alexander, 1888, Three cruises of the "Blake," 1: Harvard Univ., Mus. Comp. Zoology Bull., v. 14, 314 p., 194 figs.

——— 1795, A reconnaissance of the Bahamas and of the elevated reefs of Cuba in the steam yacht "Wild Duck" January to April 1893: Harvard Univ., Mus. Com. Zoology Bull., v. 26, no. 1, p. 1–203, pls. 1–47.

Alderman, A. R., 1959, Aspects of carbonate sedimentation: Geol. Soc. Australia Journ., v. 6, pt. 1, p. 1–10, figs. 1–3.

Alderman, A. R., and Skinner, H. C. W., 1957, Dolomite sedimentation in the southeast of Australia: Am. Jour. Sci., v. 255, p. 561–567, fig. 1.

Alekin, O. A. and Moricheva, N. P., 1957, The problem of the stability of the carbonate system in natural water: Proc. Acad. Sci. USSR, Geochemistry Sec., v. 117, p. 103–106, figs. 1–2 (Consultants Bureau translation).

American Public Health Association and American Water Works Association, 1946, Standard methods for the examination of water and sewage: Lancaster, Pa., Lancaster Press, Inc., 9th ed., 286 p.

Baas Becking, L. G. M, 1956, Biological processes in the estuarine environment IX observations on total base: Koninkl. Nederlandse Akad. Wetensch. Proc., ser. B, v. 59, No. 5, p. 408–420, figs. 1–7.

——— 1958, The influence of algae on the natural environment: Blumea, suppl. 4, p. 87–90.

Bäckström, H. L. J., 1925, The thermodynamic properties of calcite and aragonite: Am. Chem. Soc. Jour., v. 47, no. 10, p. 2432–2442, fig. 1.

Baier, C. R., 1937, Die Bedeutung der Bakterien für den Kalktransport in den Gewässern: Geol. Meere u. Binnengewässer, v. 1, p. 75–005.

Banewicz, J. J., and Kenner, C. T., 1952, Determination of calcium and magnesium in limestones and dolomites: Anal. Chemistry, v. 24, p. 1186–1187.

Bavendamm, W., 1932, Die mikrobiologische Kalkfällung in der tropischen See: Arkiv für Microbiologie, Zeitschr. Erforschung pflanzlichen Mikroörganismen, v. 3, no. 2, p. 205–276.

Berkeley, C., 1919, A study of marine bacteria, Straits of Georgia, B. C.: Royal Soc. Canada Proc. and Trans., 3d ser., sec. 5, v. 13, p. 15–43.

Betz, J. B., and Noll, C. A., 1950, Total-hardness determination by direct colorimetric titration: Am. Water Works Assoc. Jour., v. 42, p. 49–56.

Black, Maurice, 1933a, The precipitation of calcium carbonate on the Great Bahama Bank: Geol. Mag. [Great Britain], v. 70, p. 455–466.

——— 1933b, The algal sediments of Andros Island, Bahamas: Royal Soc. London Philos. Trans., ser. B, v. 222, p. 165–192: figs. 1–16, pls. 21, 22.

Bramlette, M. N., 1926, Some marine bottom samples from Pago Pago Harbor, Samoa: Carnegie Inst. Washington, Papers Dept. Marine Biology, v. 23, p. 1–35, figs. 1–8.

——— 1958, Significance of coccolithophorids in calcium-carbonate deposition: Geol. Soc. America Bull., v. 69, p. 121–126.

Bsharah, Lewis, 1957, Plankton of the Florida Current. V. Environmental conditions, standing crop, seasonal and diurnal changes at a station forty miles east of Miami: Marine Science of the Gulf and Caribbean Bull., v. 7, no. 3, p. 201–251, fig. 1–45.

Buch, Kurt, 1933, Der Borsäuregehalt des Meerwassers und seine Bedeutung bei der Berechnung des Kohlensäure systems im Meerwasser: Conseil Permanent Internat. Exploration de la Mer, v. 85, pt. 3, p. 71–75.

——— 1938, New determination of the second dissociation constant of carbonic acid in sea water: Acad. Aboensis Acta, Math. et Phys., v. 11, no. 5, p. 1–18, fig. 1.

——— 1951, Das Kohlensäure Gleichgewichtssysem im Meerwasser, Kritische Durchsicht und Neuberechnungen der Konstituenten: Havforskningsinstitutets Skr., Meren-tutkimuslaitoksen Julkaisu, no. 151, p. 1–18.

Buch, Kurt, Harvey, H. S., Wattenberg, Hermann, and Gripenberg, Stina, 1932, Über das Kohlensäuresystem im Meerwasser: Conseil Permanent Internat. Exploration de la Mer, v. 79, p. 1–70, fig. 1–9.

Buchan, J. L. 1927a, The free energy of transition in the system calcite-aragonite: Faraday Soc. Trans., v. 23, no. 79, p. 668–671.

——— 1927b, The free energies of solid compounds, deduced from their crystal structure: with special reference to calcite and aragonite: Faraday Soc. Trans., v. 23, no. 79, p. 672–676, fig. 1.

Bunting, W. E., 1944, Determination of soluble silica in low concentrations: Anal. Chemistry, v. 16, p. 612–615, figs. 1, 2.

Campbell, D. N., and Kenner, C. T., 1954, Separation of magnesium from calcium by ion exchange chromatography. Application to determination of CaO and magnesia in limestones and dolomites: Anal. Chemistry, v. 26, p. 560–561.

Carroll, Dorothy, 1959, Sedimentary studies in the Shenandoah Valley of Virginia: U.S. Geol. Survey Prof. Paper 314–F, p. 125–154.

Chave, K. E., 1952, A solid solution between calcite and dolomite: Jour. Geology, v. 60, p. 190–192, fig. 1.

——— 1954a, Aspects of the biogeochemistry of magnesium. 1, Calcareous marine organisms: Jour. Geology, v. 62, p. 266–283, figs. 1–16.

——— 1954b, Aspects of the biogeochemistry of magnesium. 2, Calcareous sediments and rocks: Jour. Geology, v. 62, p. 587–599, figs. 1–4.

Chilingar, G. V., 1956a, Relationship between Ca/Mg ratio and geologic age: Am. Assoc. Petroleum Geologists Bull., v. 40, no. 6, p. 2256–2266, figs. 1–3.

[†] Such information was issued (while this report was in press) in the important series of papers by D. L. Graf, 1960, Geochemistry of carbonate sediments and sedimentary carbonate rocks: Illinois Geol. Survey Circ. 301, 308, 297, 298, and 309.

Chilingar, G. V., 1956b, Use of Ca/Mg ratio in porosity studies: Am. Assoc. Petroleum Geologists Bull., v. 40, no. 10, p. 2489–2493.

Chow, J. J., and Thompson, T. G., 1955, Flame photometric determination of calcium in sea water and marine organisms: Anal. Chemistry, v. 27, p. 910–913.

Cloud, P. E. Jr., 1959, Geology of Saipan, Mariana Islands; Part 4, Submarine topography and shoal water ecology: U.S. Geol. Survey Prof. Paper 280–K, p. 361–445.

——— 1960, Gas as a sedimentary and diagenetic agent: Am. Jour. Sci., Bradley Volume (v. 258–A), p. 35–45, fig. 1, pls. 1–3.

Cloud, P. E., Jr., and Barnes, V. E., 1948, The Ellenburger group of central Texas: Texas Univ. Bur. Econ. Geology Pub. 4621, 473 p., 8 figs., 45 pls.

——— 1957, Early Ordovician sea in central Texas: Geol. Soc. America Mem. 67, v. 2, chap. 9, p. 163–214, figs. 1–3.

Cloud, P. E., Jr., Friedman, Irving, Sisler, F. D., and Dibeler, V. H., 1958, Microbiological fractionation of the hydrogen isotopes: Science, v. 127, p. 1394–1395.

Conway, B. E., 1952, Electrochemical data: Amsterdam, N. Y., Elsevier Pub. Co., 374 p.

Cuvillier, Jean, and Sacal, Vincent, 1951, Corrélations stratigraphiques par microfaciès en Aquitaine occidentale: Leiden, E. J. Brill, 23 p., 90 pls.

Dall, W. H., and Harris, G. D., 1892, The Neocene of North America: U.S. Geol. Survey Bull. 84, 349 p., 43 figs., 3 pls.

Deflandre, Georges, and Deflandre-Rigaud, Marthe, 1956, *Micrascidites* manip. nov., sclérites de Didemnidés (Ascidies, Tuniciers) fossiles du Lutétien du Bassin parisien et du Balcombien d'Australie: Soc. géol. France Compte rendu, no. 4, p. 47–49, figs. 1–5.

DeKeyser, W. L., and Degueldre, L., 1950, Contribution à l'étude de la formation de la calcite, aragonite et vaterite: Soc. Chimiques Belges Bull. 59, p. 40–71, figs. 1–11.

Dittmar, William, 1884, Report on researches into the composition of ocean water collected by H. M. S. *Challenger*: *Challenger* Repts., v. 1, Physics and Chemistry, pt. 1, p. 1–251.

Drew, G. H., 1911, The action of some marine denitrifying bacteria in tropical and temperate seas, and the bacterial precipitation of calcium carbonate in the sea: Marine Biol. Assoc. United Kingdom Jour., new ser., v. 9, no. 2, p. 142–155.

——— 1912, Report of investigations on marine bacteria carried on at Andros Island, Bahamas, British West Indies in May 1912: Carnegie Inst. Washington Yearbook, no. 11, p. 136–144.

——— 1913, On the precipitation of calcium carbonate in the sea by marine bacteria, and on the action of denitrifying bacteria in tropical and temperate seas: Marine Biol. Assoc. United Kingdom Jour., new ser., v. 9, no. 4, p. 479–524, figs. 1, 2.

——— 1914, On the precipitation of calcium carbonate in the sea by marine bacteria, and on the action of denitrifying bacteria in tropical and temperate seas: Carnegie Inst. Washington Pub. 182, p. 7–45, figs. 1–4.

Dunbar, C. O., and Rodgers, John, 1957, Principles of stratigraphy: New York, John Wiley & Sons, Inc., 356 p.

Eardley, A. J., 1951, Structural geology of North America: New York, Harper & Bros., 624 p.

Eitel, Wilhelm, 1954, The physical chemistry of the silicates: Univ. Chicago Press, 1592 p.

Ellis, A. J., 1959, The solubility of calcite in carbon dioxide solutions: Am. Jour. Sci., v. 257, no. 5, p. 354–365, fig. 1.

Ellis, M. M., Westfall, B. A., and Ellis, M. D., 1945, Determination of water quality: U.S. Fish and Wildlife Rept. 9, 122 p.

Elving, P. J., and Van Atta, R. E., 1950, Precipitation in homogeneous solution. Separation and determination of barium, strontium, and calcium: Anal. Chemistry, v. 22, p. 1375–1378.

Emery, K.O., and Rittenberg, S. C., 1952, Early diagenesis of California basin sediments in relation to origin of oil: Am. Assoc. Petroleum Geologists Bull., v. 36, no. 5, p. 735–806, figs. 1–30.

Eyster, Clyde, 1958, Bioassay of water from a concretion-forming marl lake: Limnology and oceanography, v. 3, no. 4, p. 455–458.

Field, R. M., and others, 1931, Geology of the Bahamas: Geol. Soc. America Bull., v. 42, p. 759–784, figs. 1–26, pls. 18–21.

Finckh, A. E., 1904, Biology of the reef-forming organisms at Funafuti Atoll: The Atoll of Funafuti, Report of the Coral Reef Committee, Royal Soc. London, sec. 6, p. 125–150, fig. 19.

Findlay, Alexander, and Campbell, A. N., 1938, The phase rule and its applications: London, New York, Toronto; Longmans, Green and Co. (8th ed. of work originally under sole authorship of Findlay), 327 p.

Flint, R. F., 1957, Glacial and Pleistocene geology: New York, John Wiley & Sons, Inc., 553 p., illus.

Fondeur, Catherine, Gottis, Maurice, Rouire, Jacques, and Vatan, André, 1954, Quelques aspects de la dolomitisation au Jurassique en France: Internat. Geol. Cong., 19th sess., Algeria, Comptes rendus., sec. 13, pt. 15, p. 471–491, figs. 1–10.

Foote, F. J., 1932, Determination of boron in waters: Anal. Chemistry, v. 4, p. 39–42, figs. 1–3.

Fugilister, F. C., 1947, Average monthly sea surface temperatures of the western North Atlantic Ocean: Mass. Inst. Technology and Woods Hole Oceanog. Inst., Papers in Phys. Oceanography and Meteorology, v. 10, no. 2, p. 1–25, pls. 1–16.

Garrels, R. M., 1960, Mineral equilibria: New York, Harper and brothers, 254 p.

Garrels, R. M., and Dreyer, R. M., 1952, Mechanism of limestone replacement at low temperatures and pressures: Geol. Soc. America Bull., v. 63, p. 325–380, figs. 1–36, pls. 1–3.

Garrels, R. M., and Siever, Raymond, 1958, Stability of some carbonates in aqueous solutions: Geol. Soc. America Bull., v. 69, p. 1569.

Garrels, R. M., Thompson, M. E., and Siever, Raymond, 1959, Solubility of carbonates in sea water; control by carbonate complexes: Geol. Soc. America Bull., v. 70, p. 1608.

Gee, Haldane, 1932, Lime deposition and the bacteria: Carnegie Inst. Washington Pub. 435, p. 67–91.

Ginsburg, R. N., 1956, Environmental relationships of grain size and constituent particles in some south Florida carbonate sediments: Am. Assoc. Petroleum Geologists Bull., v. 40, no. 10, p. 2384–2427, figs. 1–10.

———1957, Early diagenesis and lithification of shallow-water carbonate sediments in South Florida: Soc. Econ. Paleontologists and Mineralogists Spec. Pub. 5, p. 80–99. figs 1–18.

Glasstone, Samuel, 1947, Thermodynamics for chemists: New York, D. van Nostrand Co., Inc., 522 p.

Glasstone, Samuel, Laidler, K. J., and Eyring, Henry, 1941, The theory of rate processes: New York, McGraw-Hill Book Co., Inc., 611 p.

Goldman, M. I., 1926, Proportions of detrital organic calcareous constituents and their chemical alteration in a reef sand from the Bahamas: Carnegie Inst. Washington Pub. 344, p. 37–66, fig. 1.

Goldsmith, J. R., 1953, A "simplexity principle" and its relation to ease of crystallization: Jour. Geology, v. 61, no. 5, p. 439–451.

Goldsmith, J. R., Graf, D. L., and Joensuu, O. I., 1955, The occurrence of magnesian calcites in nature: Geochim. et Cosmochem. Acta, v. 7, p. 212–230.

Gordon, Louis, and Wroczynski, A. F., 1952, Precipitation of calcium from homogeneous solution with methyloxalate: Anal. Chemistry, v. 24, p. 896–897.

Gotzinger, G., 1912, Die Lunzer Seen, I. Physik A. Geomorphologie der Lunzer Seen: Internat. Rev. Hydrobiologie und Hydrographie, Suppl. v. 3, p. 1–156, figs. 1–23, pls. 1–20, maps 1–4.

Grim, R. E., 1953, Clay mineralogy: New York, McGraw-Hill Book Co., Inc., 384 p.

Gripenberg, Stina, 1937, A simplified method for the determination of calcium in sea water: Jour. du Conseil, v. 12, no. 3, p. 284–292.

Harned, E. S., and Owen, B. B., 1958, The physical chemistry of electrolytic solutions: Am. Chem. Soc. Mon. 137, 803 p.

Harvey, H. W., 1948, The estimation of phosphate and of total phosphorus in sea waters: Marine Biol. Assoc. United Kingdom Jour., v. 27, p. 337–359, figs. 1–11, tables 1–3.

——— 1955, The chemistry and fertility of sea waters: Cambridge England, Cambridge Univ. Press, 224 p.

Hatcher, J. T., and Wilcox, L. V., 1950, Colorimetric determination of boron using carmine: Anal. Chemistry, v. 22, p. 567–569, figs. 1, 2.

Hess, H. H., 1933, Submerged river valleys of the Bahamas: Am. Geophys. Union Trans., 14th Ann. Mtg., p. 168–170, figs. 1, 2.

Hindman, J. C., 1943, Properties of the system $CaCO_3-CO_2-H_2O$ in sea water and sodium chloride solutions: Univ. Calif. at Los Angeles, PhD Thesis GC3.U3, S34d, no. 20609, 153 p. (Available on loan upon request to Director, Scripps Inst. Oceanography, La Jolla; Calif.)

Hodgman, C. D., [ed.], 1947, Handbook of Chemistry and Physics: Cleveland, Ohio, Chemical Rubber Publishing Co., 30th ed., 2686 p.

Holth, Tore, 1949, Separation of calcium from magnesium by oxalate method, a critical study: Anal. Chemistry, v. 21, p. 1221–1226.

Hood, D. W., Park, Kilho, and Smith, J. B., 1959, Evidence for utilization of bicarbonate ion for photosynthesis by marine phytoplankton: A. & M. College of Texas, Dept. Oceanography and Meteorology, Final Report, The calcium carbonate solubility equilibrium in sea water, pt. 6, 12 p.

Houbolt, J. J. H. C., 1957, Surface sediments of the Persian Gulf near the Qatar Peninsula: The Hague, Mouton & Co., 113 p.

Illing, L. V., 1954, Bahama calcareous sands: Am. Assoc. Petroleum Geologists Bull., v. 38, no. 1, p. 1–95, figs. 1–13, pls. 1–9.

Ingols, R. S., and Murray, P. E., 1949, Urea hydrolysis for precipitating calcium oxalate: Anal. Chemistry, v. 21, p. 525–527.

Jamieson, J. C., 1953, Phase equilibrium in the system calcite-aragonite: Jour. Chemistry and Physics, v. 21, no. 8, p. 1385–1390, figs. 1–3.

Johnston, John, Merwin, H. E., and Williamson, E. D., 1916, The several forms of calcium carbonate: Am. Jour. Sci., 4th ser., v. 41, p. 473–512.

Kazakov, A. V., Tikhomirova, M. M., and Plotnikova, V. I., 1957, The system of carbonate equilbiria (dolomite, magnesite) [in Russian]: Trudy Inst. Geol. Nauk, v. 152, geol. ser. (no. 64); p. 13–58, figs. 1–17. Republished in English, 1959, International Geology Review, v. 1, no. 10, p. 1–39.

Kellerman, K. F., 1916, Halophytic and lime precipitating bacteria: Centralbl. Bakteriologie, Abt. 2, v. 45, p. 371.

Kellerman, K. F., and Smith, N. R., 1914, Bacterial precipitation of calcium carbonate: Washington Acad. Sci. Jour., v. 4, p. 400–402.

Kelley, K. K., and Anderson, C. T., 1935, Contributions to the data on theoretical metallurgy. IV. Metal carbonates—correlations and applications of thermodynamic properties: U.S. Bur. Mines Bull. 384, 73 p.

Kirk, P. L., and Moberg, E. G., 1933, Microdetermination of calcium in sea water: Jour. Indus. Eng. Chem., Anal. Ed., v. 5, p. 95–97.

Kline, W. D., 1929, The solubility of magnesium carbonate (nesquehonite) in water at 25°C and pressures of carbon dioxide up to one atmosphere: Am. Chem. Soc. Jour., v. 51, no. 7, p. 2093–2097.

Kobayashi, Koichi, 1951, The heat capacities of inorganic substances at high temperatures. Pt. 4, The heat capacity of synthetic aragonite (calcium carbonate): Tōhoku Univ. Sci. Repts., 1st ser., v. 35, no. 2, p. 111–118, figs. 1–5.

Kolthoff, I. M., and Sandell, E. B., 1943, Text book of quantitative inorganic analysis: New York, The Macmillan Co., 794 p.

Kornicker, L. S. and Purdy, E. G., 1957, A Bahamian faecal-pellet sediment: Jour. Sed. Petrology, v. 27, no. 2, p. 126–128, fig. 1.

Lalou, Claude, 1957a, Étude expérimentale de la production de carbonates par les bactéries des vases de la baie de Villefranche-sur-mer: Inst. Océanog. Annales, new ser., v. 33, pt. 4, p. 201–267, figs. 1–32, pls. 1–3.

——— 1957b, Studies on bacterial precipitation of carbonates in sea water: Jour. Sed. Petrology, v. 27, no. 2, p. 190–195, figs. 1–2.

Latimer, W. M., 1952, The oxidation states of the elements and their potentials in aqueous solution: New York, Prentice-Hall, Inc., 392 p.

Latimer, W. M., and Hildebrand, J. H., 1951, Reference book of inorganic chemistry: New York, The Macmillan Co., 547 p.

Laubenfels, M. W. de, 1936, Sponge fauna of the Dry Tortugas: Carnegie Inst. Washington, Papers from Tortugas Lab., v. 30, 225 p.

Lee, C. S., 1951, Geophysical surveys on the Bahama Banks: Inst. Petroleum Jour., v. 37, no. 334, p. 633–657, figs. 1–13.

Lerner, Morris, and Rieman, William, III, 1954, Quantitative separation of the alkaline earths by ion exchange chromatography: Anal. Chemistry, v. 26, p. 610–611.

Lipman, C. B., 1924, A critical and experimental study of Drew's bacterial hypothesis on $CaCO_3$ precipitation in the sea: Carnegie Inst. Washington Pub. 240, p. 181–191.

——— 1929a, Further studies on marine bacteria with special reference to the Drew hypothesis on $CaCO_3$ precipitation in the sea: Carnegie Inst. Washington Pub. 391, p. 231–248.

——— 1929b, Chemical composition of sea-water: Carnegie Inst. Washington Pub. 391, p. 249–257.

Lowenstam, H. A., 1954a, Environmental relations of modification compositions of certain carbonate secreting marine invertebrates: Natl. Acad. Sci. Proc., v. 40, no. 1, p. 39–48, figs. 1–3.

——— 1954b, Factors affecting the aragonite:calcite ratios in carbonate secreting marine organisms: Jour. Geology, v. 62, no. 3, p. 284–322, figs. 1–15.

Lowenstam, H. A. 1955, Aragonite needles secreted by algae and some sedimentary implications: Jour. Sed. Petrology, v. 25, no. 4, p. 270–272.

Lowenstam, H. A., and Epstein, S., 1957, On the origin of sedimentary aragonite needles of the Great Bahama Bank: Jour. Geology, v. 65, no. 4, p. 364–375, figs. 1–6.

MacDonald, G. J. F., 1956, Experimental determination of calcite-aragonite equilibrium relations at elevated temperatures and pressures: Am. Mineralogist, v. 41, nos. 9–10, p. 744–756, figs. 1, 2.

McKee, E. D., 1956, Geology of Kapingamarangi Atoll, Caroline Islands· Natl. Acad. Sci., Natl. Research Council, Atoll Research Bull. 50, 38 p.

——— 1958, Geology of Kapingamarangi Atoll, Caroline Islands: Geol. Soc. America Bull., v. 69, no. 3, p. 241–278, figs. 1–17.

Mann, Albert, 1935, Diatoms in bottom deposits from the Bahamas and the Florida Keys: Carnegie Inst. Washington Pub. 452, p. 121–128.

Manov, G. G., Bates, R. C., Hamer, W. G., and Acree, S. F., 1943, Values of the constants in the Debye-Hückel equation for activity coefficients: Am. Chem. Soc. Jour., v. 65, p. 1765–1767.

Matide, Yoshihiro, 1950, On the chemical composition of sea water in the Tokyo Bay: Oceanog. Soc. Japan Jour., v. 5, p. 105–110.

Moberg, E. G., Greenberg, D. M., Revelle, Roger, and Allen, E. C., 1934, The buffer mechanism of sea water: Scripps Inst. Oceanography Bull., Tech. Ser., v. 3, no. 11, p. 231–278.

Moellar, Therald, 1952, Inorganic chemistry: New York, John Wiley and Sons, 966 p.

Molisch, H., 1925, Ueber Kalkbakterien und Andere Kalkfällende Pilze: Centralbl. Bakteriologie, Abt. 2, v. 65, p. 130–139.

Monaghan, P. H., and Lytle, M. L., 1956, The origin of calcareous ooliths: Jour. Sed. Petrology, v. 26, no. 2, p. 111–118, figs. 1–3.

Moore, George, 1956, Aragonite speleothems as indicators of paleotemperature: Am. Jour. Sci., v. 254, p. 746–753, fig. 1.

Moore, H. B., 1933, Faecal pellets from marine deposits: *Discovery* Repts., v. 7, p. 17–26, fig. 1.

Murray, John, and Irvine, Robert, 1889, On coral reefs and other carbonate of lime formations in modern seas: Royal Soc. Edinburgh Proc., v. 17, p. 79–109.

Nadson, G. A., 1928, Beitrag zur Kenntnis der Bakteriogenen Kalkablagerungen: Archiv Hydrobiologie, v. 19, p. 154–164.

Neave, S. A., 1939, Nomenclator Zoologicus, v. 2: London, Zool. Soc. London, 1025 p.

Newell, N. D., 1955, Bahamian platforms: Geol. Soc. America, Spec, Paper 62, p. 303–316, figs. 1–4.

Newell, N. D., Imbrie, John, Purdy, E. G., and Thurber, D. L., 1959, Organism communities and bottom facies, Great Bahama Bank: Am. Mus. Nat. History Bull., v. 117, art. 4, p. 177–228, figs. 1–17, pls. 58–69.

Newell, N. D., and Rigby, J. K., 1957, Geological studies on the Great Bahama Bank: Soc. Econ. Paleontologists and Mineralogists Spec. Pub. 5, p. 15–72, figs. 1–22, pls. 1–22.

Newell, N. D., Rigby, J. K., Whiteman, A. J., and Bradley, J. S., 1951, Shoal-water geology and environments, eastern Andros Island, Bahamas: Am. Mus. Nat. History Bull., v. 97, art. 1, p. 1–29.

Ostwald, Wilhelm, 1900, Grundlinien der anorganischen Chemie: Leipzig, Wilhelm Engelmann, 795 p.

Parker, T. J., and Haswell, W. A., 1949, A text-book of zoology: London, Macmillan and Co., Ltd., 6th ed. revised, v. 1, 770 p.

Pecora, W. T., and Kerr, J. H., 1954, Whewellite from a septarian limestone concretion in marine shale near Havre, Montana: Am. Mineralogist, v. 39, p. 208–214.

Phillips, Craig, and Brady, W. H., 1953, Sea peats: Univ. Miami Press, The Marine Lab. Spec. Pub., 78 p.

Plass, G. N., 1956, Carbon dioxide and the climate: American Scientist, v. 44, p. 302–316.

Pobeguin, Thérèse, 1954, Contribution a l'étude des carbonates du calcium, précipitation du calcaire par les végétaux, comparison avec le monde animal: Annales des Sciences Naturelles, Botanique, 11th sér., v. 15, no. 5, p. 29–109, figs. 1–44.

——— 1955, Sur les concrétions calcaires observées dans la grotte de Moulis (Ariège): Acad. Sci. Paris Comptes rendus, v. 241, p. 1791–1793.

Reed, F. R. C., 1921, The geology of the British Empire: London, Edward Arnold, 480 p., 25 figs.

Revelle, Roger, and Fairbridge, Rhodes, 1957, Carbonates and carbon dioxide: Geol. Soc. America Mem. 67, v. 1, chap. 10, p. 239–295, figs. 1–8.

Revelle, Roger, and Fleming, R. H., 1934, The solubility product constant of calcium carbonate in sea water: Pacific Sci. Cong. Proc., 5th, Victoria and Vancouver, British Columbia, Canada, 1933, v. 3, p. 2089–2092.

Rich, J. L., 1948, Submarine sedimentary features on Bahama Banks and their bearing on distribution patterns of lenticular oil sands: Am. Assoc. Petroleum Geologists Bull., v. 32, p. 767–779, figs. 1–10.

Rivière, André, 1939a, Sur la dolomitisation des sédiments calcaires: Acad. Sci. Paris Comptes rendus, v. 209, p. 597–599.

——— 1939b, Observations nouvelles sur le mécanisme de dolomitisation des sédiments calcaires: Acad. Sci. Paris Comptes rendus, v. 209, p. 691–693.

Robinson, R. A., and Stokes, R. H., 1949, The role of hydration in the Debye-Hückel theory: New York Acad. Sci., Annales, v. 51, p. 593–604.

——— 1955, Electrolyte solutions: London, Butterworth Sci. Pubs., 512 p.

Roche, Jean, Ranson, Gilbert, and Eysseric-Lafon, Marcelle, 1951, Sur la composition des scléroprotéines des coquilles des Mollusques (conchiolines): Soc. Biologie Comptes rendus, v. 45, p. 1474–1477.

Rodgers, John, 1957, The distribution of marine carbonate sediments: a review: Soc. Econ. Paleontologists and Mineralogists Spec. Pub. 5, p. 2–13, figs. 1–2.

Rubey, W. W., 1951, Geologic history of sea water: Geol. Soc. America Bull., v. 62, p. 1111–1147, figs. 1–4.

Rubin, Meyer, and Alexander, Corinne, 1958, U.S. Geological Survey radiocarbon dates, IV: Science, v. 127, p. 1476–1487.

Sander, Bruno, 1936, Beiträge zur Kenntniss der Anlagerungsgefüge: Mineralog. petrog. Mitt., v. 48, p. 27–139, 141–209.

Shattuck, G. B., and others, 1905, The Bahama Islands: New York, The Macmillan Co. (for the Geog. Soc. Baltimore), 630 p.

Sisler, F. D., 1953, Critical study of the usual numeration and isolation techniques for marine bacteriology: Internat. Cong. Microbiology, 6th, Rome, 1953, v. 3, sess. 22, no. 1006.

——— 1954, Bacteriology and biochemistry of the sediments: U.S. Geol. Survey, Lake Mead Comprehensive Survey of 1948–49, v. 3, p. (VIII)266–281.

Sisler, F. D., and ZoBell, C. E., 1950, Hydrogen–utilizing, sulfate-reducing bacteria in marine sediments: Jour. Bacteriology, v. 60, p. 747–756.

——— 1951a, Hydrogen utilization by some marine sulfate-reducing bacteria: Jour. Bacteriology, 62, p. 117–127.

——— 151b, Nitrogen fixation by sulfate-reducing bacteria indicated by nitrogen-argon ratios: Science, v. 113, p. 511–512.

Sitter, L. U. de, 1947, Diagensis of oil-field brines: Am. Assoc. Petroleum Geologists Bull., v. 31, no. 11, p. 2030–2040, figs. 1–4.

Smith, C. L., 1940, The Great Bahama Bank. 1, General hydrographical and chemical features. 2, Calcium carbonate precipitation: Yale Univ., Bingham Oceanographic Lab., Sears Found. Marine Research, Jour. Marine Research, v. 3, no. 2, p. 147–189, figs. 44–51.

——— 1941, The solubility of calcium carbonate in tropical sea water: Marine Biol. Assoc. United Kingdom Jour., v. 25, no. 2, p. 235–242.

Smith, J. L. B., 1949, The sea fishes of southern Africa: South Africa, Central News Agency, Ltd., 550 p.

Smith, N. R., 1926, Report on a bacteriological examination of "Chalky Mud" and sea-water from the Bahama Banks: Carnegie Inst. Washington Pub. 344, p. 69–72.

Sorby, H. C., 1879, The anniversary address of the President: Geol. Soc. London Quart. Jour. proc., v. 35, p. 39–95, figs. 1–11.

Squires, D. F., 1958, Stony corals from the vicinity of Bimini, Bahamas, B. W. I.: Am. Mus. Nat. History Bull., v. 115, no. 4, p. 217–262, figs. 1–4, pls. 28–43.

Steidtmann, Edward, 1911, The evolution of limestone and dolomite: Jour. Geology, v. 19, p. 323–345, 392–428.

Strakhov, N. M., 1947, Carbonates in contemporary lagoon basin and their importance for the problem of dolomite formation: Soc. Naturalistes Moscow Bull., new ser., v. 52, Sec. Geol., v. 22, no. 4, p. 3–38, figs. 1–13.

Sverdrup, H. U., Johnson, M. W., and Fleming, R. H., 1942, The oceans; their physics, chemistry, and general biology: New York, Prentice-Hall, Inc., 1087 p.

Sweetser, P. B., and Bricker, C. E., 1954, Spectrophotometric titrations with ethylenediaminetetraacetic acid. Determination of magnesium, calcium, zinc, cadmium, titanium, and zirconium: Anal. Chemistry, v. 26, p. 195–199.

Terzaghi, Ruth D., 1940, Compaction of lime mud as a cause of secondary structure: Jour. Sed. Petrology, v. 10, no. 2, p. 78–90, figs. 1–5.

Taylor, W. R., 1928, The marine algae of Florida: Carnegie Inst. Washington, Papers from Tortugas Lab., v. 25, 219 p.

Thompson, T. G., and Wright, C. C., 1930, Ionic ratios of the waters of the North Pacific Ocean: Am. Chem. Soc. Jour., v. 52, p. 915–921.

Thorp, E. M., 1936, Calcareous shallow-water marine deposits of Florida and the Bahamas: Carnegie Inst. Washington, Papers from the Tortugas Lab., v. 29, p. 37–120, figs. 1–10, pls. 1–4.

——— 1939, Florida and Bahama marine calcareous deposits *in* Trask, P. D., and others, Recent marine sediments: London, Thomas Murby and Co. (for Am. Assoc. Petroleum Geologists), p. 283–297, fig. 1.

Thurber, David, Purdy, Edward, and Broecker, Wallace, 1958, Radiocarbon studies of the Bahama Bank: Geol. Soc. America Bull., v. 69, p. 1652.

Togari, Kenji, and Togari, Susumu, 1955, Conditions controlling the crystal form of calcium carbonate minerals (1); On the influences of the temperature and the presence of the magnesium ion: Hokkaido Univ., Fac. Sci. Jour., ser. 4, v. 9, no. 1, p. 55–65, figs. 1–4.

——— 1959, Conditions controlling the crystal form of calcium carbonate minerals (2); Mineralogical study of Molluska: Hokkaido Univ., Fac. Sci. Jour., ser. 4, v. 10, no. 2, p. 447–456, figs. 1–3.

Twenhofel, W. H. and McKelvey, V. E., 1941, Sediments of fresh-water lakes: Am. Assoc. Petroleum Geologists Bull., v. 25, no. 5, p. 826–849.

Urey, H. C., 1956, Regarding the early history of the earth's atmosphere: Geol. Soc. American Bull., v. 67, p. 1125–1128.

U.S. Coast and Geodetic Survey, 1941, Manual of tide observations: U.S. Coast and Geodetic Survey Spec. Pub. 196 (revised), 91 p.

Usiglio, J., 1849, Études sur la composition de l'eau de la Méditerranée et sur l'exploitation des sels qu'elle continent: Annales Chime et Physique, 3d ser., v. 27, p. 172–191.

Van Name, W. G., 1930, The ascidians of Porto Rico and the Virgin Islands: New York Acad. Sci., Scientific Survey of Porto Rico and the Virgin Islands, v. 10, pt. 403–535, figs. 1–73, pls. 5–8.

Vaughan, T. W., 1914a, Preliminary remarks on the geology of the Bahamas with special reference to the origin of the Bahaman and Floridian oolites: Carnegie Inst. Washington Pub. 182, p. 47–54.

——— 1914b, Geological investigations in the Bahamas and southern Florida: Carnegie Inst. Washington Yearbook, no. 13, p. 227–233.

——— 1917, Chemical and organic deposits of the sea: Geol. Soc. America Bull., v. 28, p. 933–944.

——— 1918, Some shoal-water bottom samples from Murray Island Australia, and comparisons of them with samples from Florida and the Bahamas: Carnegie Inst. Washington Pub. 213, p. 235–288, figs. 1–4, pls. 94, 95.

——— 1924, Present status of studies on the causes of the precipitation of finely divided calcium carbonate: Natl. Research Council, Rept. Comm. Sedimentation, p. 53–58.

Wassall, Harry and Dalton, Howard, 1959, Oil prospects in the Bahamas: World Oil, Feb. 1, 1959, p. 85–89, fig.1.

Wattenberg, Hermann, 1933, Kalziumkarbonat- und Kohlensäurgehalt des Meerwassers: Wiss. Ergebnisse Atlantischen Exped. "Meteor" (1925–27), v. 8, p. 1–333, figs. 1–43, pls. 1, 2, 27.

——— 1936, Kohlensäure und Kalziumkarbonat in Meere: Fortschr. Mineralogie, Kristallographie, u. Petrographie, v. 20, p. 168–195, figs. 1–7.

Wattenberg, Hermann, and Timmerman, E., 1936, Über die Sättigung des Seewassers an $CaCO_3$ und die anorganogene Bildung von Kalksedimenten: Annalen Hydrographie u. Maritimen Meteorologie, Zeitschr. für Seefahrt- u. Meereskunde, v. 64, no. 1, p. 23–31.

Webb, D. A., 1938, Strontium in sea water and its effect on calcium determinations: Nature, v. 142, p. 751–752.

Williams, M. B., and Moser, J. H., 1953, Colorimetric determination of calcium with ammonium purpurate: Anal. Chemistry, v. 25, p. 1414–1417.

Willstätter, R. M., and Stoll, Arthur, 1928, Investigations on chlorophyll, methods and results [English translation by Schertz, F. M., and Merz, A. R.]: Lancaster, Pa., Science Press Printing Co., 385 p.

Wray, J. L., and Daniels, Farrington, 1957, Precipitation of calcite and aragonite: Am. Chem. Soc. Jour., v. 79, p. 2031–2034, fig. 1.

Zeller, E. J., and Wray, J. L., 1956, Factors influencing precipitation of calcium carbonate: Am. Assoc. Petroleum Geologists Bull., 40, no. 1, p. 140–152, figs. 1, 2.

Zeuner, F. E., 1952, Dating the past: London, Methuen & Co., Ltd., 495 p.

ZoBell, C. E., 1946a, Studies on redox potential of marine sediments: Am. Assoc. Petroleum Geologists Bull., v. 30, no. 4, p. 477–513, figs. 1–5.

——— 1946b, Marine microbiology: Waltham, Mass., Chronica Botanica, 240 p.

——— 1947, Microbial transformation of molecular hydrogen in marine sediments with particular reference to petroleum: Am. Assoc. Petroleum Geologists Bull., v. 31, no. 10, p. 1709–1751.

ZoBell, C. E., Sisler, F. D., and Oppenheimer, C. H., 1953, Evidence of biochemical heating in Lake Mead mud: Jour. Sed. Petrology, v. 23, no. 1, p. 13–17.

INDEX

PLATES 1–10

PLATE 1

[All photographs taken in May 1955]

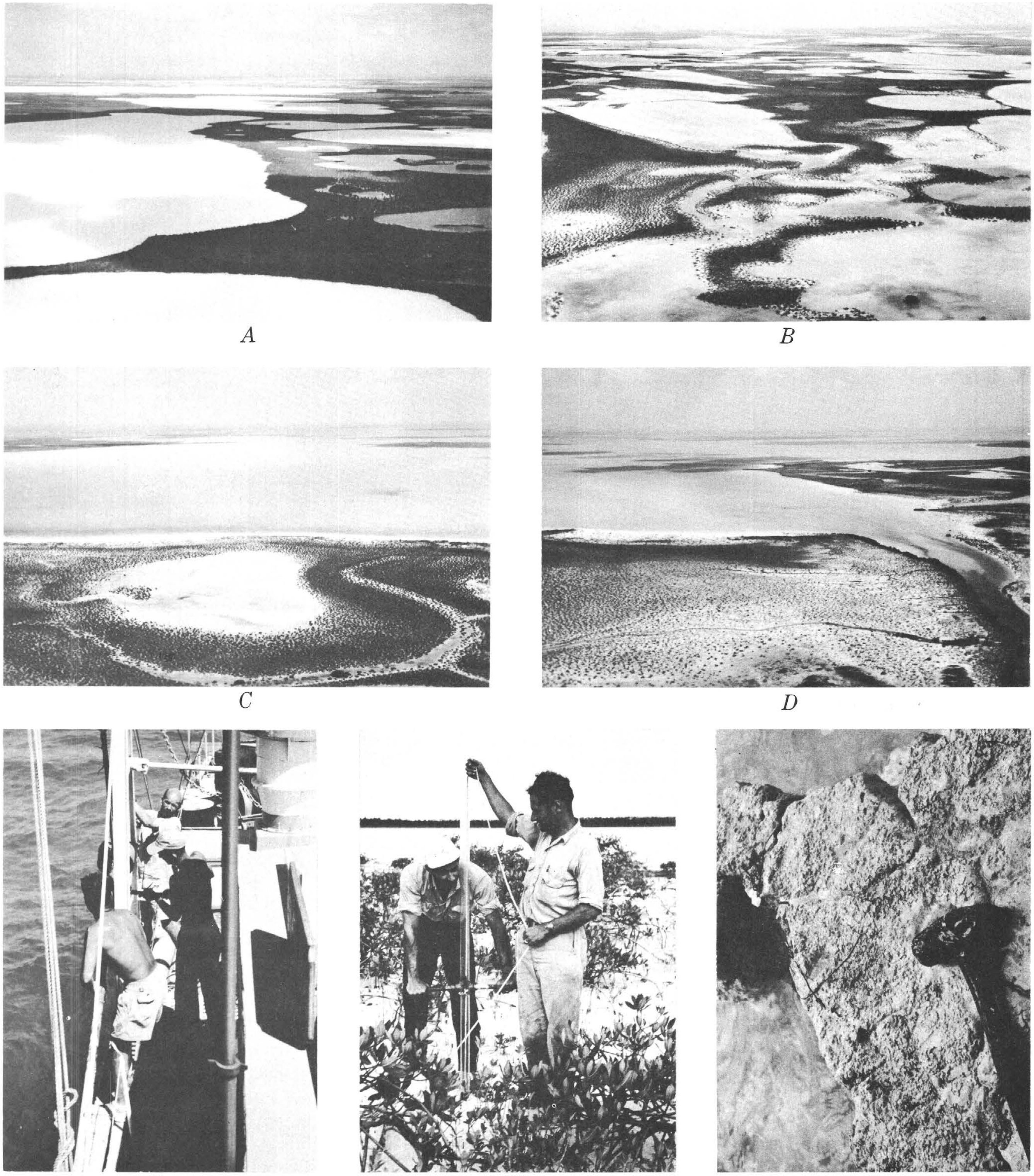
A–B. Western third of Andros Island, between Fresh Creek and Williams Island. The lakes are reported to be mostly very shallow to only a few centimeters deep, and to contain brackish to fresh water. (Pilot L. M. Thompson of Nassau asserted while these photographs were being taken that the series in fig. *A* is drinkable.)

C–D. Western shore of Andros Island; Williams Island is at the left of fig. *C*.

E. Rigging the piston corer aboard M. V. *Physalia*.

F. Ginsburg coring technique in a mangrove swamp in South Bight.

G. Emerged aragonite mud at sta. *C7a*.



A B C D E F G

AIRVIEWS OF WESTERN ANDROS ISLAND, CORING OPERATIONS, AND EMERGED LIMEMUD

PLATE 2

[All photographs taken in May 1955]

A. Airview of underwater dunes off northwestern end of Andros Island. Individual dunes are up to several kilometers long.

B–C. Airviews of whitings (white-water areas) at midbank west of Andros Island. The whiting in fig. *B* is about 0.5 km wide and 2.5 km long. That in fig. *C* is much larger.

D. Northwestern shore of Andros Island from M. V. *Physalia* at sta. *A11*. A broad beach ridge separates the sea from extensive mangrove swamp.

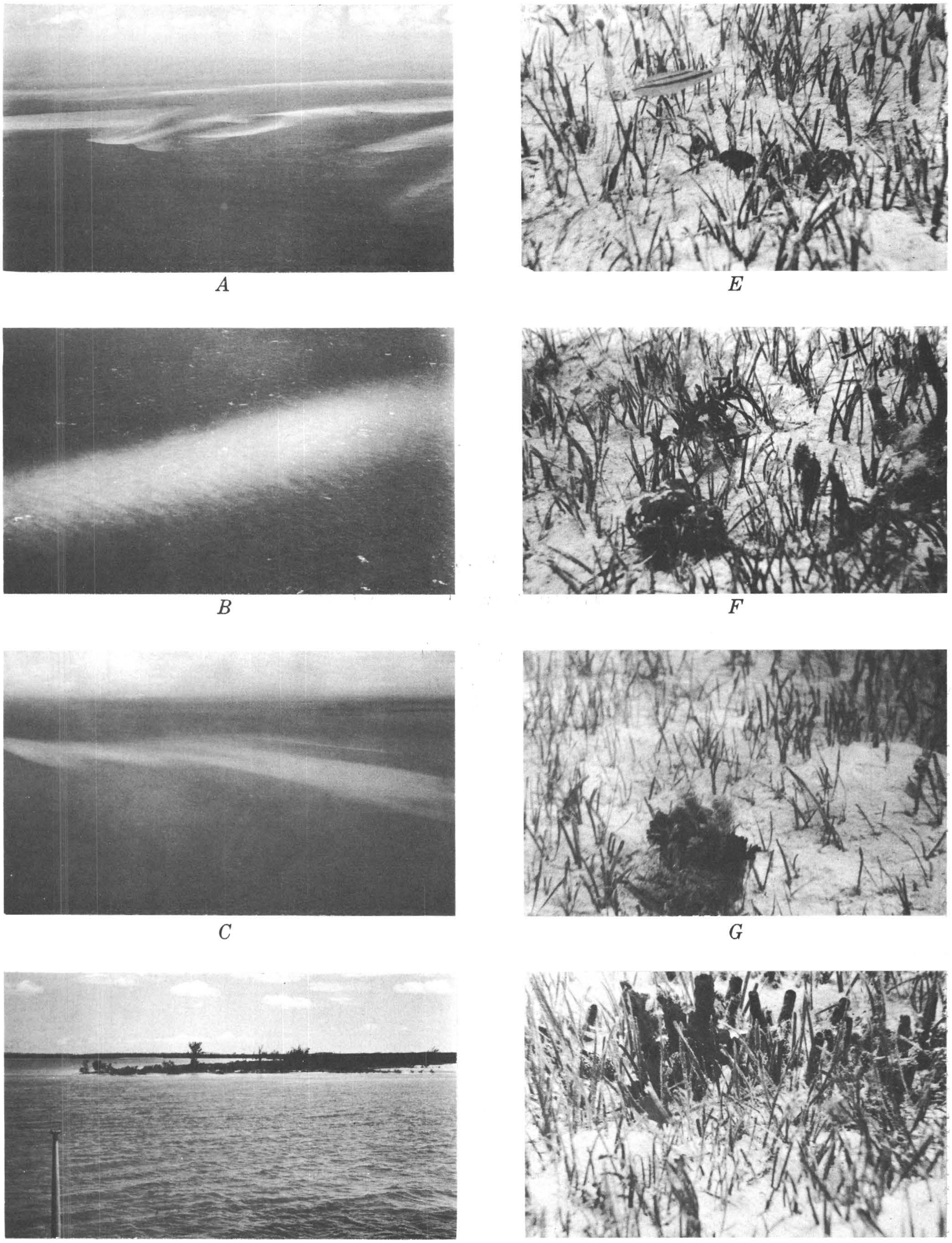
E–H. Bottom views in 7 m of water at sta. *G4*. The grasslike plant in all views is the marine phanerogam *Thalassia testudinum* Koenig and Sims, a *Zostera* relative called turtle "grass".

E. Beneath the 20-cm labrid fish (*Halichoeres*) is a fan-shaped species of the green alga *Avrainvillea*.

F. The loaf-shaped sponge about 20 cm across is the commercial *Spongia obliqua* Duchassaing and Michelloti, rare in the area. Behind is a cluster of the common branching candle sponge *Veronia longissima* (Carter). The pagoda-shaped alga to the right of and below center is a common species of *Rhipocephalus*, and to the right of it is the sponge *Haliclona*.

G. At the right is one of the common burrow mounds, about 1 m across at the base; in the foreground an alga-sponge complex of branching *Avrainvillea* cf. *A. nigricans* Decaisne at the center, surrounded by the common black sponge *Hircinia*. A cluster of the brown alga *Laurencia*, tumbleweedlike, has lodged against the sponge.

H. A hollow organ-pipe sponge, with individual cylinders rising from a common basal connective layer in the mud, is similar in form and habit to *Archaeoscyphia* of the Early Ordovician limemud banks of central Texas.



A E

B F

C G

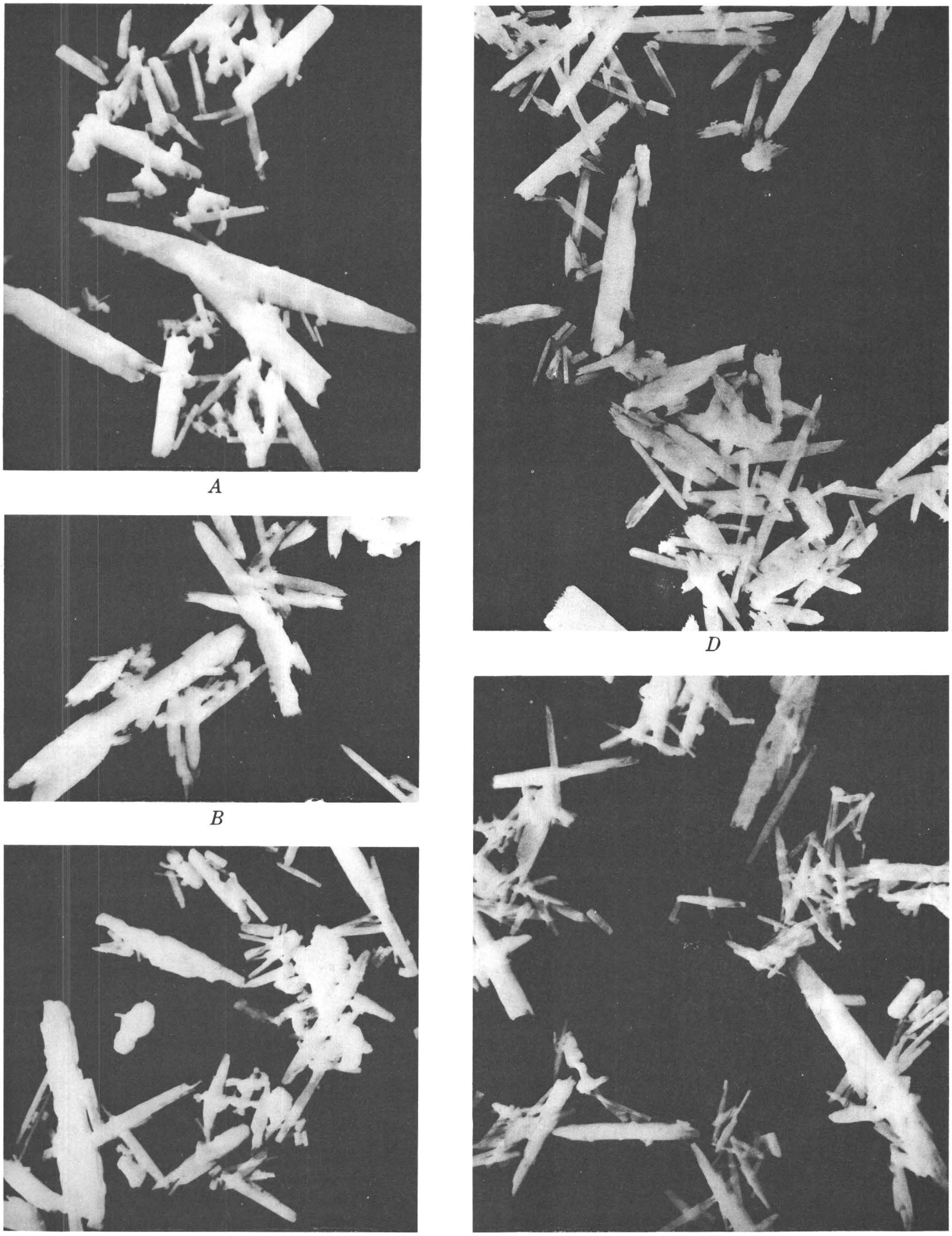
D H

THE SEA WEST OF ANDROS ISLAND

PLATE 3

[All electron micrographs at magnification of 11,500]

A. Sta. *A11*.
B. Sta. *D1a*.
C. Sta. *E9*.
D. Sta. *B3*.
E. Sta. *G4*.



A

B

C

D

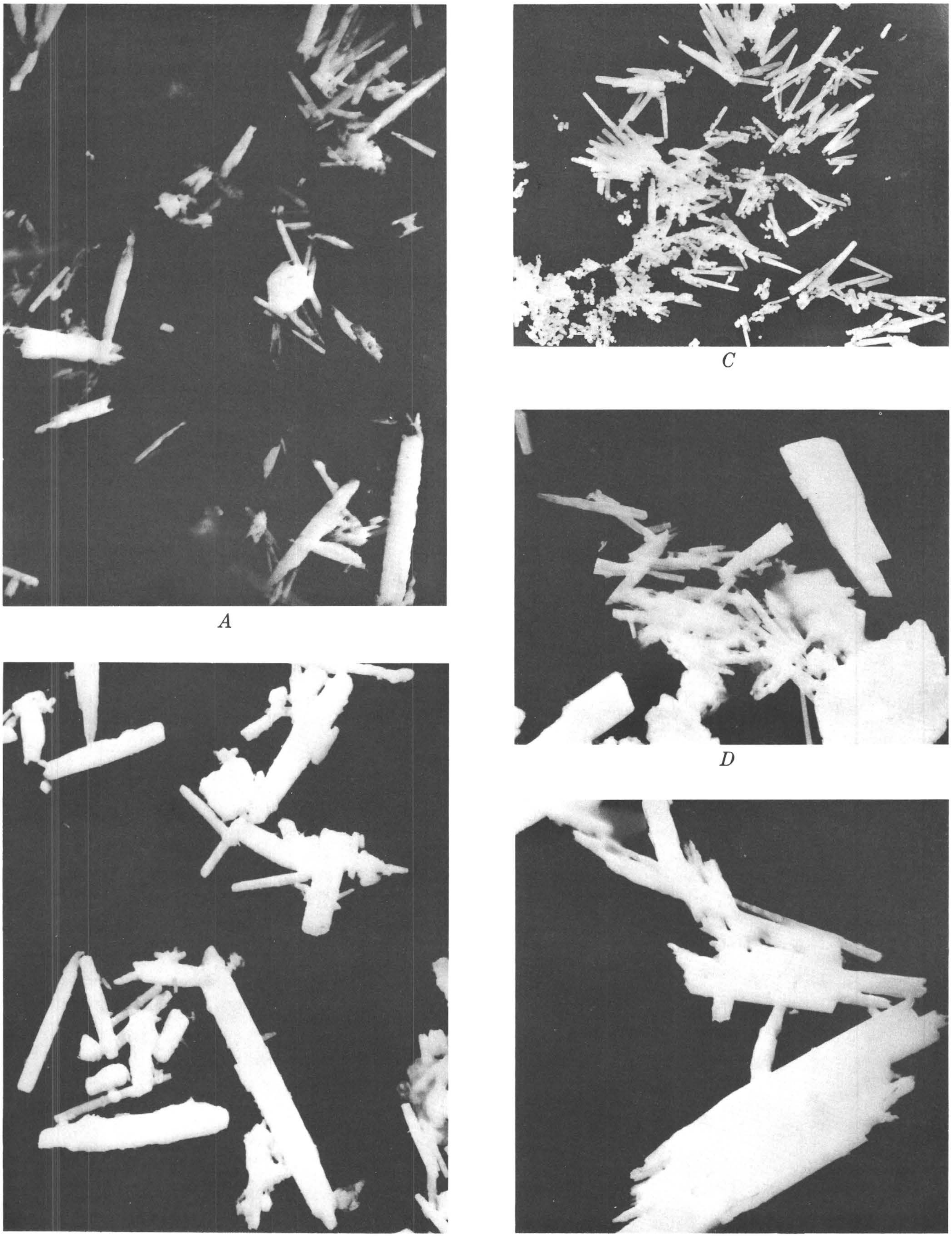
E

ARAGONITE NEEDLES FROM TOP SEDIMENTS

PLATE 4

[All electron micrographs at magnification of 11,750]

A. Suspension from surface water at sta. *C6.*
B. From clay fraction of top sediment at sta. *C6.*
C. Precipitate from slow (overnight) mixing of $CaNO_3$ and $NaCO_3$ solutions at 50°C.
D. Precipitate from passing CO_2 free air through surface water from bank-edge sta. *A1′* for 3 weeks at 26°C.
E. Precipitate from passing CO_2 free air through surface water from Straits of Florida sta. *GSz* for 2 weeks at 24°C.



A

B

C

D

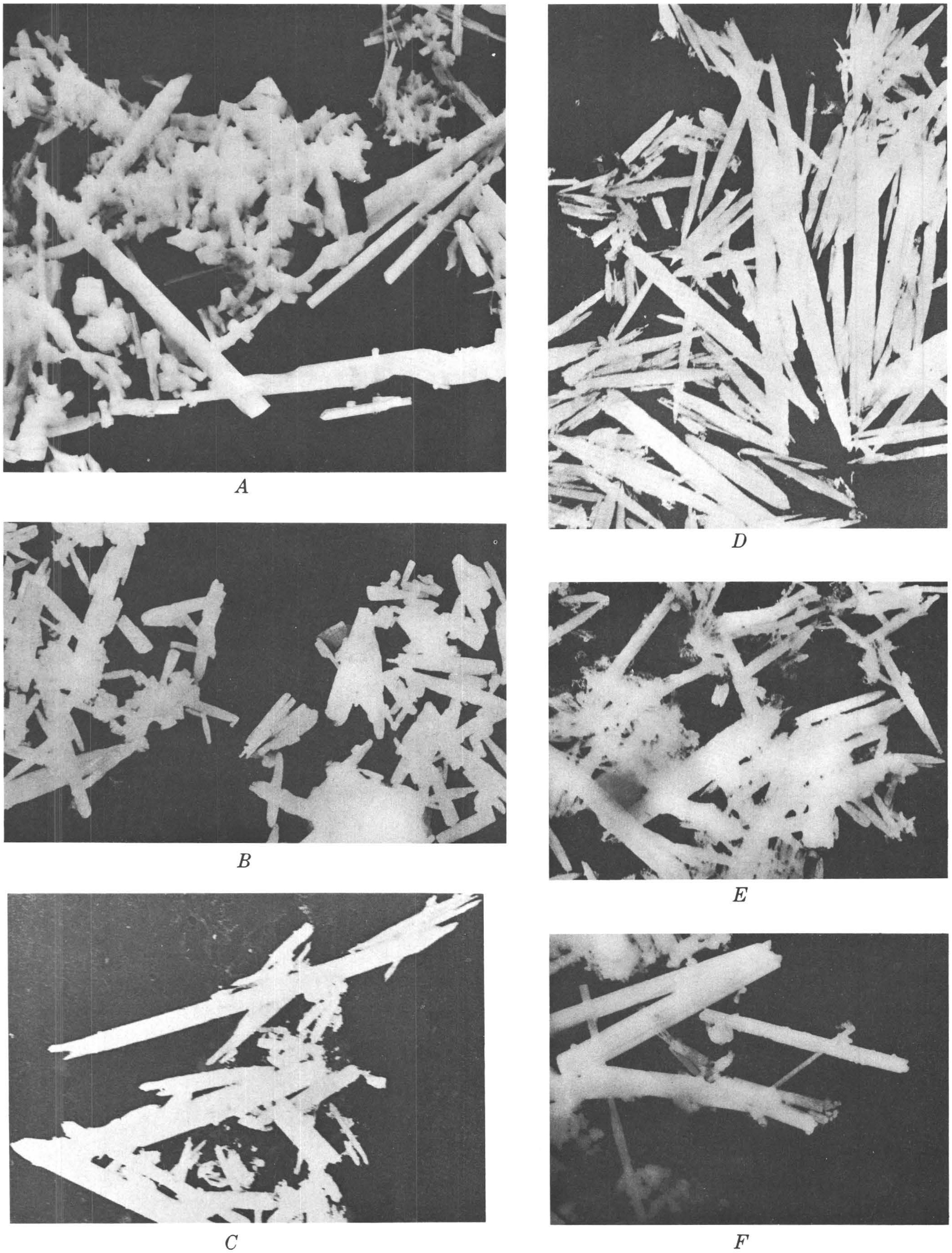
E

ARAGONITE NEEDLES FROM SUSPENSION AND TOP SEDIMENTS AT STATION *C6* AND PRECIPITATED FROM NATURAL WATERS AND SYNTHETIC SOLUTION

PLATE 5

[All electron micrographs at magnification of 11,750]

A. *Halimeda*, sta. *D3*.
B. *Batophora*, sta. *C7a*.
C. *Rhipocephalus*, sta. *C3*.
D. *Penicillus*, sta. *C3*.
E. *Avrainvillea*, sta. *C3*.
F. *Udotea*, sta. *C3*.


A B C D E F

ARAGONITE NEEDLES OF ALGAL ORIGIN

PLATE 6

A, Fragments of dasycladacean algae (upper left) and *Halimeda* (right and bottom margins), × 22. From top sediment at sta. *A6*.

B, Fresh *Halimeda* fragments, × 11. From surface sediment at sta. *A6*.

C. Small mollusk shells, × 8. From top sediment at sta. *A6*.

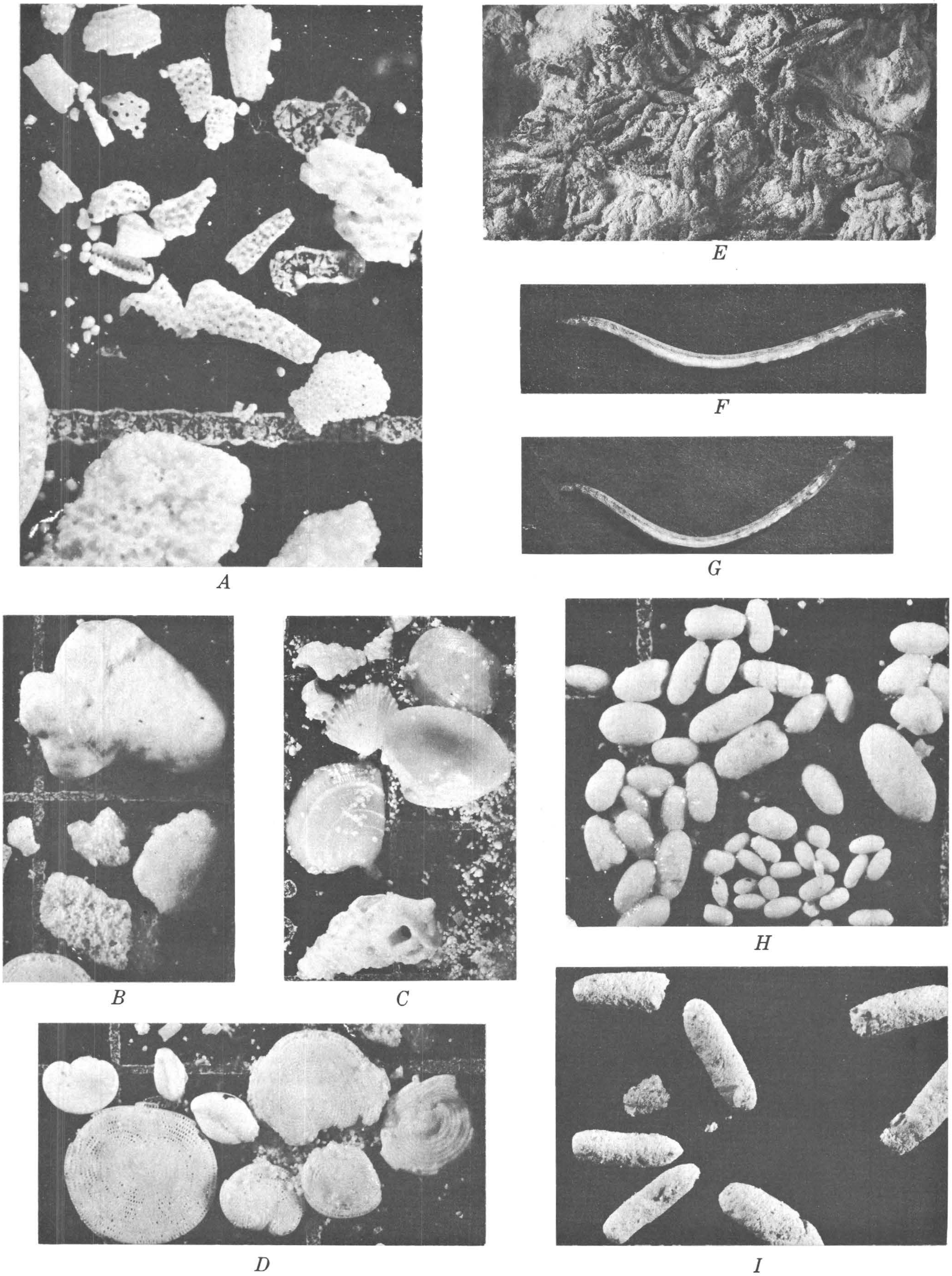
D. Foraminifera (*Archaias* and miliolids), × 11. From top sediment at sta. *A6*.

E. Loose slab, × 1, of indurated sediment from sta. *C7*, after drying, showing cover of now prone but formerly erect cylindrical dasycladacean algae (*Batophora* sp.) and a few individuals of the small cerithiid gastropod *Batillaria* (*Lampanella*) *minima* Gmelin.

F–G. The principal ovoid pellet maker, *Armandia maculata* (Webster), a polychaete annelid of the family Opheliidae (identified by Dr. Marion Pettibone). Both photographs show the same animal at the same magnification (× 2.5) at successive stages of shrinkage under the camera lights. Resultant constriction of the mud-filled gut produced or emphasized the pellets seen to the right in fig. 7. From sta. *It′*.

H. Ovoid pellets of different sizes, × 15. From top sediment at sta. *A6*. The pellets at the lower left are stuck together with gum tragacanth.

I. Fecal pellets of *Chiton tuberculatus* Linné, × 8. From seaward shore at south end of South Cat Cay.



SOME COMPONENTS OF THE SAND FRACTION

PLATE 7

A. Pellets from top sediment at sta. *E6*, × 70, thick section in polarized light, matrix synthetic.

B. Radial aragonite growth at small pellet boundaries and contacts in new grapestone lump from top sediment at sta. *D9*, × 250, crossed nicols; enlargment of part at upper left of fig. *C*.

C. Part of new grapestone lump from top sediment at sta. *D9*, × 50, thick section in plain transmitted light. (See fig. *B*.)

D. Old grapestone lump and pellets from top sediment at sta. *E6*, × 25, thick section in synthetic matrix, plain transmitted light.

E. Superficial ooids with original pelletal centers recrystallized to clear fine-grained calcite and surrounded by fine-grained calcite matrix. Rock floor beneath thin sediment cover at sta. *D1*, × 50, thin section in plain transmitted light.

F. Pellets and ooids with pelletal centers surrounded by fine-grained calcite matrix; sample from rock floor beneath thin sediment cover at sta. *D1*, × 50, thin section in plain transmitted light.

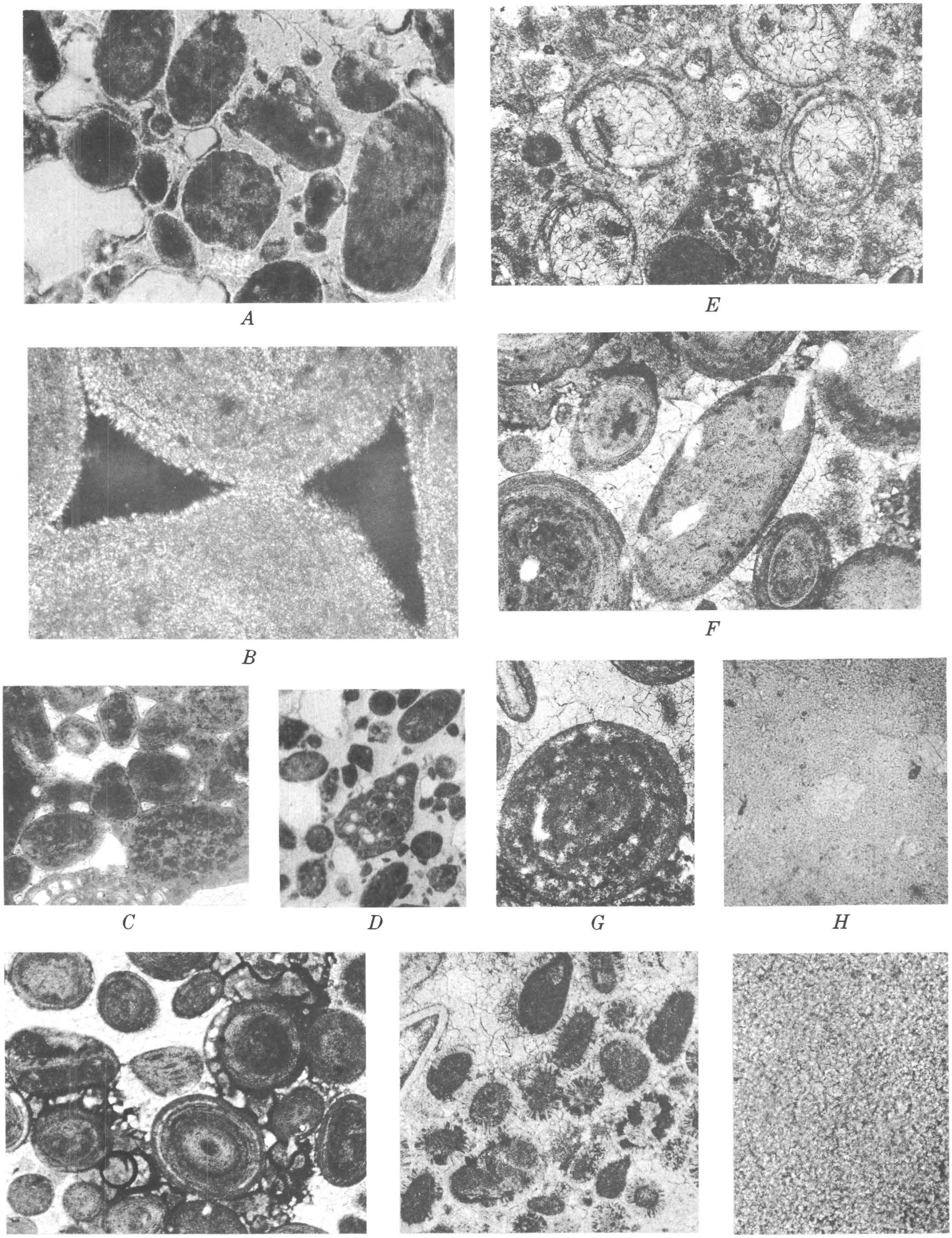
G. Ooid with recrystallization centers and in calcitic matrix, × 50, thin section in plain transmitted light. Slightly emerged oolitic limestone from Fresh Creek entrance, east side Andros Island.

H. Thin section of limestone made experimentally from limemud from sta. *G1*; pressure 350 kg/cm^2 (5,000 psi), temperature 200°C, time 27 days; compressive strength 170 kg/cm^2 (2,400 psi). Plain transmitted light at × 300. Stellate object near center is a section of a burrlike didemnid tunicate spicule. Compare with fig. *J*.

I. Thin section of slightly emerged oolitic limestone from Fresh Creek entrance, east side Andros Island, × 25, plain transmitted light.

J. Pelletal and oolitic limestone of Early Ordovician age, × 25, thin section in plain transmitted light. Note recrystallization of ooidal rims and matrix but preservation of fine grain and organic coloration of pellets. Sample from 22 feet above base of calcitic facies of Gorman formation, Ellenburger group, Warren Springs section, central Texas (Cloud and Barnes, 1948, p. 273).

K. Subaphanitic limestone of Early Ordovician age for comparison with fig. *H*; thin section at × 250 in plain transmitted light. Sample from 240 feet above base of calcitic facies of Gorman formation, Ellenburger group, Warren Springs section, central Texas (Cloud and Barnes, 1948, p. 270).



A *E*

B *F*

C *D* *G* *H*

I *J* *K*

SECTIONS OF PELLETS AND LUMPS AND OF NATURAL AND MADE ROCK

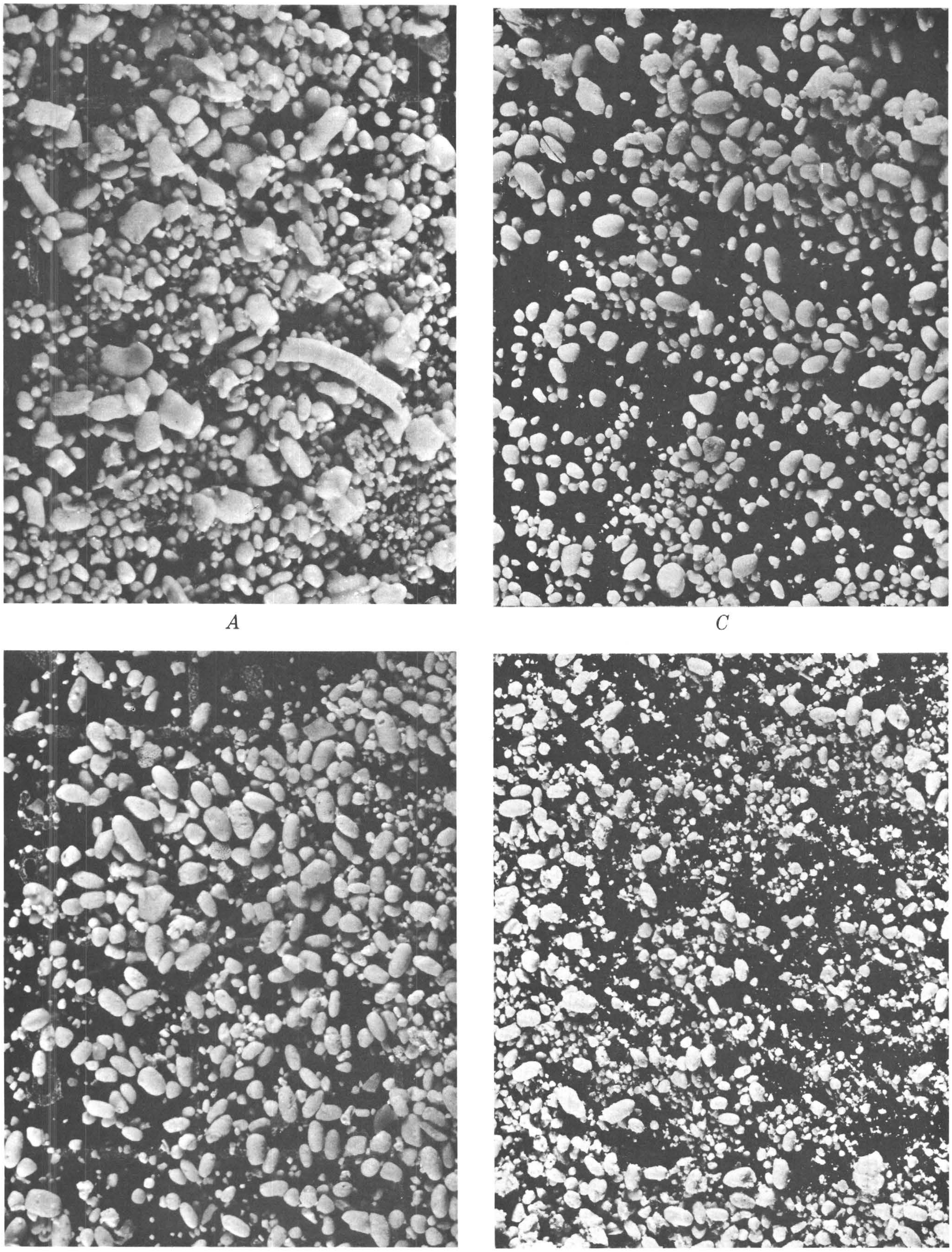
PLATE 8

A. Pellet and skeletal sand with numerous calcium carbonate impregnated and "polished" *Halimeda* fragments, × 10. Washed and screened surface sediment from sta. *D8*.

B. Washed and screened sand fraction, × 10, from sta. *A6*, showing dominance of only moderately indurated ovoid pellets and a few unimpregnated *Halimeda* fragments.

C. Pellet sand, × 10. Unwashed, unscreened top sediment from sta. *E4*. Grapestone lumps (of Illing 1954) in upper quarter.

D. Pellet sand, × 10. Unwashed, unscreened top sediment from sta. *E6*.



A *C*

B *D*

SAND FRACTION OF BANK SEDIMENTS

PLATE 9

A. Sand fraction with pellets, aggregates, and occasional *Halimeda* and dasycladacean fragments, × 10. Top sediment from sta. *B7*.

B. Unwashed top sediment from sta. *G3*, × 20.

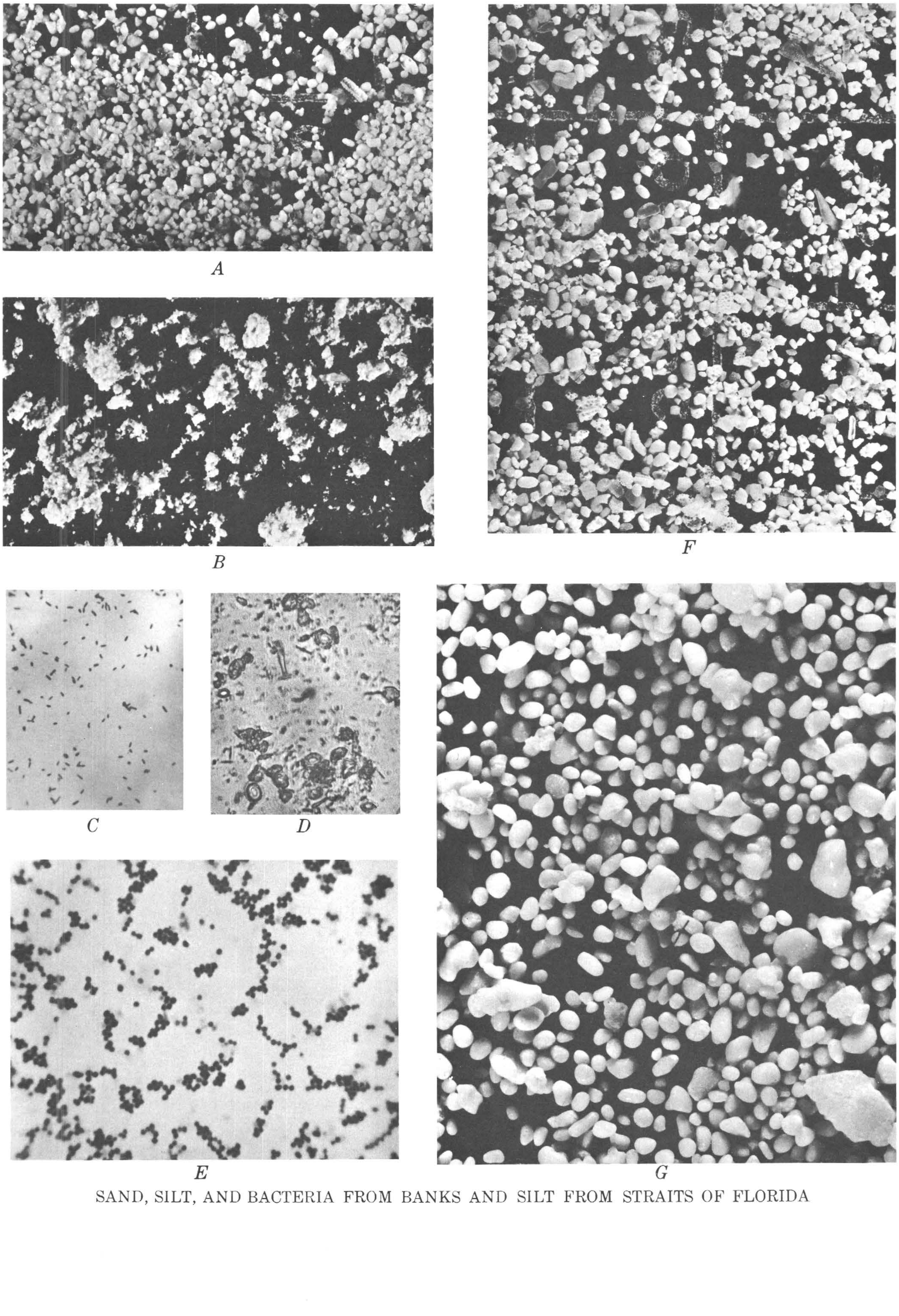
C. Hydrogen fractionating and CO_2 producing bacterium, cf. *Pseudomonas* sp., from 15 cm below sediment-water interface at sta. *G4*, × 800. Abundance in sediment sample 10^{10} per gram wet weight.

D. Silt fraction with discoasters, rhabdoliths, and aragonite needles, from top sediment at Straits of Florida sta. *GSx*, × 750.

E. Ammonium producing bacterium, *Micrococcus*, from water column at sta. *G4*, × 1000. Abundance 10^4 per liter H_2O.

F. Sand fraction with about 15 percent (about 3 percent of total sediment) *Halimeda* and other algal fragments, pellets, aggregates, Foraminifera, and rare ostracods and mollusk fragments, × 10. From top sediment at sta. *B6*.

G. Pellet sand from top sediments at sta. *D9*, × 20. Note well-indurated polished appearance of pellets and rounded *Halimeda* fragments.



A

B

C

D

E

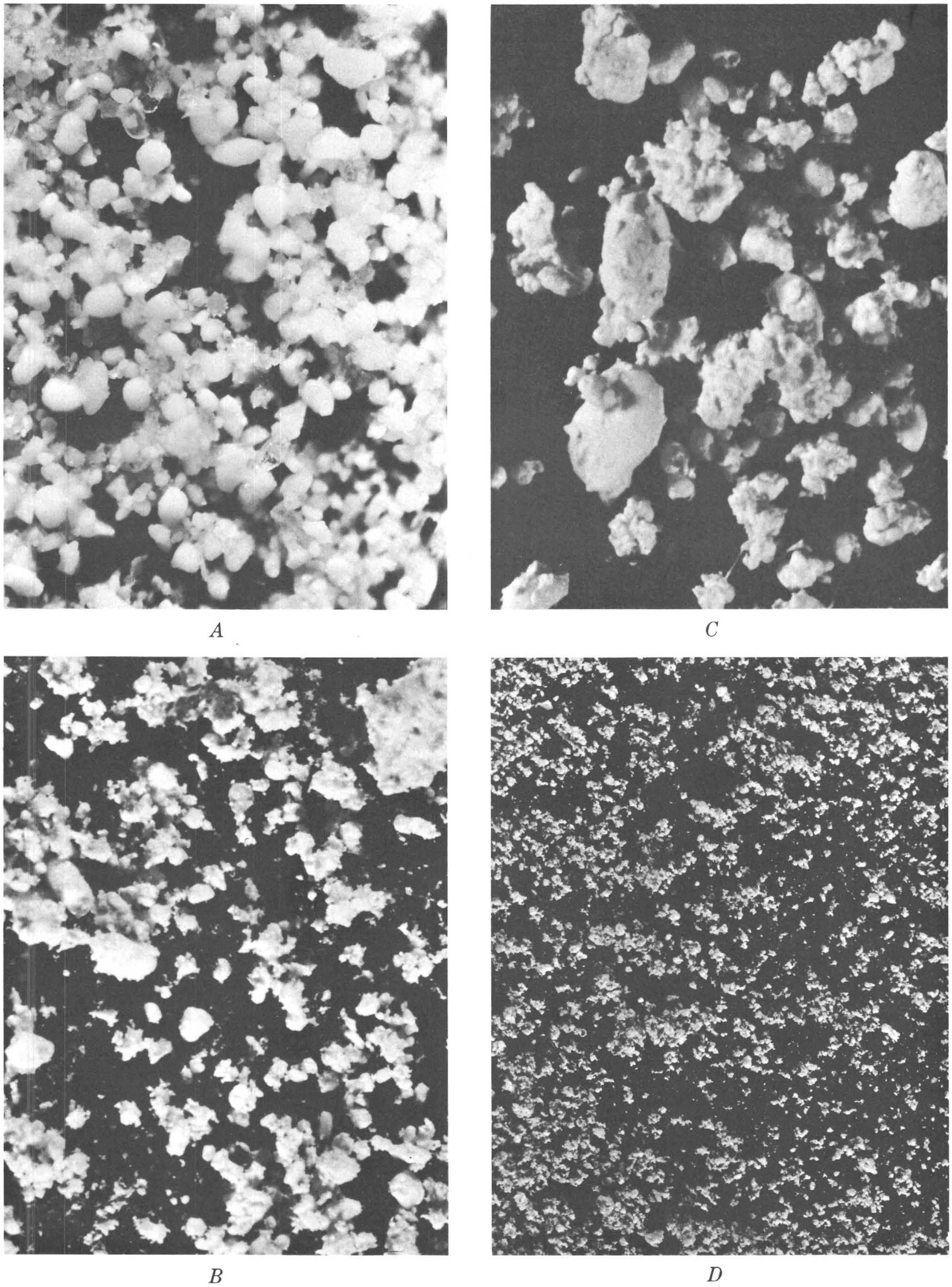
F

G

SAND, SILT, AND BACTERIA FROM BANKS AND SILT FROM STRAITS OF FLORIDA

PLATE 10

A. Silt fraction with many tiny pellets and aggregates and with scattered 50μ burrlike dermal sclerites of a didemnid tunicate cf. *Didemnum candidum* Savigny (as at center), × 100. Surface sediment at sta. *A6*.
B. Dried, raw sample from 15 cm below surface of sediment at sta. *B6*, × 40.
C. Dried, raw sample from 10 cm below surface of sediment at sta. *B4*, × 40.
D. Dried, raw sample of surface sediment at loc. 20/1, east side of South Bight, × 10.



SILT AND FINE SAND FROM MIDBANK AND SOUTH BIGHT SEDIMENTS

☆ U. S. GOVERNMENT PRINTING OFFICE: 1962 O - 576468