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RELATION OF SALINITY TO THE CALCIUM CARBONATE CONTENT OF MARINE SEDIMENTS

BY

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RELATION OF SALINITY TO THE CALCIUM CARBONATE CONTENT OF MARINE SEDIMENTS

By PARKER D. TRASK

ABSTRACT

The calcium carbonate content of sediments is influenced by many factors, such as temperature, depth, salinity, hydrogen-ion concentration of the water, degree of saturation of the water with calcium carbonate, activity of living organisms, and proportion of terrigenous debris in the sediments. Many of the factors are interrelated. The temperature, for example, affects the solubility of calcium carbonate in sea water, it influences the growth of living organisms, it varies the salinity because of its effect on evaporation, and it modifies the action of several other factors. Most of the factors that affect the formation and deposition of calcium carbonate operate simultaneously, and the relative importance of the effects of the individual factors varies in different parts of the ocean. It is difficult, therefore, to isolate a single factor and ascertain the magnitude of its effect in comparison with the effect of some other factor. This paper, however, is an attempt to discuss the relation of the calcium carbonate content of marine sediments to the salinity of the water, with particular reference to the surface layers.

The problem is approached in three ways—(1) by a discussion of the effect of the salinity upon the solubility of calcium carbonate in sea water (because of the dominant influence of the solubility on the formation of solid calcium carbonate in the sea); (2) by a statistical study of the relation of the salinity to the calcium carbonate content of sediments in many parts of the world; and (3) by the preparation of a map showing the distribution of calcium carbonate on the floor of the ocean with respect to the salinity of the surface water. In each of these lines of attack the effect of temperature is also considered, so that the influence of salinity may be compared with the effect of a factor whose influence is generally recognized.

The studies of the solubility relations indicate that in the upper layers of water, in which presumably most of the solid calcium carbonate is formed, an increase in salinity from 34 to 35 parts per thousand raises the degree of saturation of the water with respect to calcium carbonate 8.4 percent, and that an increase in temperature from 20° to 21° C. raises the degree of saturation 4.6 percent. That is, a rise of 1 part per thousand in salinity affects the solubility of calcium carbonate approximately as much as an increase of 2° in temperature. In many parts of the ocean the salinity of the surface water changes 1 part per thousand in roughly the same distance as the temperature of the surface water changes 2°. The surface temperature, however, varies more during the course of a year than the surface salinity, and the temperature decreases greatly with depth, but the salinity does not. It would seem, therefore, that in several parts of the ocean salinity has as great an effect as temperature on the solubility of calcium carbonate, but that the total effect of salinity on the solubility is less than that of temperature.

In the statistical part of the investigation the relation of the calcium carbonate content of the sediments to the surface salinity, surface temperature, and depth was ascertained by a series of averages, by graphs based on these averages, and by coefficients of correlation of the data represented by these averages. The surface salinity and surface temperature were con-

sidered because of the importance of the upper layers of water in the formation of solid calcium carbonate. However, subsequent to the compilation of the statistical results, it has been shown by other workers that the upper 200 meters of water probably represents the zone in which most of the solid calcium carbonate is formed. Consequently the results might have been more reliable if the average salinity and average temperature in this zone had been considered instead of surface salinity and temperature. The surface salinity indicates the average salinity in this zone better than the surface temperature indicates the average temperature. This difference may account for the better relation that was found between calcium carbonate and surface salinity than between calcium carbonate and surface temperature.

The series of averages and the accompanying graphs indicate that the calcium carbonate content of the sediments increases as the surface salinity rises. The rate of rise in calcium carbonate content is greatest between salinities of 34 and 36 parts per thousand. Sediments in areas in which the salinity of the surface water is less than 34 parts per thousand in general contain less than 5 percent of calcium carbonate, and those in areas in which the salinity is more than 36 parts as a rule contain more than 50 percent of calcium carbonate. The critical salinity seems to be about 35 parts per thousand, which is approximately the average for the ocean. The calcium carbonate content of the sediments likewise increases as the temperature increases and as the depth decreases.

The relation for the surface temperature is less well defined than that for salinity or that for depth. The critical depth with respect to calcium carbonate content of the sediments seems to be about 1,500 fathoms, as the calcium carbonate content of sediments in water less than 1,500 fathoms deep is much more nearly constant than that of sediments in water more than 1,500 fathoms deep, particularly for sediments that were laid down near the shore.

The results of the determination of the coefficients of correlation are similar to those based on the averages. (The coefficient of correlation is a mathematical expression of the degree of relationship between two variables, such as calcium carbonate content of sediments and surface salinity.) The coefficients of correlation indicate that the calcium carbonate content is fairly definitely related to surface salinity for both pelagic and near-shore deposits and to depth for pelagic deposits. It is less distinctly related to depth for near-shore deposits and to temperature for both near-shore and pelagic deposits.

The areal distribution of calcium carbonate on many parts of the sea floor varies in sympathy with the surface salinity and to a smaller extent with surface temperature, but on several parts, notably in the South Atlantic, it does not. The results of an empirical investigation of this type are naturally attended by a certain amount of ambiguity due to the effect of other factors, such as the proportion of clastic material, that mask the effect of salinity; but they are sufficiently reliable to indicate that the surface salinity is definitely related to the calcium carbonate content of the sediments and that its effect is similar in order

of magnitude to the effect of surface temperature. The empirical relations of the calcium carbonate content of the sediments thereby agree with the solubility relations of calcium carbonate in sea water in indicating that salinity is an important factor in the deposition of calcium carbonate.

The relation between the calcium carbonate content of sediments and the salinity, however, may in part not be a cause and effect relation. It is possible that the surface salinity may be a rough index of the degree of saturation of the water with calcium carbonate. Thus, areas of high salinity may be super-saturated, with the result that they favor the precipitation of calcium carbonate.

Two geologic applications of the results are considered—one relating to the deposition of red clay, the other to past climates. An increase in degree of saturation of the deep water in the ocean, due to an increase in temperature, may result in less calcium carbonate being dissolved from particles as they fall to the sea floor, thus causing the calcium carbonate content of the sediments to be increased. As red clay is characterized by a small calcium carbonate content, the quantity of red clay on the sea floor under such conditions would be less than at present. Consequently, the scarcity of red clay among ancient sediments may be accounted for by increases in the degree of saturation of the water in the past.

As the calcium carbonate content of sediments in areas of high salinity is generally large, and as an arid climate would favor the development of high salinity in the sea water, it is suggested that some alternations between limestone and calcareous shale or between calcareous shale and noncalcareous shale may be indicative of changes in climate. The more calcareous layers would represent more arid periods, when evaporation was high and influx of terrigenous debris was small, and the less calcareous layers would represent more humid periods, when evaporation was low and influx of terrigenous debris was great.

INTRODUCTION

The object of this report is to show that the salinity of the sea water is a factor influencing the calcium carbonate content of marine sediments. In order to ascertain the relative importance of salinity, the effect of salinity on the deposition of calcium carbonate is compared with the effect of other factors, chiefly temperature. The problem has been approached in three ways—(1) study of the factors influencing the deposition of calcium carbonate, with special emphasis on the effect of salinity and temperature upon the solubility of calcium carbonate in sea water; (2) statistical study of the relation of salinity, temperature, and depth to the calcium carbonate content of near-shore and pelagic sediments; and (3) preparation of a map showing the relation of the areal distribution of calcium carbonate on the sea floor to the surface salinity, surface temperature, and depth of water. The results obtained in all these lines of attack are in accord in indicating that salinity is definitely related to the calcium carbonate content of sediments.

I am indebted to Dr. Roger Revelle and Dr. E. G. Moberg, of the staff of the Scripps Institution of Oceanography, La Jolla, Calif., for assistance in calculating the effect of salinity and temperature on the solubility of calcium carbonate in sea water, and for their kindness in giving me access to unpublished data. I wish to thank Dr. T. Wayland Vaughan, director of the

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FACTORS INFLUENCING THE CALCIUM CARBONATE CONTENT OF SEDIMENTS

GENERAL FACTORS

The calcium carbonate content of sediments is affected by four main groups of factors—(1) the source of particles of calcium carbonate in the water, (2) the transportation of the particles while they are being deposited, (3) the changes that take place in the sediments after the particles have been deposited, and (4) the proportion of particles of clastic origin in the sediments. The source of calcareous particles in the water is the most influential of these four groups of factors and is discussed in detail below.

In the transportation of the particles the main considerations are the strength of the currents, the depth of water, the size and shape of the particles, the degree of saturation of the water with calcium carbonate, the rate of solution of calcareous particles, the shape of the ocean floor, and the buoyancy of the particles. The chief influence of salinity in the transportation of the particles is its effect on the degree of saturation of the water, which in turn controls the rate of solution of calcareous particles. Salinity influences the density of the water, and as the rate at which particles fall depends upon their buoyancy—that is, the difference in density between the particles and the liquid through which they fall—the salinity might have a very slight effect on the rate at which the particles sink. Moreover, in the ocean, currents such as the Gulf Stream are caused by the attempt of masses of water of different density to come to equilibrium, and as salinity is one of the main factors controlling density, it would therefore indirectly affect the transportation of particles.

The changes that take place in the sediments after the particles have been deposited are mainly connected with the processes of diagenesis—that is, lithification. The main factor with which salinity might be associated in the processes of diagenesis is the removal of calcium carbonate by solution of particles.

The chief factors governing the proportion of particles of clastic origin in the sediments are (1) distance from shore—near-shore sediments in general contain much clastic debris, and pelagic sediments contain relatively little; (2) climate—sediments deposited near arid regions consist of less clastic material than those near humid regions; (3) relief of land—sediments laid down near areas of low relief, like Florida, contain less clastic

material than those near areas of high relief, like California; (4) location with respect to the mouths of streams—sediments off the mouths of large streams contain much more clastic debris than those off small streams; and (5) the rate at which calcareous particles are added to the sediments. The salinity of the water, except for its effect on the rate at which calcareous particles are added to sediments, influences but slightly the quantity of clastic debris in the sediments.

Calcium carbonate gets into the water in a solid form in three ways—(1) by chemical precipitation, (2) as remains of living organisms, and (3) as detrital particles derived from limestone. The presence of limestone areas in the drainage basins of streams entering the sea may locally be the main source of calcium carbonate in sediments deposited near shore; but in general the calcium carbonate content of marine sediments is due chiefly to chemical precipitation or remains of organisms. The relative importance of these two sources is a controversial problem that has not yet been solved satisfactorily. In fact, so little is known about the processes by which organisms extract calcium carbonate from water for their bodily needs that it seems impracticable to attempt to discuss this phase of the subject in the present report. However, both chemical precipitation of calcium carbonate and the formation of calcareous material by organisms are favored by increased saturation of the sea water with calcium carbonate.

SOLUBILITY OF CALCIUM CARBONATE IN SEA WATER MAIN FACTORS

The solubility of calcium carbonate in sea water has been studied intensively in the past few years by several workers, among whom are Moberg, Revelle, and their associates at Scripps Institution; Buch, Gripenberg, and their associates at Helsingfors; and Wattenberg, who accompanied the *Meteor* expedition to the South Atlantic.¹ The discussion of the solubility relations of calcium carbonate in the present report is based on the work of these investigators. As their publications describe the problem in full and contain extensive bibliographies, only a summary of the features that relate to the question of salinity is included here.

The chemical precipitation of calcium carbonate depends upon the degree of saturation of the water with calcium carbonate. If the water is undersaturated, solid particles of calcium carbonate can pass into solution; if it is oversaturated, solid particles can be formed by precipitation from the water. Precipitation, how-

ever, does not necessarily take place as soon as the saturation point is reached. The water can become supersaturated to a considerable extent before beginning to produce solid calcium carbonate. The precipitation of calcium carbonate from solution is favored by the presence in the water of solid particles, either of calcium carbonate or of something else. The instigation of precipitation by such an action is called "seeding."

The saturation point depends upon the law of mass action. That is, the water is saturated when the product of the concentration of calcium and carbonate equals a constant, called the "apparent solubility product constant." The relation expressed symbolically is

$$[\text{Ca}^{++}][\text{CO}_3^{--}] = K'_{\text{CaCO}_3}$$

The apparent solubility product constant is practically independent of the quantity of calcium carbonate or the concentration of calcium and carbonate in the water, but it is not constant with respect to other variables, for if the temperature, salinity, pressure, or concentration or kinds of ions other than calcium or carbonate change, the apparent solubility product constant likewise changes.

If the concentration of calcium is high, a small concentration of carbonate will make the water saturated with respect to calcium carbonate, and if the concentration of calcium is low, a large concentration of carbonate is needed to make the water saturated. If the product of calcium and carbonate exceeds the apparent solubility product constant, calcium carbonate can be removed from solution by precipitation of solid calcium carbonate until the product of the calcium and carbonate ions equals the solubility product constant, but whether or not under any particular circumstances calcium carbonate will be precipitated in the sea depends on the laws governing supersaturation, which are not yet well understood.

According to the relations governing the solubility of calcium carbonate in the sea, three main factors, therefore, are concerned—(1) the concentration of calcium, (2) the concentration of carbonate, and (3) the apparent solubility product constant. The concentration of calcium at any given depth² depends almost entirely upon the salinity, because the salinity represents the concentration of total solids in solution, and if the salinity changes, then it follows that the concentration of all the salts, including those of calcium, likewise changes. The apparent solubility product constant is influenced by several factors, including temperature and salinity. It increases with rise in salinity and decreases with rise in temperature (table 1). The concentration of carbonate depends upon a large number of variables and is by far the most influential factor in the deposition of calcium carbonate.

¹ Moberg, E. G., Greenberg, D. M., Revelle, R., and Allen, E. C., The buffer mechanism of sea water: Scripps Inst. Oceanography Bull., Tech. ser., vol. 3, no. 11, pp. 231-278, 1934. Buch, K., Harvey, H. W., Wattenberg, H., and Gripenberg, S., Ueber das Kohlensäuresystem im Meerwasser: Conseil perm. expl. mer Rapports et procès-verbaux, vol. 79, pp. 1-70, 1932. Wattenberg, H., Kalziumkarbonat- und Kohlensäuregehalt des Meerwassers: Wiss. Ergeb. Deutschen Atlantischen Exped. *Meteor*, 1925-27, Band 8, Teil 2, pp. 1-333, 1933. Revelle, R., and Fleming, R. H., The solubility product constant of calcium carbonate in sea water: 5th Pacific Sci. Cong., Victoria and Vancouver, Proc., vol. 3, pp. 2089-2092, 1933. Revelle, R., Physicochemical factors affecting the solubility of calcium carbonate in sea water: Jour. Sedimentary Petrology, vol. 4, pp. 103-110, 1934.

² Revelle, R., Physicochemical factors affecting the solubility of calcium carbonate in sea water: Jour. Sedimentary Petrology, vol. 4, p. 107, 1934.

INFLUENCE OF CARBON DIOXIDE

Carbonate ions represent one of the three forms in which carbon dioxide occurs in sea water. The other two forms are bicarbonate ions and carbonic acid. For a strictly accurate discussion, carbonic acid and free carbon dioxide should be considered separately, but their effects are so nearly alike that for the purpose of this discussion they are treated as one variable.³

These three forms of carbon dioxide are related to one another according to definite laws, which are expressed symbolically as follows:

$$\frac{[\alpha H^+][HCO_3^-]}{[H_2CO_3]} = K_1' \text{-----} (1)$$

$$\frac{[\alpha H^+][CO_3^{--}]}{[HCO_3^-]} = K_2' \text{-----} (2)$$

$$B = [HCO_3^-] + 2[CO_3^{--}] \text{-----} (3)$$

In these equations B is the equivalent concentration of titratable base; αH , the activity or effective concentration of hydrogen ions as indicated by the pH; K_1' and K_2' , the respective apparent dissociation constants of the first and second steps in the ionization of carbonic acid; and the brackets denote molar concentration.⁴

The first equation indicates that the concentration of bicarbonate depends upon the concentration of hydrogen ions and undissociated carbonic acid and on a constant K_1' , called the "first apparent dissociation constant of carbonic acid." The second equation indicates that the concentration of carbonate depends upon the concentration of hydrogen and bicarbonate and upon a constant K_2' , called the "second apparent dissociation constant of carbonic acid." Thus if the concentration of any one of the three forms of carbon dioxide—namely, carbonate, bicarbonate, or carbonic acid—should change, the concentration of the other two forms must also change in order to satisfy the relations expressed in equations 1 and 2. The two apparent dissociation constants, K_1' and K_2' , similar to the apparent solubility product constant of calcium carbonate, K'_{CaCO_3} , are affected by external conditions, such as temperature, salinity, and the activity of the ions in the solution; but they are practically unaffected by the concentration of hydrogen, carbonate, and bicarbonate ions and by carbonic acid.

Sea water, being alkaline, contains an excess of base that can be balanced against a weak acid like carbonic acid. At a salinity of 34 parts per thousand the amount of carbon dioxide that can be balanced against this excess base is approximately 103 milligrams per liter.⁵ As the carbonate radical has double the valence of the bicarbonate radical, only one-half as much carbon di-

oxide—that is, 51.5 milligrams per liter—in the form of carbonate is needed to balance the excess base. If the quantity of carbon dioxide were intermediate between 51.5 and 103 milligrams per liter, part of the base could be balanced by carbonate and part by bicarbonate. The relation is expressed symbolically in equation 3. This equation, however, is not strictly accurate, because part of the excess base is balanced by acids of boron⁶ and perhaps by other acids as well. According to Revelle and Fleming, the influence of borate becomes greater as the hydrogen-ion concentration decreases—that is, as the pH increases. At a hydrogen-ion concentration of 10^{-9} —that is, at a pH of 9—about 16 percent of the excess base is balanced by borates, but at a pH of 8.0 to 8.2, which is the general average for the surface of the sea, the proportion of excess base balanced by borates is less than 4 percent,⁷ which indicates that nearly all the excess base is balanced by some form of carbonic acid. Below the surface of the ocean the pH decreases to about 7.8,⁸ and the influence of boron is insignificant. Equation 3, which shows the relation of carbonic acid to excess base, therefore seems to be approximately correct for the conditions that usually prevail in the sea, but to be strictly accurate it should include the effect of boron.

Similarly, to be strictly accurate the excess base should be corrected for the effect of hydrogen and hydroxyl ions, but according to Moberg and his associates⁹ this effect is not great for conditions that ordinarily prevail in the sea. Consequently, in order to simplify the calculations, the effect of these ions on the excess base was not considered in connection with equation 3.

The distribution of the three forms of carbon dioxide in the water therefore depends on the three fundamental relations expressed by equations 1, 2, and 3. These three equations may be solved simultaneously and the total effect expressed as follows:

$$[HCO_3^-] = \frac{K_1'}{4K_2'} [H_2CO_3] \left(\sqrt{1 + \frac{8BK_2'}{K_1'[H_2CO_3]}} - 1 \right) \text{---} (4)$$

An expression for the concentration of carbonate instead of the bicarbonate could have been given, but it would be in a form that would make numerical computation difficult.

It follows from equations 1 to 4 and also from experimental work of Moberg and his associates¹⁰ that the hydrogen-ion concentration increases—or, as generally

³ Moberg, E. G., Greenberg, D. M., Revelle, R., and Allen, E. C., The buffer mechanism of sea water: Scripps Inst. Oceanography Bull., Tech. ser., vol. 3, p. 238, 1934.

⁴ For detailed explanation of these equations see Moberg, E. G., and others, op. cit., pp. 235-268.

⁵ Moberg, E. G., and others, op. cit., p. 269.

⁶ Revelle, R., and Fleming, R. F., The solubility product constant of calcium carbonate in sea water: 5th Pacific Sci. Cong., Victoria and Vancouver, Proc., vol. 3, pp. 2089-2092, 1933.

⁷ Buch, K., Der Borsäuregehalt des Meerwassers und seine Bedeutung bei der Berechnung des Kohlensäuresystems im Meerwasser: Conseil perm. expl. mer Rapports et procès-verbaux, vol. 85, pp. 71-75, 1933.

⁸ Wattenberg, H., Kalziumkarbonat- und Kohlensäuregehalt des Meerwassers: Wiss. Ergeb. Deutschen Atlantischen Exped. Meteor, 1925-27, Band 8, Teil 2, pp. 268-308, 1933.

⁹ Moberg, E. G., and others, op. cit., pp. 243-244.

¹⁰ Idem, p. 269.

reported, the pH decreases—as the total content of carbon dioxide rises. Thus, at a pH of 8.5 the total content of carbon dioxide is about 83 milligrams per liter, of which about 20 milligrams is in the form of carbonate, 63 milligrams in the form of bicarbonate, and less than 1 milligram in the form of carbonic acid. At a pH of 8.1, which prevails at the surface of the ocean, the total content of carbon dioxide is about 93 milligrams, of which 10 milligrams occurs as carbonate, 83 milligrams as bicarbonate, and less than 1 milligram as carbonic acid; and at a pH of 7.5, the total content of carbon dioxide is about 104 milligrams, of which less than 1 milligram is carbonate, 103 milligrams bicarbonate, and about 1 milligram carbonic acid. As the pH falls below 7.5 the total content of carbon dioxide rises. This increase is almost entirely in the free carbon dioxide or carbonic acid. The content of carbon dioxide in the form of bicarbonate and carbonate remains about 103 milligrams and less than 1 milligram per liter, respectively.

The relationships expressed above indicate that between pH 7.5 and 8.5, which represents practically the entire range for the sea, each unit decrease in total quantity of carbon dioxide means a decrease of two units in bicarbonate and an increase of one unit in carbonate. That is, each decrease of 1 milligram in total content of carbon dioxide causes an increase of 1 milligram of carbon dioxide in the form of carbonate. The gain in carbonate, however, is slightly less than the loss in total content of carbon dioxide, because a decrease in total content of carbon dioxide causes an increase in the pH of the water, which in turn causes more of the excess base to be balanced by borates. Consequently, part of the base that would have to be balanced by carbonate if borates were not present is balanced by borates, and not so much carbon dioxide changes from bicarbonate to carbonate.

This relation of carbonate to total content of carbon dioxide is probably the most significant factor in the deposition of calcium carbonate, as it is most susceptible to change. The total content of carbon dioxide ranges chiefly between 90 and 95 milligrams per liter in the upper layers of the sea, where, as discussed below, most of the calcium carbonate seems to be formed.¹¹ The carbon dioxide in the form of carbonate under such conditions ranges between 8 and 12 milligrams per liter. Thus, a decrease of only 1 percent in the total content of carbon dioxide causes an increase of about 10 percent in the quantity of carbonate. It follows, therefore, that small changes in the total quantity of carbon dioxide in the water have a very pronounced influence on the solubility of calcium carbonate.

The relations governing the quantity of carbonate in the sea water, however, as indicated by the foregoing

discussion, are complicated. The controlling factors are the concentration of carbonic acid and bicarbonate, the total content of carbon dioxide, the hydrogen-ion concentration, and the two apparent dissociation constants of carbonic acid, K_1' and K_2' . These factors, in addition to being interrelated to some extent, are also influenced by other factors. The content of carbonic acid depends upon the content of free carbon dioxide, which in turn is directly affected by the solubility of carbon dioxide in sea water, by the carbon dioxide tension in the air above the water, and by the activity of the organisms in the water. The solubility of free carbon dioxide in the water and the two apparent dissociation constants, K_1' and K_2' , are influenced considerably by the temperature and salinity. The quantity of excess base in the water depends directly upon the salinity, but it is not affected significantly by small changes in temperature (table 1).

EFFECTS OF INDIVIDUAL FACTORS

The foregoing analysis shows that the deposition of calcium carbonate in the sea is affected by many factors and that several of these factors influence the deposition of calcium carbonate in different ways.

TEMPERATURE

The temperature of sea water affects the solubility of calcium carbonate in the water because of its influence on (1) the solubility of free carbon dioxide in the water, (2) the apparent solubility product constant, K'_{CaCO_3} , (3) the two apparent dissociation constants of carbonic acid, K_1' and K_2' , and (4) the hydrogen-ion concentration. It also influences the growth of living organisms, which in turn affect the deposition of calcium carbonate in several ways. Moreover, owing to its effect on evaporation, it influences the salinity of the water. As the temperature changes with depth, it also influences the relations for depth. Finally, it has some minor effects because of its influence on the viscosity and density of the water and because of its relation to the formation of detrital particles by the weathering of limestone.

SALINITY

The salinity of sea water influences the solubility of calcium carbonate in the water because of its relations to (1) the solubility of free carbon dioxide in the water, (2) the constants, K_1' , K_2' , and K'_{CaCO_3} , (3) the hydrogen-ion concentration, and (4) the quantity of calcium and excess base in the water. Like the temperature, it affects the viscosity and density of the water and the growth of living organisms. Owing to its effect on the density of water, it influences the circulation of masses of water in the ocean, with the result that bodies of warm or cold water are moved from their places of formation; and thus the salinity indirectly affects the temperature of the water.

¹¹ Moberg, E. G., and others, op. cit., p. 269.

ORGANISMS

Living organisms may remove calcium carbonate directly from the water to make shells and skeletal material. They may transport particles of calcium carbonate in their digestive tracts. Forms like bacteria may precipitate calcium carbonate directly,¹² or, as suggested by Revelle,¹³ they may instigate the precipitation of calcium carbonate from supersaturated water by a seeding action induced by the presence of their bodies in the water. Living organisms may give off waste products, such as ammonia, which may affect the solubility of calcium carbonate.¹⁴ The most important action of living things in the sea with respect to the precipitation of calcium carbonate, however, is their effect on the part played by carbon dioxide in the water.

The floating plants (phytoplankton) living in the surface layers of the water remove large quantities of carbon dioxide from the water for building organic compounds in their tissues by the aid of photosynthesis. The animals living in the sea, on the other hand, give off carbon dioxide as a waste product. The decomposition of the tissues of dead plants and animals as they fall to the bottom of the sea results in the addition of carbon dioxide to the water. The phytoplankton is confined chiefly to the upper 200 meters of water, in which light penetrates effectively for photosynthesis.¹⁵ The animals are found at nearly all depths but are largely confined to the upper layers, in the zone of phytoplankton, which forms their basic source of food. Decomposition takes place at all depths, but its effect is more evident in the water beneath the zone of phytoplankton. In the upper 100 to 200 meters of water the removal of carbon dioxide by the phytoplankton is greater than the addition of carbon dioxide to the water by animals and by decomposition;¹⁶ but below 200 meters the reverse is true. These phenomena cause the upper 200 meters of water to contain comparatively little carbon dioxide and the water below a depth of 200 meters to contain comparatively much carbon dioxide. Consequently, the surface layers are relatively rich and the lower layers relatively poor in carbonate. The upper layers, therefore, are more highly saturated with calcium carbonate than the lower layers.

Wattenberg¹⁷ has prepared maps showing the degree of saturation of the water in the South Atlantic, which presumably apply in general to the other oceans as

well. The surface water ranges from about 100 percent saturation in polar latitudes to about 150 percent saturation in equatorial latitudes. Below a depth of about 200 meters in polar latitudes and 500 meters in tropical latitudes the water everywhere is undersaturated with calcium carbonate, but in no place is the degree of saturation reported to be less than 90 percent.

Wattenberg's maps are based on a determination of the apparent solubility product constant that is about one-half as large as the determination by Revelle and Fleming,¹⁸ made by a different method.

The solubility product constant of calcium carbonate in sea water has to be determined experimentally and is very difficult to measure. It represents the point of equilibrium at which no calcium carbonate will be dissolved and none will be precipitated from the water. The solubility of calcium carbonate in sea water is very small, and the water tends to become supersaturated before precipitation begins. Consequently, it is not surprising that the results of Wattenberg should differ by 50 percent from those of Revelle and Fleming. The gratifying feature is that they are as close to one another as they are. It would seem, therefore, that the proper order of magnitude of the apparent solubility product constant has been ascertained. However, because Revelle and Fleming's determination of this constant is distinctly greater than Wattenberg's, the estimates of the degree of saturation for the South Atlantic given by Wattenberg may be too high. It nevertheless seems probable that the upper layers of water in the ocean, especially in low latitudes, are saturated with calcium carbonate and that the water below 200 meters is undersaturated.

DEPTH

The depth of water, therefore, is an important factor in the deposition of calcium carbonate. The upper layers of water, which appear to be saturated with calcium carbonate, represent the zone in which calcium carbonate is formed by chemical precipitation, and they also represent the zone in which most of the skeletal material, composed of calcium carbonate, is produced by the action of living organisms. The layers below a depth of 200 meters, where the water is undersaturated with calcium carbonate, represent a zone where calcium carbonate may be dissolved from particles as they sink to the sea floor.

Depth, because of its relation to pressure, also affects the solubility of calcium carbonate.¹⁹ In addition, the temperature of the water decreases from the surface downward, with the result that the deep water can hold more calcium carbonate in solution than the surface layers. The salinity of the deep ocean water is remark-

¹² Bavendamm, W., Die Mikrobiologische Kalkfällung in der tropische See: Archiv Mikrobiologie, Band 3, pp. 205-276, 1932. This paper contains a good bibliography.

¹³ Revelle, R., personal communication.

¹⁴ Murray, J., On the deposits of the Black Sea: Scottish Geog. Mag., vol. 16, p. 684, 1900.

¹⁵ Cf. Hentschel, E., Allgemeine Biologie des süd-Atlantischen Ozeans: Wiss. Ergeb. Deutschen Atlantischen Exped. Meteor, 1925-27, Band 11, 1933.

¹⁶ Wattenberg, H., op. cit., pp. 162, 236.

¹⁷ Idem, pp. 194-205.

¹⁸ Revelle, R., and Fleming, R. F., op. cit., p. 2091.

¹⁹ Wattenberg, H., op. cit., p. 209.

ably constant and differs but little from the general average of the ocean.²⁰ The influence of salinity on calcium carbonate because of changes in depth, therefore, is not great.

CALCULATION OF EFFECT OF CHANGE IN TEMPERATURE AND SALINITY ON SOLUBILITY OF CALCIUM CARBONATE

METHOD OF CALCULATION

The effect of changes in salinity and temperature on the solubility of calcium carbonate in sea water can be computed from the relations given in equations 1 to 4 and from the apparent solubility product constant. The quantity of carbonate in the water can be calculated from equations 3 and 4. The content of bicarbonate is determined from equation 4 by substitution of the figures for carbonic acid, excess base, and the two apparent dissociation constants, K_1' and K_2' . The carbonate content is then readily obtained by substitution of the figures for bicarbonate and excess base in equation 3.

In order to show the effect of increase in temperature and salinity, the solubility of calcium carbonate in sea water was calculated for three sets of conditions—(1) a standard condition in which the temperature was 20° C. and the salinity was 34 parts per thousand; (2) where

the temperature was 1° higher but the salinity was the same; and (3) where the salinity was 1 part per thousand higher but the temperature was the same (table 1). For the standard condition the carbonate content of a saturated solution was computed on the basis of a hydrogen ion concentration of 10^{-8} , or a pH of 8.0 (which is determined mainly by the amount of carbonic acid in the water), a first apparent dissociation constant of 1.07×10^{-6} ($pK_1' = 5.97$), a second apparent dissociation constant of 8.9×10^{-10} ($pK_2' = 9.05$), and an excess base equivalent to 103 milligrams of carbon dioxide in the form of bicarbonate. The carbonate content for the conditions of increased temperature and salinity was likewise computed by substitution of the proper figures for carbonic acid, K_1' , K_2' , and excess base in equations 3 and 4. The changes in K_1' , K_2' , and carbonic acid (in reality, in the solubility of free carbon dioxide in saline solutions) corresponding to the changes in temperature and salinity were based on data presented by Buch and his associates.²¹ The excess base was assumed to vary directly with the salinity and to be unaffected by temperature. The effect of boron was disregarded, but, as mentioned above, at a hydrogen ion concentration of 10^{-8} , the effect of boron is slight.

TABLE 1.—Effect of a small rise in salinity and temperature on the solubility of calcium carbonate in sea water

	Standard	Rise in temperature	Rise in salinity
Temperature.....°C.....	20	21	20
Salinity.....parts per thousand.....	34	34	35
Free CO ₂ (assumed to be equivalent to [H ₂ CO ₃]).....	1.000	0.974	0.996
First apparent dissociation constant of carbonic acid $\frac{[\alpha H^+][HCO_3^-]}{[H_2CO_3]} = K_1'$	1.000	1.015	1.008
Second apparent dissociation constant of carbonic acid $\frac{[\alpha H^+][CO_3^{--}]}{[HCO_3^-]} = K_2'$	1.000	1.023	1.047
Reciprocal of hydrogen-ion concentration $\frac{1}{[\alpha H^+]}$	1.000	1.007	1.016
Excess base (titration alkalinity), B	1.000	1.000	1.029
Concentration of bicarbonate [HCO ₃ ⁻].....	1.000	.995	1.020
Concentration of carbonate [CO ₃ ⁻⁻].....	1.000	1.025	1.085
Concentration of calcium [Ca ⁺⁺].....	1.000	1.000	1.029
Apparent solubility product constant of calcium carbonate in sea water K'_{CaCO_3}	1.000	.978	1.030
Degree of saturation of sea water with calcium carbonate $\frac{[Ca^{++}][CO_3^{--}]}{K'_{CaCO_3}}$	1.000	1.046	1.084

RESULTS

The results of the calculations are presented in table 1. The computations are given in the ratio form so that percentage changes in the size of the different variables will be readily apparent. For a rise in temperature of 1° C. the carbonate content increases 2.5 percent, and for a rise in salinity of 1 part per thousand the carbonate content increases 8.5 percent.

²⁰ Defant, A., Die vertikale Verteilung von Temperatur und Salzgehalt im Weltmeere: Gesell. Erdkunde Berlin Zeitschr., Jahrg. 1930, pp. 28–42. Wüst, G., Schichtung und Tiefenzirkulation des Pazifischen Ozeans: Inst. Meereskunde Veröffentlich., A, Heft 20, 1929. Sverdrup, H. W., The deep water of the Pacific, according to the observations of the Carnegie: Internat. Geod. and Geophys. Union, Repts. Stockholm meeting, pp. 87–93, Carnegie Inst. Washington, Dept. Terrestrial Magnetism, 1930.

The content of calcium ions was assumed to vary proportionately with the salinity and to be unaffected by the rise in temperature. As the salinity increased 2.9 percent, the calcium content likewise increased 2.9 percent. The changes in the apparent solubility product constant were computed from data given by Wattenberg.²² For the increased temperature the apparent solubility product constant was lowered 2.2 percent, and for the increased salinity it was raised 3.0 percent.

As the sea water is completely saturated with calcium carbonate when the product of the calcium and car-

²¹ Buch, K., and others, op. cit. (1932), pp. 46, 54, 63.

²² Wattenberg, H., op. cit., pp. 199, 203.

bonate equals the apparent solubility product constant, the degree of saturation of the water with calcium carbonate can be expressed by a ratio $\frac{[\text{Ca}^{++}][\text{CO}_3^{--}]}{K'_{\text{CaCO}_3}}$.

If the ratio is greater than 1.0 the water is oversaturated; if less than 1.0 it is undersaturated; and if equal to 1.0 it is exactly saturated.

The degree of saturation of the water for the three chosen sets of conditions can therefore be calculated by the substitution of the proper figures for $[\text{Ca}^{++}]$, $[\text{CO}_3^{--}]$, and K'_{CaCO_3} in this ratio. In the standard condition the ratio is unity and the water is exactly saturated. Where the temperature is 1° higher the water is 4.6 percent oversaturated, and where the salinity is 1 part per thousand higher the water is 8.4 percent oversaturated. That is, according to this table, at a temperature of 20° , a salinity of 34 parts per thousand, and a pH of 8.0, a rise of 1° in temperature increases the degree of saturation 4.6 percent, and a rise of 1 part per thousand in salinity increases the degree of saturation 8.4 percent.

These determinations of the effect of temperature and salinity on the solubility of calcium carbonate should be classed as estimates. They are believed to indicate the proper order of magnitude, but some of the variables on which they depend, especially the apparent solubility product constant of calcium carbonate, have not yet been worked out completely. Consequently the determinations may be modified in the future. Wattenberg,²³ using a different method of calculation, reports a rise in degree of saturation of the water of about 3.5 percent, instead of 4.6 percent, for an increase of 1° C. in temperature; and Revelle,²⁴ by a still different method in which a correction was made for boron, finds a rise of 5.2 percent for an increase of 1° C.

Wattenberg does not calculate the effect of salinity on the degree of saturation, but Revelle²⁵ reports a rise of 5.0 percent, instead of 8.4 percent, for an increase in salinity of 1 part per thousand. Revelle, though having assisted me in calculating the effect of salinity on the solubility, when he came to make his own determination took more factors into consideration and in part used different data. According to current concepts of the solubility of calcium carbonate, his estimate is therefore presumably more accurate than mine; but the greater effect of salinity indicated by my calculations is more nearly in agreement with the relation of the calcium carbonate content of sediments to the surface salinity indicated by the statistical studies described below. The two determinations, however, are of the same general order of magnitude and demonstrate that the degree of saturation of the water with calcium carbonate increases as the salinity rises.

²³ Wattenberg, H., op. cit., p. 207.

²⁴ Revelle, R., Physicochemical factors affecting the solubility of calcium carbonate in sea water: Jour. Sedimentary Petrology, vol. 4, pp. 103-110, 1934.

²⁵ Idem, p. 207.

SIGNIFICANCE

It is evident from the data given in table 1 that the salinity definitely affects the solubility of calcium carbonate in the sea and therefore influences the deposition of calcium carbonate. The magnitude of the change in degree of saturation for an increase in salinity of 1 part per thousand, compared with the magnitude of the change for a rise of 1° in temperature, demonstrates that salinity ranks with temperature as a factor controlling the solubility of calcium carbonate.

However, it is difficult to ascertain whether or not the effect of salinity on the solubility of calcium carbonate in sea water is as great as that of temperature. In the upper 200 meters of water, in which most of the solid calcium carbonate seems to be formed, the rate of change in solubility of calcium carbonate with respect to lateral changes in salinity and temperature is of the same order of magnitude. This feature is illustrated by figure 19, which shows the lines of equal temperature and salinity on the surface of the ocean. The maximum rate of change in salinity on the surface of the open ocean is about 0.4 part per thousand in 100 miles; in temperature, about 0.7° in 100 miles. The effect of this change in salinity on the solubility is $0.4 \times 8.4 = 3.3$ percent, and the effect of this change in temperature is $0.7 \times 4.6 = 3.2$ percent—that is, the effects are about the same. The relation of the areal distribution of calcium carbonate in sediments to surface temperature and to salinity, illustrated by plate 71, also supports this inference. It would seem, therefore, that in some parts of the ocean salinity would influence the solubility as much as the temperature. However, the seasonal variations of temperature on the surface of the ocean during the course of a year are relatively greater than those of salinity. Moreover, the temperature decreases greatly with depth, but the salinity does not. Consequently the total effect of salinity on the solubility of calcium carbonate in the ocean presumably is less than the effect of temperature.

STATISTICAL STUDY OF RELATIONS

METHOD OF STUDY

The relation of the salinity to the calcium carbonate content of marine sediments may also be studied statistically. In a previous investigation²⁶ I compiled a table which suggested strongly that the calcium carbonate content of marine sediments is definitely related to the salinity of the surface water. In this table the average calcium carbonate content of the sediments in 100 environments of deposition from many parts of the world was plotted against the salinity of the surface water. Table 2 is a modification of this previous table.

²⁶ Trask, P. D., Hammar, H. E., and Wu, C. C., Origin and environment of source sediments of petroleum, p. 103, Houston, Tex., Gulf Publishing Co., 1932.

TABLE 2.—*Relation of calcium carbonate content of marine sediments to salinity of surface water, as indicated by individual environments of deposition*

Average (median) CaCO ₃ content of region (percent)	Salinity (parts per thousand)			
	<34	34-35	35-36	36+
	Number of regions			
0 to 2-----	40	4	-----	-----
3 to 10-----	8	6	-----	-----
11 to 20-----	9	4	3	2
21 to 50-----	-----	1	6	6
51 to 88-----	-----	-----	6	5
Average (median) CaCO ₃ content for given salinity percent--	1	5	45	45

According to this table, the sediments in areas in which the surface salinity is less than 35 parts per thousand contain little calcium carbonate, and those in areas in which the salinity is more than 35 parts contain much calcium carbonate. This relationship, however, might be more apparent than real, because the effects of other factors, such as temperature and depth of water, the degree of saturation of the water with calcium carbonate, the action of organisms, or the proportion of clastic detritus in the sediments, were not considered. The salinity might happen to vary in the same way as some of these other factors and thus not be definitely related to the calcium carbonate content of the sediments.

If the effect of the other factors could be considered and if the salinity were then still found to vary with the calcium carbonate content, it would be evident that the relation is definite. The ideal way to undertake such an investigation would be to make all the factors except salinity constant, and then examine the relationship between salinity and calcium carbonate. Unfortunately, it is impossible to make all the other factors constant, but the effect of some of them can be determined to a certain extent by means of a statistical study of a large number of samples.

CONTROL OF EXTRANEEOUS FACTORS

The sea floor can be divided into several areal groups representing different conditions of temperature, depth of water, and distance from shore; and the relation of the salinity to the calcium carbonate content of the sediments in each group can then be examined. The size of the groups into which it is practicable to divide the sea floor depends upon the number of samples available. If the number of samples is large, the size of the groups can be small; but if the number of samples is small, the size of the groups must be large, because each group should be represented by enough samples to counterbalance the effects of factors not considered in the selection of the groups. About 2,000

samples were available for study, and the most practicable number of groups into which the sea floor could be divided seemed to be 32. The average number of samples in each group, therefore, was about 60, which should be sufficient to counterbalance to a considerable extent the effect of the factors that were not evaluated, such as the degree of saturation of the water with calcium carbonate.

If there are 32 groups, the most practicable grouping seems to be to divide the sea into 4 temperature groups; divide each of these temperature groups into 4 depth groups, making 16 groups; and then divide each of these depth groups into 2 groups according to distance from shore, making 32 groups in all.

The mean annual temperature of the surface of the sea ranges chiefly between 0° and 30° C., but over a large area it ranges mainly between 20° and 30°. Consequently, instead of making four equal groups based on surface temperature, it seemed better to make the areal distribution of the groups more nearly equal and have the limits of the groups 0°-10°, 10°-20°, 20°-25°, and 25°-30°. The limits of the four depth groups were 0 to 1,000, 1,000 to 2,000, 2,000 to 3,000, and 3,000 to 4,000 fathoms. In reference to distance from shore, the samples were divided into near-shore and pelagic groups. All the samples in the near-shore group were obtained less than 500 miles from shore and most of them within 200 miles of shore. For the most part they represent "terrigenous deposits" in the Murray classification.²⁷ The pelagic samples represent sediments far from land and are characterized by material of chemical and organic origin, in contrast with the near-shore deposits, which contain considerable material of clastic origin in addition to that of chemical and organic origin. The effect of detrital particles on the proportion of calcium carbonate in the sediments is compensated to some extent by means of this division of the sediments into near-shore and pelagic deposits, but it would be better if it had been practicable to make more than two divisions of the sediments with respect to distance from shore, because of the possibility that variations in the proportion of detrital particles within either the near-shore or the pelagic group might obscure the effect of other variables, such as temperature or salinity.

In fact, in the entire grouping of the samples the limits of the individual groups are so wide that variations within any one of them may mask the relation of salinity to calcium carbonate. Ordinarily, variations in calcium carbonate arising from variations within a group will tend to counterbalance one another, but if the effect of some particular factor, such as temperature, or proportion of clastic material, or degree of saturation of the water with calcium carbonate,

²⁷ Murray, J., and Renard, A. F., *Challenger Rept.*, Deep-sea deposits, pp. 228-240, 1891.

should vary in some of the individual groups in the same way as the salinity, the relation of salinity to calcium carbonate might be completely obscured. For example, in certain parts of the sea, notably in latitudes greater than 40°, the surface temperature and salinity vary in the same way with respect to latitude (fig. 19). If within the areal confines of a temperature group the salinity should be found to vary with respect to horizontal distance in the same way as temperature, and if a relation between salinity and calcium carbonate of the sediments were found, it would not follow necessarily that the variations in calcium carbonate were due to variations in salinity. They might be due in part or wholly to variations in temperature within the group. A similar degree of indefiniteness would arise in areas where the salinity increases away from shore, because it would not be certain whether the increase in calcium carbonate in the sediments were due to the increased salinity or to the smaller proportion of clastic material in the sediments.

The possibility of sympathetic variations of this type is an inevitable result of a system of grouping in which the range within the individual groups is considerable. The conclusions obtained from a study of such groups, however, though not completely satisfactory, are certainly more definite than if no grouping had been made. Moreover, it is evident from plate 71 and figure 19 that surface salinity in most parts of the ocean does not vary in the same way in a horizontal direction as surface temperature, depth of water, or distance from shore. Furthermore, each of the 32 individual groups represents several different parts of the sea in which the conditions are not everywhere the same. The number of samples in the individual groups is fairly large, and the samples are distributed over many parts of the sea. Therefore, according to the laws of probability, the chances are against the possibility that the relation of surface salinity to the calcium carbonate content of the sediments might be obscured by the effect of variations of other factors in any individual group, and still more in a large number of groups. Consequently, if a consistent relationship between salinity and calcium carbonate is found for nearly all the groups, the chances are much in favor of its being a true relationship, though not necessarily one of cause and effect.

It seems evident, therefore, that if there is such a relationship for salinity, its existence will be indicated by a statistical study of this type, but it does not necessarily follow that the true degree of the relationship will be indicated. For example, as pointed out below, the extent to which the water is saturated with calcium carbonate may possibly be related to the surface salinity and thus may have influenced in part the relation between salinity and calcium carbonate content of the sediments brought out by the statistical study.

METHOD OF COMPARING SALINITY AND CALCIUM CARBONATE CONTENT

In the determination of the relation of salinity to calcium carbonate, the samples likewise were classed according to groups. Each of the 32 groups for temperature, depth, and distance from shore was divided into 4 groups based on salinity and into 8 groups based on calcium carbonate content. The limits of the salinity groups, in parts per thousand, were less than 34, 34 to 35, 35 to 36, and more than 36. This type of grouping was adopted because of the suggestion indicated by table 1 that the critical salinity was about 35 parts per thousand and that salinities of less than 34 or more than 36 parts did not seem to affect appreciably the calcium carbonate content of sediments. The limits of the calcium carbonate groups, in percent, were 0 to 2, 2 to 5, 5 to 10, 10 to 20, 20 to 30, 30 to 50, 50 to 75, and more than 75. The object of this grouping was to separate the samples into varying grades of content of calcium carbonate, ranging from carbonate-free to limestone-forming sediments. The subsequent calculations, however, would have been simpler if the limits of the groups had been geometric instead of arbitrary.

It would also probably have been better if the average salinity and average temperature in the upper 200 meters of water had been considered instead of the surface salinity and temperature. The statistical part of this report was prepared in 1931, primarily for the purpose of ascertaining whether or not the relationship expressed by table 2 was real. The papers of Wattenberg,²⁸ Buch and others,²⁹ and Moberg and others,³⁰ which emphasize the importance of the upper 200 meters of water with respect to the formation of calcium carbonate, had not yet appeared, and at that time there was no reason to presume that the average salinity or temperature of any particular depth zone would be better to consider than the surface salinity or temperature. In many parts of the sea—notably in low latitudes—the surface salinity represents the average salinity in the upper 200 meters of water more closely than the surface temperature represents the average temperature of that zone.³¹ The conditions in the upper 200 meters of water depend largely upon the circulation of water in the ocean. Heat derived from the sun raises the temperature of the surface water

²⁸ Wattenberg, H., Kalziumkarbonat- und Kohlensäuregehalt des Meerwassers: Wiss. Ergeb. Deutschen Atlantischen Exped. *Meteor*, 1925-27, Band 8, Teil 2, pp. 1-333, 1933.

²⁹ Buch, K., Harvey, H. W., Wattenberg, H., and Gripenberg, S., Ueber das Kohlensäuresystem im Meerwasser: Conseil perm. expl. mer Rapports et procès-verbaux, vol. 79, pp. 1-70, 1932.

³⁰ Moberg, E. G., Greenberg, D. M., Reville, R., and Allen, E. C., The buffer mechanism of sea water: Scripps Inst. Oceanography Bull., Tech. ser., vol. 3, no. 11, 231-278, 1934.

³¹ Defant, A., Die systematische Erforschung des Weltmeeres: Gesell. Erdkunde Berlin Zeitschr., Sonderband zur Hundertjahrfeier der Gesellschaft, p. 485, 1928. Wüst, G., Der Ursprung der Atlantischen Tiefenwässer: Idem, p. 520; Schichtungen und Tiefenzirkulation des Pazifischen Ozeans: Meereskunde Veröffentlich., A, Heft 20, 1929. Schott, G., Geographie des Atlantischen Ozeans, p. 144, Hamburg, C. Boysen, 1926. Schott, G., and Schu, F., Die Wärmeverteilung in den Tiefen des Stilles Ozeans: Annalen der Hydrographie, Band 38, pls. 2, 3, p. 48, 1910.

more readily than it raises the salinity of the surface water by means of its effect on evaporation. These features may account in part for the apparently closer relation of the calcium carbonate content of the sediments to the surface salinity than to the surface temperature.

SOURCE OF DATA

About 3,000 samples were considered, of which 1,953 were selected for study. The samples are described in Murray's *Challenger*,³² Pacific,³³ and Atlantic³⁴ reports and in my report on source beds.³⁵ These publications give the calcium content, the depth, and the position of the samples. Pratje³⁶ and Correns³⁷ have published maps of the distribution of calcium carbonate in the South Atlantic, but the data from these maps were not used for the statistical study, because they were not presented in a form readily applicable to the statistical groups that were used.

The data for salinity were derived from Schott's map³⁸ showing the mean annual salinity of the surface of the oceans; and the data for temperature from maps by Schott,³⁹ Schott and Schu,⁴⁰ Krümmel,⁴¹ and Shokalsky,⁴² showing the mean annual isotherms of the surface water.

The samples available for study cover the world more or less satisfactorily. The Pacific and Atlantic Oceans are fairly well represented, but the Indian and Antarctic Oceans are not. No pelagic samples from the Arctic Ocean were available, but several samples were procured off the northern coast of Canada and Alaska. Most of the inland and semienlosed seas are represented—namely, the Arabian, Baltic, Bering, Black, Caribbean, Japan, Java, Mediterranean, Red, and Yellow Seas and the Gulfs of California, Maine, Mexico, Panama, and Venezuela. The near-shore samples came from many parts of the Arctic, Atlantic, and Pacific coasts of North and South America, the entire west coast of Africa, and the coasts of parts of Arabia, Antarctica, Australia, Europe, India, Japan, Java, and the Philippine Islands.

Some areas were represented by many samples, and others by few. In order to make the results of the statistical study of these areas comparable, the number of samples from areas represented by many samples was reduced. In this process of reduction, an attempt was made to select samples proportionately with respect to area, so that the sediments chosen for study would represent an approximately equal distribution. This process of elimination lowered the number of samples to 1,953, of which 928 were typically pelagic deposits and 1,035 were near-shore sediments or deposits from inland seas or lakes.

About 4 percent of the near-shore sediments represent samples of fresh-water and saline lakes that had been studied previously.⁴³ The sediments of saline lakes contain considerable calcium carbonate, but those from nearly all the fresh-water lakes contain less than 2 percent. It is probable, however, that the proportion of fresh-water lakes characterized by calcareous deposits is greater than was indicated by the previous work, which was based on relatively few lakes; and it is also probable that the calcium carbonate content of lacustrine sediments is ordinarily influenced more by other factors than it is by the salinity of the water.⁴⁴

The relation of the salinity to the calcium carbonate content of lacustrine sediments is not discussed in this paper, but in order to make the study of the effect of salinity representative of general conditions, a few lacustrine samples were included in the statistical study. As this paper is restricted mainly to the discussion of marine conditions, it might be better if this had not been done. The lacustrine samples, however, form so small a proportion of the total number of samples, and the relationships they exhibit are so similar to those indicated by marine sediments, that the statistical results are not significantly different from what they would have been if the lacustrine samples had been omitted.

METHOD OF COMPILING DATA

The method of recording the data was to use 32 cards, 16 for near-shore sediments and 16 for pelagic deposits. The 16 cards in each of these groups were divided into 4 series of temperature groups and 4 series of salinity groups. For example, there were 4 cards for the salinity group of less than 34 parts per thousand, 1 for each of the 4 temperature subgrades. Similarly there were 4 cards for the salinity group of 34 to 35 parts per thousand, 1 for each temperature grade; and so on. On each card the depth was plotted against the calcium carbonate content. Each of the 1,953 samples was placed in the proper category on one of these cards. Table 3 illustrates the manner of plotting.

³² Murray, J., and Renard, A. F., *Challenger Rept.*, Deep-sea deposits, pp. 34-147, 1891.

³³ Murray, J., and Lee, G. V., The depth and marine deposits of the Pacific: Harvard Coll. Mus. Comp. Zoology Mem., vol. 38, pp. 40-148, 1909.

³⁴ Murray, J., and Chumley, J., The deep-sea deposits of the Atlantic Ocean: Royal Soc. Edinburgh Trans., vol. 54, pp. 1-216, 1924.

³⁵ Trask, P. D., Hammar, H. E., and Wu, C. C., Origin and environment of source sediments of petroleum, pp. 249-273, Houston, Tex., Gulf Publishing Co., 1932.

³⁶ Pratje, O., Geologische Tiefseeforschungen auf der Deutschen Atlantischen Expedition: Deutsche geol. Gesell. Monatsber., Band 79, p. 202, 1927.

³⁷ Correns, C. W., Mineralogisch-geologische Arbeiten der Deutschen Atlantischen Expedition: Gesell. Erdkunde Berlin Zeitschr., Jahrg. 1928, Ergänzungsheft 3, p. 127.

³⁸ Schott, G., Die Verteilung des Salzgehaltes im Oberflächwasser der Ozeane: Annalen der Hydrographie, Band 56, Heft 5, p. 184, 1928.

³⁹ Schott, G., Geographie des Atlantischen Ozeans, pl. 10, p. 144, Hamburg, C. Boysen, 1926.

⁴⁰ Schott, G., and Schu, F., Die Wärmeverteilung in den Tiefen des Stillen Ozeans: Annalen der Hydrographie, Band 38, Heft 1, pp. 2-25, 44, 1910.

⁴¹ Krümmel, O., Handbuch der Ozeanographie, Band 1, pp. 400-406, 1907 (for Indian Ocean).

⁴² Shokalsky, J., Oceanography [in Russian], pp. 134, 135, Petrograd, 1917.

⁴³ Trask, P. D., Hammar, H. E., and Wu, C. C., op cit., pp. 100, 281.

⁴⁴ Naumann, E., Die Bodenablagerungen der Seen: Internat. Ver. theor. u. angew. Limnologie Verh., Band 4, 1929. Pia, J., Die rezente Kalksteine; Min. pet. Mitt., Ergänzungsband, 1933.

TABLE 3.—*Relation of calcium carbonate content of pelagic deposits to depth of water in areas in which the surface water has a salinity greater than 36 parts per thousand and a temperature higher than 25° C.*

CaCO ₃ (percent)	Depth (fathoms)								Total number of samples
	0 to 500	500 to 1,000	1,000 to 1,500	1,500 to 2,000	2,000 to 2,500	2,500 to 3,000	3,000 to 3,500	3,500 to 4,000	
	Number of samples								
0 to 2-----						1	9	1	11
2 to 5-----						6	4		10
5 to 10-----					1	2	3	1	7
10 to 20-----					1	5	1		7
20 to 30-----				1	1	8	1		11
30 to 50-----			1	5	9	4	2		21
50 to 75-----	2	1	8	7	22	7			47
75+-----	2	6	3	7	12				30
Total-----	4	7	12	20	46	33	20	2	144
Average percent of CaCO ₃ -----	77	79	66	62	60	28	9	4	47

The cards could just as well have been arranged in a form in which the salinity or the temperature instead of the depth was plotted against the calcium carbonate content of the sediments, but the depth was used because of the time saved thereby in compilation.

In order to study the relationship of surface salinity and surface temperature to the calcium carbonate content of the sediments the figures on these cards were rearranged on 64 other cards—32 for salinity and 32 for temperature. The salinity and temperature groups were subdivided into near-shore and pelagic groups, and these in turn were segregated into four depth groups, each representing an interval of 1,000 fathoms. That is, for salinity there were 32 cards to cover all possible variations of two groups based on distance from shore, four temperature groups, and four depth groups. Similarly there were 32 cards for surface temperature, representing all possible combinations of two groups based on distance from shore, four depth groups, and four salinity groups. These 64 cards, together with the 32 cards that showed the relation of depth to calcium carbonate content, formed the basis for the statistical study of the problem.

ARITHMETIC MEANS

METHOD OF PRESENTING DATA

It is not practicable to present in this paper the 96 size distributions⁴⁵ represented by these cards. Instead, the significant features are summarized in three ways—first, in tables 4 to 6, which show the average⁴⁶ calcium carbonate content for different combinations of depth, surface salinity, and surface temperature; second, in figures 12 to 18, which show graphically the relation of the average calcium carbonate content of the sediments for given surface salinity, surface temperature, and depth; and third, in table 7, which indicates for each of the 96 subgroups the coefficients of correlation between the calcium carbonate content of the sediments and the salinity, the temperature, and the depth.

⁴⁵ A "size distribution" is a numerical classification of items according to a number of groups of different sizes. Table 3 represents the size distribution of calcium carbonate and depth for a particular temperature and salinity. It shows the distribution of the samples with respect to calcium carbonate and depth on the basis of the number of samples in each of several categories.

⁴⁶ "Mean" and "average" unless otherwise stated are used interchangeably in the present report to indicate the arithmetic mean.

TABLE 4.—Mean calcium carbonate content of marine sediments for different salinity and temperature of the surface water and for different depth of water; data arranged to show relation for depth

[Figures in *italics* are averages based on 5 samples or less; figures without indication of probable error represent single samples]

Near-shore sediments									
Salinity (parts per thousand)	Temperature (°C.)	Depth (fathoms)							
		0 to 100	100 to 250	250 to 500	500 to 1,000	1,000 to 1,500	1,500 to 2,000	2,000 to 3,000	3,000 to 4,000
		Mean percentage of calcium carbonate							
< 34	0 to 10	6 ± 4	7 ± 4	4 ± 1	3 ± 1	3 ± 2	10 ± 8	1 ± 0	1 ± 0
	10 to 20	7 ± 4	10 ± 8	8 ± 8	15 ± 10	20 ± 5	1 ± ?	6 ± 3	1 ± ?
	20 to 25	3 ± 3		62 ± 5	62 ± 5	62 ± ?			
	25 to 30	19 ± 13	24 ± 8	13 ± 7	12 ± 6	20 ± 6	19 ± 14	13 ± 8	
34 to 35	0 to 10	3 ± 2	1 ± 1	1 ± ?	14 ± 6	26 ± 6	17 ± 4		
	10 to 20	3 ± 3	15 ± ?	16 ± 5	17 ± 6	20 ± 10	5 ± 1	4 ± 2	
	20 to 25	13 ± 7	1 ± ?	12 ± 8	12 ± 9		3 ± 2	4 ± 2	
	25 to 30	14 ± 18	16 ± 13	26 ± 18	18 ± 10	28 ± 18	10 ± 8	9 ± 7	
35 to 36	0 to 10		20 ± 3	12 ± 3	17 ± 7		25 ± ?		
	10 to 20	30 ± 4	41 ± 13	27 ± 14	24 ± 9	18 ± 6	19 ± 11	11 ± 6	
	20 to 25	45 ± 21	62 ± ?	39 ± 15	35 ± 12	23 ± 8	20 ± 9	9 ± 4	
	25 to 30	53 ± 31	60 ± 19	82 ± ?	38 ± 10	51 ± 15	19 ± 11	16 ± 6	
36 +	0 to 10								
	10 to 20	37 ± 30	46 ± 22	27 ± 9	32 ± 11	33 ± 12	29 ± 5	29 ± 5	
	20 to 25	28 ± 9		15 ± ?	13 ± 7	16 ± 6	16 ± 4		
	25 to 30	46 ± 28	62 ± 10	57 ± 18	49 ± 26	41 ± 24	37 ± 12	24 ± 9	
Mean		23 ± 13	25 ± 10	24 ± 10	23 ± 9	26 ± 9	16 ± 8	12 ± 5	1 ± 0

Pelagic deposits									
Salinity (parts per thousand)	Temperature (°C.)	Depth (fathoms)							
		0 to 500	500 to 1,000	1,000 to 1,500	1,500 to 2,000	2,000 to 2,500	2,500 to 3,000	3,000 to 3,500	3,500 to 4,000
		Mean percentage of calcium carbonate							
< 34	0 to 10		40 ± ?	36 ± 23	12 ± 9	1 ± 0	1 ± 0	1 ± ?	
	10 to 20			72 ± 7	38 ± 25	11 ± 8	1 ± 0		
	20 to 25								
	25 to 30				21 ± 14				
34 to 35	0 to 10		62 ± ?	62 ± 5	77 ± 6	33 ± 20	49 ± 11		
	10 to 20		51 ± 7	62 ± ?	71 ± 12	38 ± 33	2 ± 1	1 ± 0	1 ± 0
	20 to 25			25 ± ?	2 ± 1	1 ± 0	1 ± 0	1 ± ?	
	25 to 30	54 ± 19	48 ± 8	48 ± 10	43 ± 10	51 ± 19	21 ± 20		1 ± ?
35 to 36	0 to 10		57 ± 6			40 ± ?			
	10 to 20	82 ± 4	65 ± 6	60 ± 8	67 ± 10	50 ± 15	28 ± 24	1 ± 0	
	20 to 25	82 ± ?		82 ± ?	56 ± 7	40 ± 30	39 ± 30		1 ± ?
	25 to 30		77 ± 5	74 ± 7	76 ± 6	57 ± 14	40 ± 19	18 ± 11	
36 +	0 to 10								
	10 to 20		63 ± 13	62 ± 15	68 ± 12	68 ± 11	45 ± 17	40 ± ?	
	20 to 25	75 ± 6	74 ± 6	76 ± 6	63 ± 12	58 ± 11	32 ± 21	4 ± 2	
	25 to 30	77 ± 8	77 ± 5	66 ± 8	62 ± 16	60 ± 14	28 ± 18	9 ± 4	4 ± 2
Mean		73 ± 9	63 ± 7	62 ± 10	53 ± 10	44 ± 15	25 ± 15	9 ± 4	2 ± 1

The mean calcium carbonate content of each depth group for all combinations of surface salinity and temperature is shown in table 4. The figures for the probable error⁴⁷ given after the figure for the mean represent the semi-interquartile range⁴⁷ when more than 10 samples were averaged, and two-thirds the standard deviation⁴⁷ when less than 10 samples were averaged.

⁴⁷ For detailed discussion of these statistical terms, see Chaddock, R. E., Principles and methods of statistics, pp. 153-163, 235-238, New York, Houghton Mifflin Co., 1925.

The probable errors obtained in this way indicate only the order of magnitude of the scatter⁴⁸ of the items averaged. For example, in table 4 the mean representing the column for the depth group of 2,500 to 3,000 fathoms in table 3 is given as 28 ± 18 percent, which indicates that the calcium carbonate content of

⁴⁸ The "scatter" is a measure of the deviation of the samples from the mean. For example, if the items in a size distribution range between 28 and 32 percent the maximum deviation from the mean (30 percent) is 2 percent, which is small; but if the items range between 10 and 50 percent the mean is still 30 percent, but the maximum deviation from the mean is 20 percent, which is large. The scatter in the first case would be small and in the second large.

one-half the samples that were averaged lies within a range of $2 \times 18 = 36$ percent, distributed on both sides of the mean of 28 percent. Actually, one-half the samples have a calcium carbonate content ranging between 8 and 44 percent. This average of 28 ± 18 in table 4 is not to be confused with the average of 25 ± 15 just below, which refers to the general average for all pelagic samples in the depth interval 2,500 to 3,000 fathoms, regardless of temperature or salinity.

RESULTS

It is evident from table 4 that the calcium carbonate content of the sediments in general decreases with increase in depth of water, especially below 2,000 fathoms. The amount of scatter, however, is high, which indicates that for this group of sediments the relationship is not close or that factors which have not been considered mask the effect of depth.

The relationship of surface temperature to the calcium carbonate content is illustrated better by table 5. This table was compiled from the 32 cards for temperature. The probable error was obtained in the same way as in table 4. The table indicates that the calcium carbonate content rises as the surface temperature increases. However, the amount of scatter, as shown by the figures for probable error, is high, which indicates that the relationship is to a certain extent indefinite.

A similar table for surface salinity could be compiled by a rearrangement of the items in table 5, and it would show a rise in calcium carbonate content for rise in salinity. However, as the relations for salinity are expressed in detail by figures 12 to 16, a table especially arranged to illustrate the effect of salinity was not prepared.

TABLE 5.—Mean calcium carbonate content of marine sediments for different salinity and temperature of the surface water and for different depth of water; data arranged to show relation for temperature

[Italic figures represent averages based on 5 samples or less. Numbers without indication of probable error represent single samples]

Salinity (parts per thousand)	Depth (fathoms)	Temperature (°C.)							
		Near-shore deposits				Pelagic deposits			
		0 to 10	10 to 20	20 to 25	25 to 30	0 to 10	10 to 20	20 to 25	25 to 30
		Mean percentage of calcium carbonate							
<34	0 to 1,000	5±2	9±6	17±16	17±8	40±0	47±22		21±14
	1,000 to 2,000	8±7	16±5	62±?	20±12	21±15			
	2,000 to 3,000	1±0	6±3		13±8	1±0	7±4		
	3,000 to 4,000	1±0	1±?			1±?			
34 to 35	0 to 1,000	5±2	11±6	12±8	21±15	62±?	51±7		49±14
	1,000 to 2,000	21±6	16±10	3±2	22±13	71±6	68±12	6±5	45±10
	2,000 to 3,000		4±2	4±2	9±7	42±19	18±9	1±0	37±26
	3,000 to 4,000						1±0	1±?	1±?
35 to 36	0 to 1,000	14±5	30±10	40±16	53±29	57±6	68±6	82±?	77±5
	1,000 to 2,000	25±?	19±8	22±9	44±13		65±10	57±10	75±6
	2,000 to 3,000		11±6	9±4	16±6	40±?	43±21	40±30	48±23
	3,000 to 4,000						1±0	1±?	18±11
36+	0 to 1,000		33±11	22±7	50±25		63±13	75±6	77±6
	1,000 to 2,000		32±9	16±6	44±20		65±13	66±11	63±13
	2,000 to 3,000		29±5		24±9		55±17	44±22	47±18
	3,000 to 4,000						40±?	4±2	8±4
Mean		9±4	17±7	20±9	28±14	40±9	45±11	36±11	46±13

A comparison of the relations for surface salinity, surface temperature, and depth is presented in table 6. Each number representing the percentage of calcium carbonate in this table is the average of two or more numbers in tables 4 and 5. In the process of averaging, in order to make the data in table 6 as comparable as possible, numbers in tables 4 and 5 based on five to two samples were weighted one-half and numbers based on only one sample were weighted one-fourth. The means shown at the bottom of each of the three main divisions of table 6 represent the average of all the numbers given for the particular grouping in tables 4 and 5, not the average of the four or less averages repre-

senting the particular grouping in table 6. For example, the general average of the calcium carbonate content of the pelagic sediments in areas in which the surface salinity is less than 34 parts per thousand is given as 22 ± 12 in table 6. This is not the mean of the two numbers (31 ± 18 and 5 ± 3) given for this grouping in table 6; it is the mean of the seven numbers representing this grouping in table 5. It was hoped by this process of averaging to minimize irregularities caused by the small number of samples in some subgroups. However, because of the large probable error the averages indicated in tables 4 to 6 are to be considered as indicating only the order of magnitude.

TABLE 6.—Comparison of the relation of the calcium carbonate content of marine sediments to the salinity of the surface water, the temperature of the surface water, and the depth of water, as indicated by arithmetic means

[Italic figures represent averages based on less than 5 samples. Numbers without indication of probable error represent single samples]

Temperature (°C.)	Depth (fathoms)	Salinity (parts per thousand)							
		Near-shore deposits				Pelagic deposits			
		<34	34 to 35	35 to 36	36+	<34	34 to 35	35 to 36	36+
		Mean percentage of calcium carbonate							
0 to 30-----	0 to 1,000-----	13±9	12±8	34±15	37±14	53±12	69±6	72±9	
	1,000 to 2,000-----	18±9	17±9	28±10	33±13	47±8	66±9	65±12	
	2,000 to 3,000-----	7±4	6±4	12±5	27±7	5±3	22±13	43±24	49±19
	3,000 to 4,000-----	1±0				1±0	11±7	10±3	
Mean-----		12±7	13±7	28±11	33±14	22±12	35±11	50±12	51±12
Temperature (°C.)	Salinity (parts per thousand)	Depth (fathoms)							
		Near-shore deposits				Pelagic deposits			
		0 to 1,000	1,000 to 2,000	2,000 to 3,000	3,000 to 4,000	0 to 1,000	1,000 to 2,000	2,000 to 3,000	3,000 to 4,000
		Mean percentage of calcium carbonate							
0 to 10-----	<34 to 36+-----	9±3	15±7	1±0	1±?	54±6	46±10	25±10	
10 to 20-----		21±8	21±9	14±4		63±9	61±14	31±13	9±?
20 to 25-----		23±12	21±6	7±3		77±7	43±9	34±17	3±2
25 to 30-----		35±19	33±15	15±7		66±9	56±10	44±22	12±8
Mean-----		23±11	22±10	12±5	1±?	66±7	57±11	35±17	7±4
Depth (fathoms)	Salinity (parts per thousand)	Temperature (°C.)							
		Near-shore deposits				Pelagic deposits			
		0 to 10	10 to 20	20 to 25	25 to 30	0 to 10	10 to 20	20 to 25	25 to 30
		Mean percentage of calcium carbonate							
0 to 4,000-----	<34-----	4±3	9±5	26±16	17±9	17±10	27±13		21±14
	34 to 35-----	13±4	10±6	8±5	17±12	62±10	37±8	3±3	40±16
	35 to 36-----	16±5	22±8	26±10	42±16	49±6	50±11	47±20	52±12
	36+-----		31±9	19±7	39±18		58±14	47±11	49±10
Mean-----		9±4	17±7	20±9	28±14	40±9	45±11	36±11	46±13

Table 6, like tables 4 and 5, exhibits a rise in calcium carbonate content of the sediments as the surface salinity and surface temperature increase and as the depth decreases. Because the averages are based on more samples than in tables 4 and 5, the respective relationships of salinity, temperature, and depth to calcium carbonate content are more regular.

GRAPHIC PRESENTATION

METHOD OF PLOTTING

Although most of the essential features of the statistical study of the data are presented in tables 4 to 6, the general relations are illustrated more clearly by diagrams. Figures 12 to 18 represent the main features given in these tables. Figures 12 to 15 show the relation of surface salinity to the calcium carbonate content of the sediments for different combinations of

depth of water and surface temperature. These figures are based on the means shown in table 5. Size groups in which the mean was based on only one sample are not represented in the figures. In the preparation of the figures, the averages of the groups representing salinities less than 34 and more than 36 parts per thousand were arbitrarily taken as 33.5 and 36.5, respectively.

RELATION FOR SALINITY

Figure 12 shows the relations for salinity in areas in which the surface temperature ranges between 0° and 10° C., for two depth intervals of both near-shore and pelagic deposits. The number of samples was insufficient to illustrate the relation for the other depth intervals in this temperature group. The calcium carbonate content for each depth interval represented

on this figure rises with increase in salinity. In the near-shore deposits in the depth interval 0 to 1,000 fathoms the mean calcium carbonate content rises from 5 percent for salinities less than 34 parts per

thousand to 21 percent for salinities between 34 and 35 parts; and in the interval 1,000 to 2,000 fathoms from 8 percent for salinities less than 34 parts per thousand to 21 percent for salinities ranging between 34 and 35 parts. In the pelagic group, for the depth interval of 1,000 to 2,000 fathoms, the mean calcium carbonate content rises from 21 percent for salinities less than 34 parts per thousand to 71 percent for salinities between 34 and 35 parts; and in the interval 2,000 to 3,000 fathoms it rises from 1 to 42 percent between these salinity limits.

carbonate content for each depth interval, except the interval 3,000 to 4,000 fathoms, which is represented by only a few samples, rises with increase in surface salinity. However, in the pelagic sediments from intervals of 0 to 1,000 and 1,000 to 2,000 fathoms the calcium carbonate content is approximately constant for a salinity in excess of 35 parts per thousand. It is greater for the pelagic group than for the near-shore group, and it is greater for depth intervals of less than 2,000 fathoms than for intervals of more than 2,000 fathoms. The calcium carbonate content of the sediments in the interval 0 to 1,000 fathoms is approximately equal to that in the interval 1,000 to 2,000 fathoms for both the near-shore and the pelagic groups, but in both depth intervals it is distinctly greater in the pelagic than in the near-shore group.

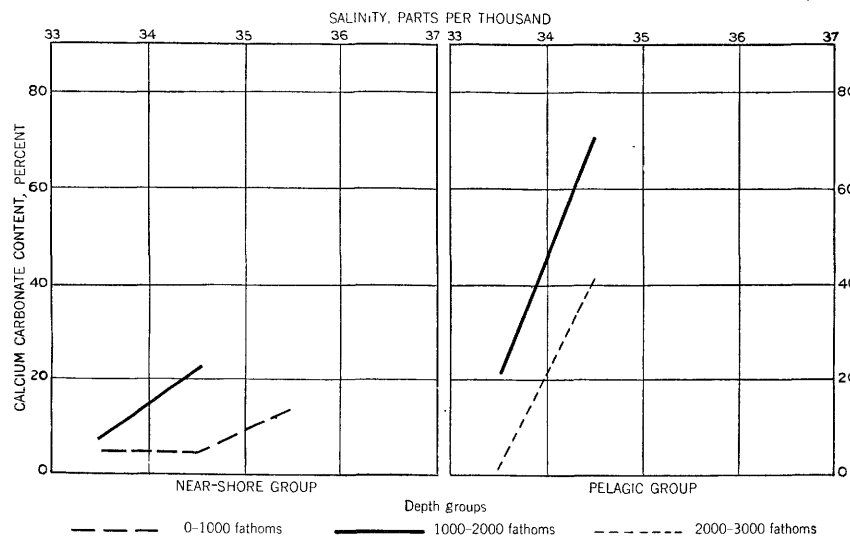


FIGURE 12.—Relation of calcium carbonate content of marine sediments to the salinity of the surface water for temperatures of 0° to 10° C. In this and the next four figures the lines represent mean calcium carbonate content of the sediment for the given salinity of the surface water, for water of different depths. The depths are classified into four groups of 1,000 fathoms each, and each depth group is represented by one line—for example, the dashed line for the 0–1,000 fathom group refers to all areas in which the water ranges in depth between 0 and 1,000 fathoms. This figure represents all areas in which the mean annual temperature of the surface water is between 0° and 10° C.; figures 13, 14, and 15 refer respectively to areas in which the temperature is 10° to 20°, 20° to 25°, and 25° to 30° C.; and figure 16 refers to the average of the four temperature groups—that is, to all areas, regardless of temperature.

thousand to 14 percent for salinities ranging between 35 and 36 parts; and in the interval 1,000 to 2,000 fathoms from 8 percent for salinities less than 34 parts per thousand to 21 percent for salinities ranging between 34 and 35 parts. In the pelagic group, for the depth interval of 1,000 to 2,000 fathoms, the mean calcium carbonate content rises from 21 percent for salinities less than 34 parts per thousand to 71 percent for salinities between 34 and 35 parts; and in the interval 2,000 to 3,000 fathoms it rises from 1 to 42 percent between these salinity limits.

The pelagic deposits contain more calcium carbonate than the near-shore deposits. In the near-shore group the sediments in the interval 1,000 to 2,000 fathoms have a greater calcium carbonate content than those in the interval 0 to 1,000 fathoms, thus presumably reflecting the effect of masking on the calcium carbonate content by terrigenous detritus. In the pelagic group the sediments in the interval 1,000 to 2,000 fathoms contain more calcium carbonate than those in the interval 2,000 to 3,000 fathoms, thus presumably representing the effect of solution of particles as they fall to the bottom in deep water.

The same phenomena apply to the temperature group 10° to 20°, illustrated by figure 13. The calcium

bonate content of pelagic sediments is slight as the salinity rises above 35 parts per thousand. The decrease with increasing depth is well illustrated by this temperature interval, for both near-shore and pelagic sediments.

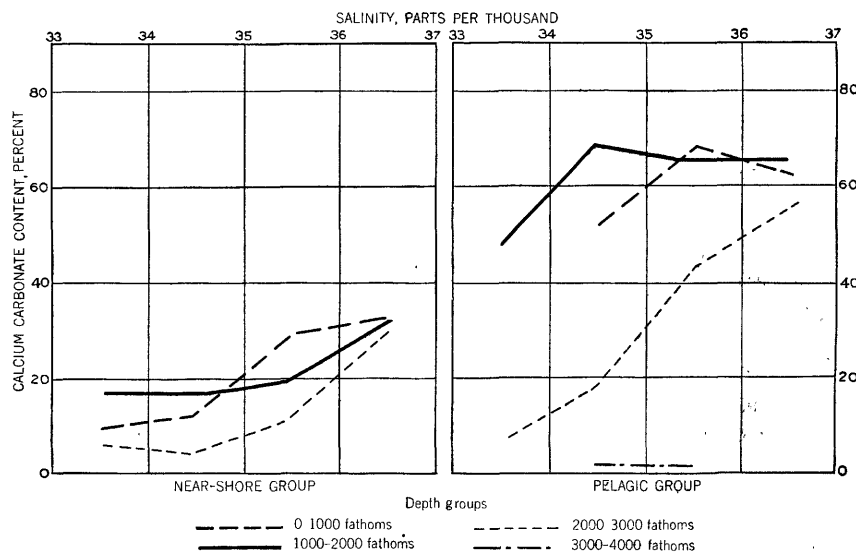


FIGURE 13.—Relation of calcium carbonate content of marine sediments to the salinity of the surface water for temperatures of 10° to 20° C. (See fig. 12 for explanation.)

The calcium carbonate content of sediments of the temperature group 25° to 30°, illustrated by figure 15, in general increases as the salinity rises. The increase here, as in the lower-temperature groups, is small above a salinity of 35 parts per thousand. In fact, in two of

the seven groups shown in figure 15, the mean calcium carbonate content decreases significantly as the salinity rises above 35 parts.

This figure illustrates well the loss in calcium carbonate content with increase in depth. The decrease is small above 2,000 fathoms and large below 2,000 fathoms. The pelagic deposits contain more calcium carbonate than the near-shore sediments.

The calcium carbonate content of all groups above 3,000 fathoms, represented in figures 12 to 15, rises with increase in salinity, but in one of the two groups for the interval 3,000 to 4,000 fathoms it decreases as the salinity rises above 35 parts per thousand, and in the other it is constant between salinities of 34 and 36 parts per thousand, which represent the limits of the samples available. This rise in calcium carbonate content for increased salinity for depths less than 3,000 fathoms is so consistent in so many different groups of temperature and depth that it seems evident that surface salinity is definitely related to the calcium carbonate content of the sediments.

A summary of all the temperature groups illustrated by figures 12 to 15 is presented in figure 16, which is based on table 6. The heavy broken line in this figure represents the average of all the depth groups shown

The rate of increase of calcium carbonate with respect to salinity apparently decreases as the salinity rises above 35 parts per thousand, as indicated by the flattening of the general curves for both the near-shore and pelagic groups for salinities greater than 35 parts.

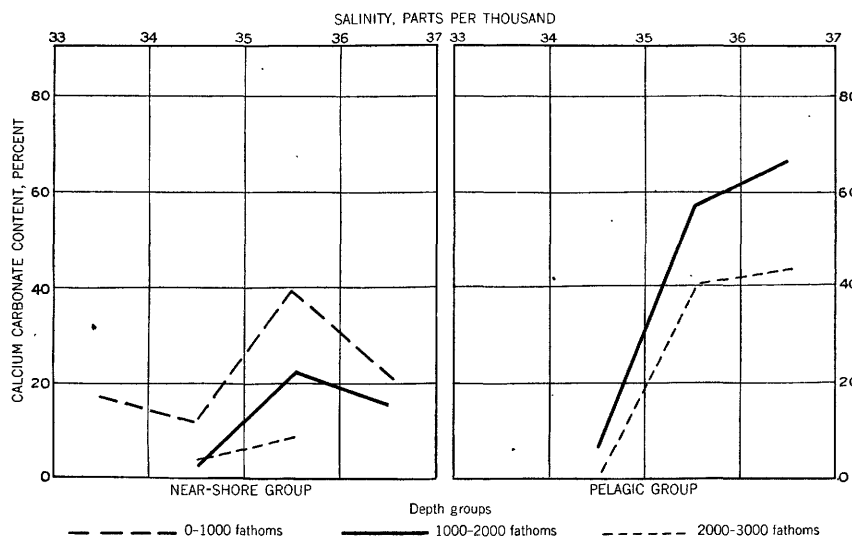


FIGURE 14.—Relation of calcium carbonate content of marine sediments to the salinity of the surface water for temperatures of 20° to 25° C. (See fig. 12 for explanation.)

The increase in calcium carbonate between salinities of 34.5 and 35.5 parts per thousand is 15 percent, compared with 5 percent between 35.5 and 36.5 parts in the near-shore sediments and with 1 percent for the same interval in the pelagic sediments.

RELATION FOR DEPTH

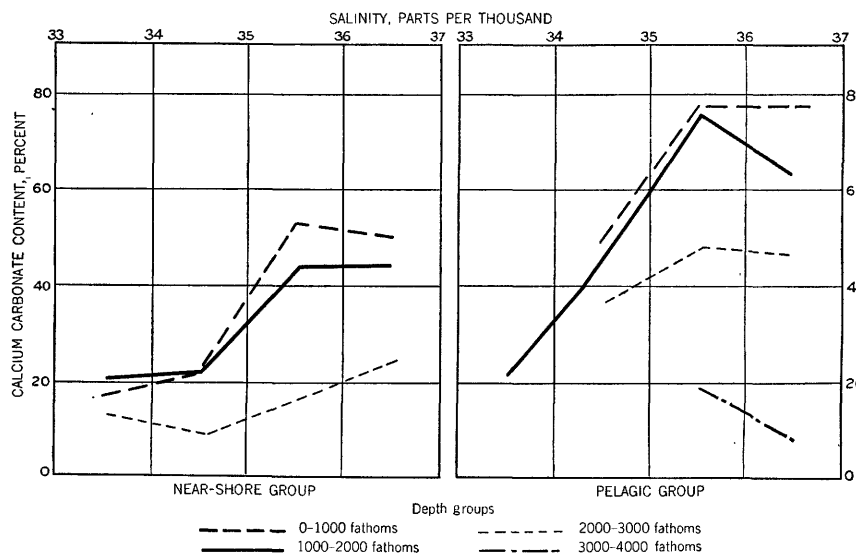


FIGURE 15.—Relation of calcium carbonate content of marine sediments to the salinity of the surface water for temperatures of 25° to 30° C. (See fig. 12 for explanation.)

and is based on the general means given for salinity in table 6. This figure shows the general increase in calcium carbonate content with rise in salinity. The average calcium carbonate content for all temperatures and all depths, in the near-shore group, increases from 12 to 33 percent with the increase from low to high salinity, and in the pelagic group it increases from 22 to 51 percent.

Figure 16 shows also the decrease in calcium carbonate content of the sediments as the depth increases. The two lines for the depth intervals above 2,000 fathoms are close together, and those for the depth intervals below 2,000 fathoms are relatively far apart. This feature indicates that the loss in calcium carbonate with increasing depth is greater below than above 2,000 fathoms.

The loss with increasing depth is illustrated better by figure 17, which shows the relation of depth to calcium carbonate for various salinities. Each salinity curve in this figure represents the average of the four temperature groups for the particular salinity and is based on data presented in table 4.

In the pelagic sediments the rate of decrease of calcium carbonate with respect to depth is fairly regular for all depths, although it is slightly less above 2,000 fathoms than below 2,000 fathoms. In the near-shore deposits, however, the rate of decrease with respect to depth is distinctly less above 1,500 fathoms than below 1,500 fathoms. This feature is indicated by the increase in the slope of the curve for the general average at a depth of about 1,500 fathoms.

In fact, in the near-shore group the mean calcium carbonate content for all salinities and temperatures is nearly constant between depths of 0 and 1,500 fathoms. The average calcium carbonate content for

carbonate content of the sediments is less closely related to surface temperature than to surface salinity. In the near-shore group, however, as indicated by figures 16 and 18, the relation for surface temperature seems to be about as definite as the relation for surface salinity.

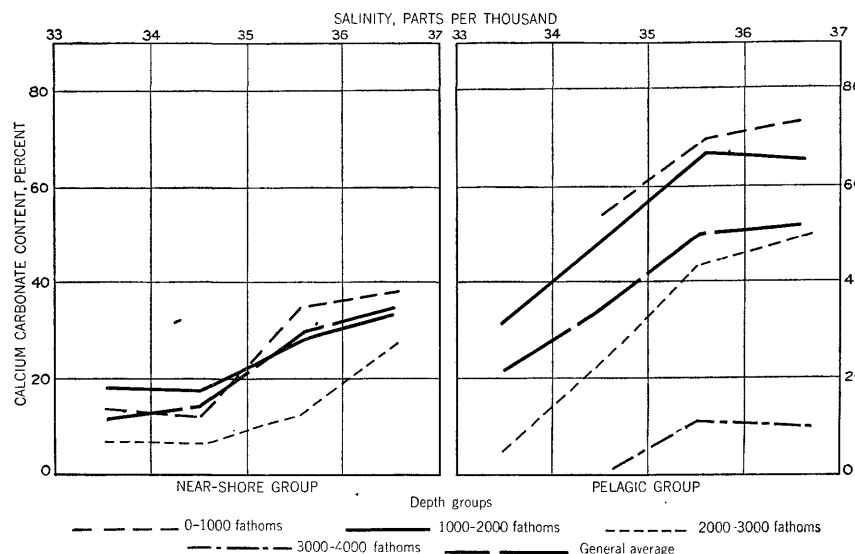


FIGURE 16.—Relation of calcium carbonate content of marine sediments to the salinity of the surface water; average for all temperatures. (See fig. 12 for explanation.)

depth intervals of 0 to 1,000, 1,000 to 2,000, 2,000 to 3,000, and 3,000 to 4,000 fathoms for the near-shore sediments is 23, 22, 12, and 1 percent, respectively; for the pelagic deposits, 66, 57, 35, and 7 percent. The curves shown in figure 17 illustrate also the large calcium carbonate content for high salinity in pelagic deposits compared with near-shore deposits.

RELATION FOR SURFACE TEMPERATURE

The relation of the surface temperature to the calcium carbonate content of sediments is illustrated by figure 18, which is based on data presented in tables 5 and 6. The figure shows that the calcium carbonate content of the sediments in general increases as the temperature rises. The rate of increase, however, is more regular for near-shore than for pelagic deposits. In the near-shore sediments the general average for all depths and salinities increases from 9 percent in the temperature group 0° to 10° to 28 percent in the group 25° to 30°, and in the pelagic deposits it rises from 40 to 46 percent between these two temperature groups. The rate of increase in the near-shore sediments is fairly regular, but in the pelagic sediments it is irregular, and the curve showing the relationship is W-shaped. The average calcium carbonate content of the four temperature groups 0° to 10°, 10° to 20°, 20° to 25°, and 25° to 30° for the pelagic sediments is 40, 45, 36, and 46 percent, respectively. It would seem, therefore, that in the pelagic group the calcium

more than 0.7 the degree of association is very good; if it is between 0.5 and 0.7 the degree of association is good; if it is between 0.3 and 0.5 the degree of association is fair; and if it is below 0.3 the degree of association is poor. Negative coefficients indicate inverse relationships.

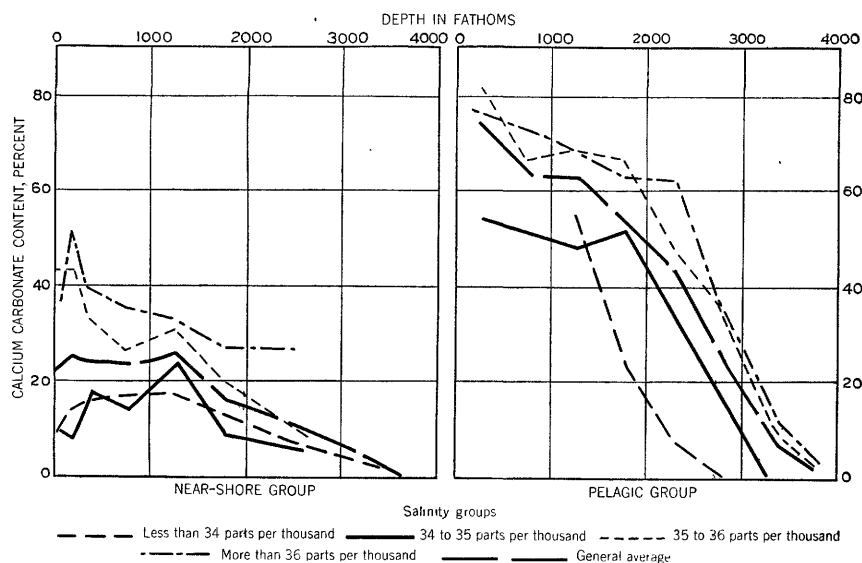


FIGURE 17.—Relation of calcium carbonate content of marine sediments to the depth of water. The lines in this figure represent mean calcium carbonate content of the sediments for the given depth of water in areas of different salinity of the surface water. The salinity is classified according to four groups, and each salinity group is represented by one line. Temperature is not considered in this figure; each line represents the average for all temperatures in the particular salinity group.

The coefficient of correlation is determined with a certain amount of unreliability, which is called the probable error. The probable error is greatest when the coefficient is 0, and it decreases in magnitude as the

⁴⁹ Chaddock, R. E., Principles and methods of statistics, pp. 286-305, New York, Houghton Mifflin Co., 1925.

⁵⁰ The term "association" seems better than "relationship", because it implies no cause and effect relation.

coefficient approaches 1.0 or -1.0 . It also decreases as the number of samples increases. A coefficient of correlation ordinarily is not regarded as significant unless it is at least four times as great as the probable

error. Thus if the coefficient and the probable error are 0.30 ± 0.10 the relation may not be significant, but if they are 0.30 ± 0.04 , the relation, or rather the degree of association, though not particularly good, is significant.

TABLE 7.—Comparison of the relation of the calcium carbonate content of marine sediments to the salinity of the surface water, the temperature of the surface water, and the depth of water, as indicated by coefficients of correlation

Near-shore deposits											
Salinity				Depth				Temperature			
Temperature (° C.)	Depth (fathoms)	Coefficient of correlation	Number of samples	Temperature (° C.)	Salinity (parts per thousand)	Coefficient of correlation	Number of samples	Depth (fathoms)	Salinity (parts per thousand)	Coefficient of correlation	Number of samples
0-10	0-1, 000	0.31 ± 0.04	190	0-10	<34	-0.07 ± 0.05	184	0-1, 000	<34	0.36 ± 0.03	317
	1, 000-2, 000	$.45 \pm .08$	48		34-35	$-.75 \pm .06$	23		34-35	$.17 \pm .06$	131
	2, 000-3, 000	-----	11		35-36	$.09 \pm .12$	31		35-36	$.45 \pm .04$	144
	3, 000-4, 000	-----	3		36+	-----	0		36+	$.38 \pm .05$	150
10-20	0-1, 000	$.56 \pm .03$	234	10-20	<34	$-.21 \pm .07$	96	1, 000-2, 000	<34	$.40 \pm .07$	63
	1, 000-2, 000	$.37 \pm .08$	55		34-35	$-.29 \pm .08$	36		34-35	$.02 \pm .09$	55
	2, 000-3, 000	$.76 \pm .06$	24		35-36	$.31 \pm .07$	78		35-36	$.50 \pm .07$	56
	3, 000-4, 000	-----	1		36+	$.14 \pm .07$	79		36+	$.20 \pm .11$	36
20-25	0-1, 000	$.28 \pm .07$	85	20-25	<34	$-.84 \pm .04$	24	2, 000-3, 000	<34	$.68 \pm .08$	23
	1, 000-2, 000	$.38 \pm .11$	29		34-35	$.26 \pm .13$	24		34-35	$.31 \pm .13$	23
	2, 000-3, 000	$.50 \pm .18$	8		35-36	$.27 \pm .09$	44		35-36	$.18 \pm .20$	11
	3, 000-4, 000	-----	0		36+	$.38 \pm .12$	22		36+	$-.31 \pm .17$	12
25-30	0-1, 000	$.48 \pm .03$	233	25-30	<34	$.03 \pm .08$	76	3, 000-4, 000	<34	$.00 \pm .34$	4
	1, 000-2, 000	$.39 \pm .06$	78		34-35	$.02 \pm .07$	103		34-35	-----	0
	2, 000-3, 000	$.39 \pm .11$	26		35-36	$.21 \pm .09$	47		35-36	-----	0
	3, 000-4, 000	-----	0		36+	$.09 \pm .07$	85		36+	-----	0
General average	-----	$.44 \pm .02$	^a 1, 025	-----	-----	$.01 \pm .06$	^b 952	-----	-----	$.32 \pm .04$	1, 025
Pelagic deposits											
0-10	0-1, 000	0.47 ± 0.21	6	0-10	<34	0.48 ± 0.14	14	0-1, 000	<34	-----	1
	1, 000-2, 000	$.79 \pm .07$	15		34-35	$.35 \pm .17$	12		34-35	$-.18 \pm 0.20$	11
	2, 000-3, 000	$.65 \pm .12$	11		35-36	-----	1		35-36	$.58 \pm .10$	19
	3, 000-4, 000	-----	1		36+	-----	0		36+	$.18 \pm .10$	40
10-20	0-1, 000	$.04 \pm .12$	33	10-20	<34	$.62 \pm .08$	26	1, 000-2, 000	<34	$.30 \pm .15$	17
	1, 000-2, 000	$.19 \pm .06$	133		34-35	$.49 \pm .07$	50		34-35	$-.55 \pm .07$	50
	2, 000-3, 000	$.58 \pm .03$	165		35-36	$.48 \pm .05$	117		35-36	$.30 \pm .06$	95
	3, 000-4, 000	$.77 \pm .10$	8		36+	$.32 \pm .05$	113		36+	$-.04 \pm .06$	135
20-25	0-1, 000	$-.24 \pm .21$	9	20-25	<34	-----	0	2, 000-3, 000	<34	$.20 \pm .13$	24
	1, 000-2, 000	$.63 \pm .05$	63		34-35	$.59 \pm .10$	18		34-35	$.28 \pm .06$	99
	2, 000-3, 000	$.32 \pm .05$	135		35-36	$.35 \pm .08$	54		35-36	$.13 \pm .05$	172
	3, 000-4, 000	$.29 \pm .22$	8		36+	$.68 \pm .03$	134		36+	$-.10 \pm .05$	216
25-30	0-1, 000	$.67 \pm .08$	23	25-30	<34	-----	2	3, 000-4, 000	<34	-----	1
	1, 000-2, 000	$.50 \pm .05$	86		34-35	$.36 \pm .07$	76		34-35	$.00 \pm .25$	7
	2, 000-3, 000	$.05 \pm .05$	200		35-36	$.52 \pm .05$	107		35-36	$.47 \pm .15$	12
	3, 000-4, 000	$-.19 \pm .11$	32		36+	$.71 \pm .03$	133		36+	$-.21 \pm .12$	29
General average	-----	$.45 \pm .06$	928	-----	-----	$.50 \pm .03$	^c 857	-----	-----	$.13 \pm .05$	928

^a Total number of samples.

^b Depths greater than 2,000 fathoms excluded.

^c Depths less than 1,000 fathoms excluded.

The coefficient of correlation was determined for each of the 96 original size distributions except for a few that were represented by a small number of samples. The results are shown in table 7. The coefficients varied so much that in the determination of the general averages, four types of averages—the mean, the median, a weighted mean, and a weighted median—were averaged together to determine the general average. In the computation of the weighted averages the coefficients were weighted inversely as the probable error. The probable error of the averages represents the semi-interquartile range divided by the square root of the number of groups averaged.

The average coefficient of correlation of the 11 near-shore groups showing the relation of surface salinity to calcium carbonate content is $.44 \pm .02$. The range is from $.28 \pm .07$ to $.76 \pm .06$. These data indicate a definite but not particularly close association between the calcium carbonate content of near-shore sediments and the salinity of the surface water. The average coefficient of correlation between surface salinity and calcium carbonate content of the 15 groups of pelagic sediments is $.45 \pm .06$. The range is from $-.24 \pm .21$ to $.79 \pm .07$. The numerical value of the average coefficient of correlation is nearly the same as for the near-shore deposits, but the larger probable error for

the pelagic group indicates that the degree of association is less certain for pelagic deposits than for near-shore deposits.

The average coefficient of correlation between depth and calcium carbonate content for the 15 groups of near-shore deposits is $.01 \pm .06$, and for the 12 groups of pelagic deposits it is $.50 \pm .03$. The smallness of the coefficient for the near-shore deposits indicates that they show no apparent relationship between depth and calcium carbonate content, but the figure for the pelagic deposits indicates a fairly good degree of asso-

relationship between depth and calcium carbonate content in near-shore deposits, where the quantity of terrigenous detritus may obscure the effect of depth. A large coefficient, on the other hand, suggests strongly that there is a relationship.

The relation between the surface salinity and the calcium carbonate of sediments seems to be fairly definite, because the average coefficient for all the groups is about .45. The relation, however, is more definite for near-shore than it is for pelagic deposits because of the larger probable error for the pelagic deposits. The relation between depth and calcium carbonate content for pelagic deposits, but not for near-shore deposits, likewise is fairly definite. The relation for surface temperature, on the other hand, seems to be less certainly established. The apparent lack of relationship between surface temperature and the calcium carbonate content of the sediments, however, does not necessarily indicate a poor relation for temperature in general, because calcium carbonate is presumably formed chiefly in the upper 50 or 100 meters of water in the sea, and lateral variations in temperature in this zone do not necessarily occur in the same way as in the surface water above.

The statistical data therefore must be interpreted as not demonstrating the existence of a relationship between temperature and calcium carbonate content of the sediments; but they most certainly do not indicate that no relationship exists. In fact, the averages represented by figure 18, although associated with a large amount of scatter, suggest that the calcium carbonate content of marine

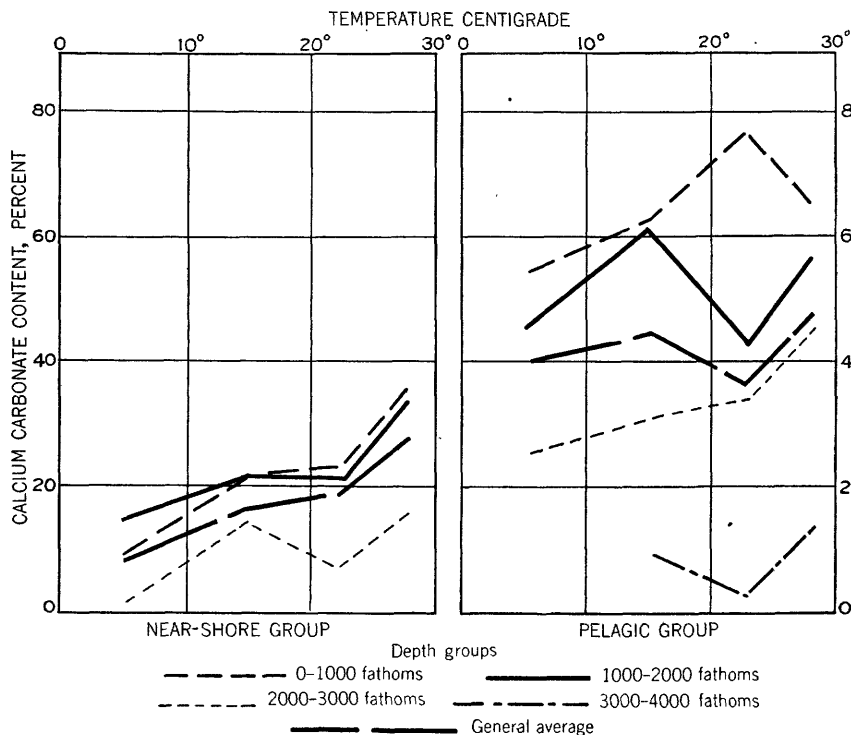


FIGURE 18.—Relation of calcium carbonate content of marine sediments to the temperature of the surface water. The lines in this figure represent mean calcium carbonate content of the sediments for the given temperature of the surface water in water of different depths. The depths are classified according to four depth groups, as in figures 12 to 16. The salinity is not considered in this figure; each line represents the average for all salinities in each particular depth group.

ciation between depth and calcium carbonate content. The average coefficient of correlation between surface temperature and calcium carbonate content for the 13 near-shore groups is $.32 \pm .04$, which indicates at best only a slight degree of association; for the 14 pelagic groups it is $.13 \pm .05$, which indicates very little association.

SIGNIFICANCE OF STATISTICAL DATA

The coefficient of correlation does not demonstrate a cause and effect relationship. Neither does a low coefficient necessarily indicate lack of relationship, as a small coefficient may be due to the effect of variables other than the two variables upon which the coefficient is based—that is, the real relationship may be masked by the effect of other factors. Such, for instance, might be the cause of the apparent poor

sediments increases as the surface temperature of the overlying water rises.

The most definite conclusion derived from this statistical study is that the calcium carbonate content of the sediments seems to be definitely related to the salinity of the overlying surface water; the calcium carbonate content of the sediments increases with the surface salinity.

The increase in calcium carbonate content of the sediments is greatest between salinities of 34 and 36 parts per thousand. Sediments in areas where the salinity is less than 34 parts in general contain less than 5 percent of calcium carbonate, and those in areas in which the salinity is more than 36 parts as a rule contain more than 50 percent of calcium carbonate. The calcium carbonate content increases but slightly as the salinity rises above 36 parts. The critical salinity seems to be about 35 parts per thousand, which is approximately the average salinity of the ocean.

AREAL RELATIONS OF CALCIUM CARBONATE CONTENT OF SEDIMENTS

PREPARATION OF MAP

In order to ascertain the extent to which the relationships of calcium carbonate to surface salinity, surface temperature, and depth might be affected by extraneous factors, a map was prepared showing the distribution of calcium carbonate in marine sediments throughout the world with respect to depth of water and surface salinity (pl. 71). The surface temperature should also be shown on this map, but in order to make the map clearer the temperature was indicated on another map (fig. 19). The surface salinity was also shown on figure 19, so that the relation of the temperature to the calcium carbonate content of the sediments could be ascertained easily by comparison with the salinity lines on the two maps.

SOURCE OF DATA

The salinities shown on plate 71 and figure 19 are taken from Schott⁵¹ and the temperatures shown on figure 19 from Shokalsky.⁵² The depths are taken from Murray and Hjort,⁵³ except those in the south Atlantic, which are based largely on Wüst.⁵⁴ The depth contours on Wüst's map are given in kilometers, which, although roughly equal to multiples of 500 fathoms, cause difficulty in the construction of a map based on fathoms, especially in regions such as the ocean off southern Brazil, where a large area lies between a depth of 2,000 fathoms and 4 kilometers.

The distribution of calcium carbonate was compiled from three sources—(1) the calcium carbonate content of nearly 4,000 samples reported by several workers;⁵⁵ (2) maps of the areal distribution of calcium carbonate in the Pacific Ocean by Murray and Lee,⁵⁶

in the north Atlantic south of latitude 25° by Correns,⁵⁷ and in the south Atlantic by Pratje;⁵⁸ and (3) maps of the distribution of the deep-sea deposits in the Atlantic and Indian Oceans by Murray and Philippi,⁵⁹ in the Pacific Ocean by Murray and Lee,⁶⁰ and in the north-west Pacific by Hanzawa.⁶¹ The data from all these sources were placed on a single map, and the lines of equal calcium carbonate content shown on plate 71 were drawn upon the basis of the data so plotted.

CLASSIFICATION OF DATA

On plate 71 the calcium carbonate content of the sediments is separated into three groups—50 to 100 percent, 10 to 50 percent, and 0 to 10 percent. If sufficient data were available it would be desirable to make more subdivisions, but as several large areas were represented only by a few bottom samples it seemed practicable to make only three groups. Furthermore, in many areas the calcium carbonate content of the sediments changes from high to low within a short distance; consequently, because of the relatively small scale of the map, it would be confusing to increase the number of subdivisions in these areas.

The threefold classification presented here separates the sediments into groups of rich, intermediate, and poor calcium carbonate content, or, in terms of rocks which the sediments would form when lithified, into (1) limestones, (2) calcareous shales or sands, and (3) slightly calcareous or noncalcareous shales or sands.

RELIABILITY OF MAP

The distribution of calcium carbonate has been indicated over the entire map, but as many areas are represented by only a few data the map should be interpreted with an understanding of the conditions under which it was made.

In the Atlantic Ocean the mapping is based on a large number of samples and is fairly reliable between 40° N. and 40° S. In the Pacific, however, it is based on fewer samples than in the Atlantic. Murray and Lee present a map of the distribution of calcium carbonate in the Pacific, but their map contains large areas unrepresented by samples. Hanzawa⁶² and I⁶³ present additional data, but still several large areas are represented by only a few samples—notably north of 40° N., south of 50° S., and in the southwest Pacific south of 20° S.

⁵¹ Schott, G., Die Verteilung des Salzgehaltes im Oberflächenwasser der Ozeane: *Annalen der Hydrographie*, Band 56, Heft 5, p. 184, 1928.

⁵² Shokalsky, J., *Oceanography* [in Russian], pp. 134-135, Petrograd, 1917. See also Schott, G., *Geographie des Atlantischen Ozeans*, pl. 10, p. 144, Hamburg, C. Boysen, 1926. Schott, G., and Schu, F., *Die Wärmeverteilung in den Tiefen des Stillen Ozeans: Annalen der Hydrographie*, Band 38, Heft 1, p. 44, 1910. Krümmel, O., *Handbuch der Ozeanographie*, Band 1, pp. 400-406, 1907.

⁵³ Murray, J., and Hjort, J., *The depths of the ocean*, p. 128, New York, Macmillan Co., 1912.

⁵⁴ Wüst, G., *Schichtung und Zirkulation des Atlantischen Ozeans: Wiss. Ergeb. Deutschen Atlantischen Exped. Meteor*, 1925-27, Band 6, Lief. 1, p. 84, 1933.

⁵⁵ Von Gimbel, *Geologisch-mineralogische Untersuchung der Meeresgrundproben aus der Nordsee: Ergebn. Untersuchungsfahrten S. M. Knbt. Drache in der Nordsee*, 1881, 1882, 1884, pp. 23-47, Berlin, 1886. Murray, J., and Renard, A. F., *Challenger Rept., Deep-sea deposits*, pp. 34-147, 1891. Murray, J., and Philippi, E., *Die Grundproben der Deutschen Tiefsee Expedition: Wiss. Ergeb. Deutschen Tiefsee Exped. Valdivia*, 1899-1900, pp. 98-136, 1908. Murray, J., and Lee, G. V., *The depth and marine deposits of the Pacific: Harvard Coll. Mus. Comp. Zoology Mem.*, vol. 38, pp. 40-148, 1909. Philippi, E., *Die Grundproben der Deutschen Südpolar-Expedition: Deutschen Südpolar-Exped., 1901-3, Repts.*, vol. 2, pp. 437-557, 1910. Spethmann, H., *Studien über die Bodenzusammensetzung der Baltischen Depression vom Kattegat bis zur Insel Gotland: Wiss. Meeresuntersuchungen, neue Folge*, Band 12, Abt. Kiel, pp. 309-312, 1910. Murray, J., and Chumley, J., *The deep-sea deposits of the Atlantic Ocean: Royal Soc. Edinburgh Trans.*, vol. 54, pp. 1-216, 1924. Samoiloff, J. V., and Gorskova, T. I., *The deposits of the Barents and Kara Seas* [in Russian, with English summary]: *Trudy Plovuchnevo Morskovo Nauchnovo Inst. Vyp. 14*, pp. 36-39, 1924. Pratje, O., *Die Sedimente der Deutschen Bucht: Wiss. Meeresuntersuchungen, neue Folge*, Band 18, Abt. Helgoland, Heft 6, p. 126, 1931. Trask, P. D., Hammar, H. E., and Wu, C. C., *Origin and environment of source sediments of petroleum*, pp. 249-273, Houston, Tex., Gulf Publishing Co., 1932.

⁵⁶ Murray, J., and Lee, G. V., *op. cit.*, map 3, p. 169.

⁵⁷ Correns, C. W., *Mineralogisch-geologische Arbeiten der Deutschen Atlantischen Expedition: Gesell. Erdkunde Berlin Zeitschr.*, Jahrg. 1928, Ergänzungsheft 3, p. 127.

⁵⁸ Pratje, O., *Geologische Tiefseeforschungen auf der Deutschen Atlantischen Expedition: Deutsch geol. Gesell. Zeitschr.*, Monatsber., Band 79, p. 202, 1927.

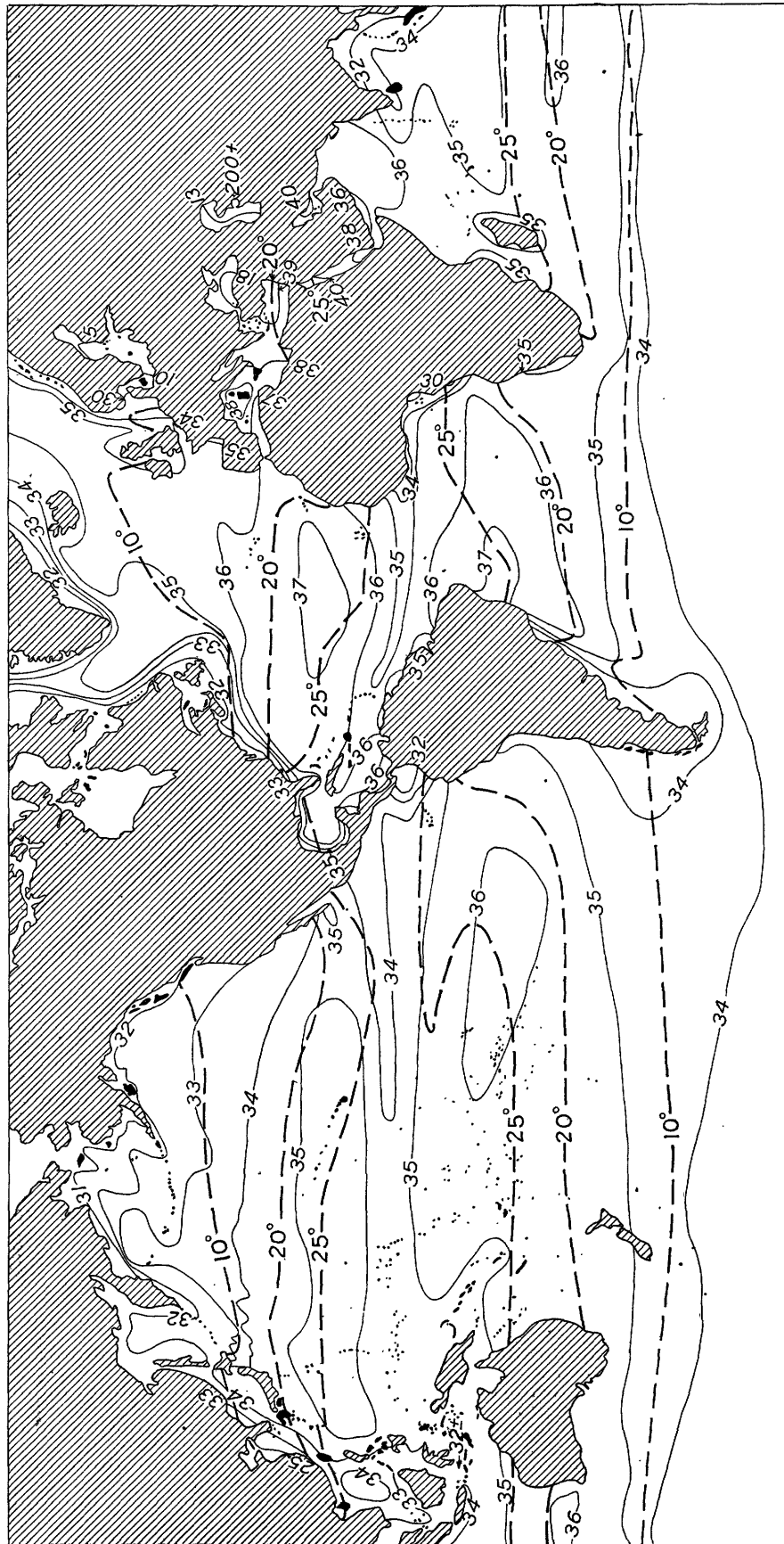
⁵⁹ Murray, J., and Philippi, E., *op. cit.*, maps 1 and 2, p. 206.

⁶⁰ Murray, J., and Lee, G. V., *op. cit.*, map 2, p. 169.

⁶¹ Hanzawa, S., *Preliminary report on marine deposits from the southwestern North Pacific Ocean, in Records of oceanographic works in Japan*, pp. 59-77, Nat. Research Council Japan, 1928.

⁶² Hanzawa, S., *op. cit.*

⁶³ Trask, P. D., Hammar, H. E., and Wu, C. C., *op. cit.*



EXPLANATION

— 34 —
Salinity in parts per thousand
(after Schott)

— 10° —
Temperature Centigrade
(after Shokalsky)

FIGURE 19.—Map of the ocean showing the mean annual salinity and temperature of the surface water. (After Schott and Shokalsky.)

Murray and Lee⁶⁴ show three lines of equal calcium carbonate content—namely, 25, 50, and 75 percent. On plate 71 the 50-percent line in the Pacific Ocean is based largely on Murray and Lee's 50-percent line, but the 10-percent line lies within the limits of Murray and Lee's 25-percent line. In general, deposits classified by Murray⁶⁵ as red clay contain less than 10 percent of calcium carbonate. He places the upper limit at 30 percent and states that the average calcium carbonate content of red clay in the Atlantic Ocean is about 8 percent and in the Pacific 5.3 percent.⁶⁶ Consequently, unless there were data to the contrary, the line for 10-percent calcium carbonate on plate 71 is placed slightly within the limits for red clay shown by Murray and Lee.⁶⁷ Similarly, in the south Atlantic the line for 10 percent is drawn within Pratje's line for 30 percent.⁶⁸

Some parts of the map are based on very little information. The Indian Ocean, in latitudes south of 50°, and the area off the west coast of France are not well represented by samples. Maps of the distribution of bottom deposits by Murray and his coworkers were the main guides for these parts of plate 71. In the China Sea some deposits may contain more than 10 percent of calcium carbonate, and in the East Indies and the Mediterranean Sea some sediments contain more than 50 percent. The calcium carbonate content indicated in the vicinity of the islands of the western Pacific should be considered only rough estimates.

RESULTS

AREAS IN WHICH RELATIONS ARE DEFINITE

The data presented on plate 71 show that the calcium carbonate content of the sediments in many parts of the sea is related to surface salinity, surface temperature, and depth. The calcium carbonate content, the surface salinity, and the surface temperature in general increase from the poles toward the Equator. However, in large areas on both sides of the Equator the calcium carbonate content is more closely related to the surface salinity than to the surface temperature.

In the north Pacific the surface salinity and the calcium carbonate content of the sediments are low. The area of maximum salinity in the Pacific is in the southeastern part, which likewise is characterized by deposits rich in calcium carbonate. The western part of the south Pacific has a lower surface salinity than the eastern part and the sediments contain less calcium carbonate in the west than in the east, except for an area east of the northern part of Australia, where the water in general is less than 2,000 fathoms deep. In

the northern part of the Indian Ocean, the western part is more saline than the eastern part, and its sediments have a greater content of calcium carbonate. The Mediterranean and Red Seas have a high salinity and the sediments are rich in calcium carbonate. The tongue of high calcium carbonate extending southward from Brazil is in an area of high salinity. The salinity of the north Atlantic is relatively high even in areas where the temperature of the surface water is less than 20° C., and the sediments in general are rich in calcium carbonate. The deposits along the west coast of Africa contain considerable calcium carbonate in the higher latitudes, but little in the vicinity of the Equator. The sediments in the Bay of Panama likewise contain little calcium carbonate. In both the Bay of Panama and off the west coast of equatorial Africa the surface salinity is comparatively low. The surface salinity in these areas, therefore, is fairly closely related to the calcium carbonate content of the sediments.

The map also shows clearly the influence of depth of water on the calcium carbonate content of the sediments. Almost every area having a depth of more than 3,000 fathoms is characterized by deposits containing less than 10 percent of calcium carbonate, and no area of this depth contains deposits having more than 50 percent of calcium carbonate.

AREAS IN WHICH RELATIONS DO NOT SEEM TO HOLD

However, though this map indicates that the relation of calcium carbonate content of the sediments to the surface salinity, surface temperature, and depth seems to hold for many areas in the sea, it also shows that the relation does not hold for all areas. The relation for surface temperature, for example, does not apply very well to low latitudes. It is evident also that deposits of equal depth differ considerably in content of calcium carbonate. In most of the Pacific Ocean, except the southeastern part, the sediments lying between depths of 2,000 and 3,000 fathoms contain little calcium carbonate, whereas in most of the Atlantic and in the southeastern Pacific the sediments in that depth interval contain much calcium carbonate. The sediments in the northwestern part of the Indian Ocean are richer in calcium carbonate than the deposits of equal depth in the northeastern part. The sediments on the east side of the mid-Atlantic ridge in general are richer than those lying at similar depth on the west side.

The relation for salinity likewise does not apply to areas near the mid-Atlantic ridge. The surface salinity is greater on the west side than on the east side of the ridge in the south Atlantic and equal on the two sides in the north Atlantic. Wüst's concept that the Antarctic bottom current causes a low content of calcium carbonate in the sediments⁶⁹ may account for

⁶⁴ Murray, J., and Lee, G. V., *The depth and marine deposits of the Pacific*: Harvard Coll. Mus. Comp. Zoology Mem., vol. 38, map 3, p. 169, 1909.

⁶⁵ Murray, J., and Renard, A. F., *Challenger Rept.*, Deep-sea deposits, pp. 192, 213, 1891. Murray, J., and Hjort, J., *The depths of the ocean*, p. 166, New York, Macmillan Co., 1912.

⁶⁶ Murray, J., and Lee, G. V., *op. cit.*, p. 20.

⁶⁷ *Idem*, map 2, p. 169.

⁶⁸ Pratje, O., *op. cit.*, p. 202.

⁶⁹ Wüst, G., *Schichtung und Zirkulation des Atlantischen Ozeans*: Wiss. Ergeb. Deutschen Atlantischen Exped. *Meteor*, 1925-27, Band 6, Lief. 1, pp. 59-64, 1933.

the distribution of calcium carbonate among the deposits of the Atlantic Ocean, as he suggests, but it does not seem to apply to the Pacific Ocean, where the sediments in southern latitudes contain more calcium carbonate than those in northern latitudes.

It would also seem that if the surface salinity influenced the deposition of calcium carbonate, the sediments underlying the Atlantic equatorial current, which is composed of water of relatively low surface salinity, should contain comparatively little calcium carbonate. The map does not indicate any such low calcium carbonate content in this area. The equatorial current in the Pacific, however, though likewise characterized by relatively low surface salinity, is underlain by sediments low in calcium carbonate. The deposits north of the Pacific equatorial current, underlying the area having a salinity of 35 parts per thousand, are represented by very few samples, but the data available suggest that the sediments are slightly richer in calcium carbonate in this area than in the vicinity of the equatorial current. However, if the calcium carbonate content of the sediments is related to the surface salinity, it would seem as if the sediments in the north Pacific in the area underlain by water having a salinity of 35 parts per thousand should contain more calcium carbonate than they do.

The calcium carbonate content of the deposits off southern California and Baja California is about 15 percent, which is higher than usual for areas having a salinity as low as in this region. These sediments are fairly rich in bottom-living Foraminifera, which may be a contributing cause to the somewhat greater calcium carbonate content than would be expected. The sediments off the Mackenzie Delta, in northern Canada, contain about 12 percent of calcium carbonate or dolomite. As a considerable proportion of the carbonate in these sediments seems to be dolomite,⁷⁰ it is probable that much of the carbonate is derived from particles of limestone or dolomite transported from adjacent land areas. The sediments of the Black Sea are fairly rich in calcium carbonate, but the surface salinity is low, being only 18 parts per thousand.

It would seem, therefore, that the relations of surface salinity, surface temperature, and depth to the calcium carbonate content of the sediments are not demonstrated definitely by the areal relations shown on plate 71. However, as explained above, the deposition of calcium carbonate is a very complicated process and is affected by a large number of factors, many of which operate simultaneously. The individual factors vary in their effect in different parts of the ocean. In some areas the influence of any particular factor may be obscured by the effect of some other factor. A relation between the calcium carbonate content of the sediments

and the salinity therefore would not be apparent for all areas in the ocean. The surprising feature is that a relation is found for so many areas.

COMPARISON WITH RESULTS OF OTHER LINES OF ATTACK

The relation of the areal distribution of calcium carbonate content to surface salinity accords fairly satisfactorily with the relation indicated by the statistical study of the individual samples. The relation indicated by both of these empirical lines of attack agrees with the relation indicated by the study of the solubility of calcium carbonate in sea water. It seems evident, therefore, that the calcium carbonate content of the sediments is definitely related to the salinity of the water. Areas of high salinity are associated with sediments rich in calcium carbonate, and areas of low salinity are associated with sediments poor in calcium carbonate.

EXPLANATION OF RELATIONSHIPS

The relation of salinity to the calcium carbonate content of sediments may be only in part a cause and effect relation. The notable increase in calcium carbonate content of sediments as the surface salinity rises from 34 to 36 parts per thousand is considerably greater than would be indicated by the increase in degree of saturation of the water caused by such a rise in salinity. The salinity associated with the greatest change in calcium carbonate content of the sediments is about 35 parts per thousand, which is approximately the average salinity of the ocean. It is possible that the surface isohalines of 35 parts per thousand may roughly mark the line between oversaturation and undersaturation of calcium carbonate in the upper layers in the sea. That is, areas in which the salinity is more than 35 parts per thousand are likely to be supersaturated, thus favoring the precipitation of calcium carbonate, and areas in which the salinity is less than 35 parts are likely to be undersaturated, thus inhibiting the precipitation of calcium carbonate. The salinity would thus be only an index of the degree of saturation of the water—that is, the relation between the salinity and calcium carbonate content of the sediments might to a considerable extent be a relation that was not one of cause and effect.

Similarly, it is possible that as the salinity rises above 35 parts per thousand it affects the activity of organisms in a manner not yet known, thus indirectly influencing the deposition of calcium carbonate; for, as explained above, living organisms, because of their effect on the carbon dioxide content of the water, constitute one of the most influential factors affecting the deposition of calcium carbonate in the sea.

Furthermore, though the salinity in different parts of the ocean remains fairly constant from year to year, the water in any particular area, in the course of time,

⁷⁰ Trask, P. D., Hammar, H. E., and Wu, C. C., *Origin and environment of source beds of petroleum*, p. 104, Houston, Tex., Gulf Publishing Co., 1932.

moves to another area in which the salinity is different—that is, the water in the ocean circulates in a more or less definite way. The salinity tends to increase in certain areas because of evaporation and tends to decrease in other areas because of influx of water from land or from the sky. The water in areas in which evaporation prevails is relatively dense and strives to move to areas where the water is less saline and therefore less dense. The sea water, consequently, is constantly but in general very slowly moving in its effort to maintain equilibrium; but because of the effects of evaporation and precipitation equilibrium is never attained.⁷¹ However, a sort of balance is obtained which causes the salinity in different parts of the ocean to remain nearly constant, even though the water in those areas continues to move.

Consequently, in areas of high salinity, where the degree of saturation presumably is greater than 100 percent, precipitation of calcium carbonate can continue more or less indefinitely, thus favoring the deposition of calcareous sediments. If the water did not move, only a comparatively small quantity of calcium carbonate could be precipitated, because the degree of saturation of the water would soon be lowered to 100 percent and no more calcium carbonate could be precipitated until the degree of saturation increased again. However, because of this slow circulation of the water, the physical conditions in any one area remain more or less constant, and calcium carbonate can be precipitated continually from areas in which the degree of saturation of the water is greater than 100 percent. The relation of calcium carbonate content of sediments to salinity therefore may to a considerable extent be influenced by the effect of salinity on oceanic circulation.

The relation of the salinity to the calcium carbonate content of sediments may also be due in part to the relation of salinity to time. Experimental data of investigators at the Scripps Institution of Oceanography seem to indicate that the precipitation of calcium carbonate from sea water is influenced by the length of time the water has remained in a state of supersaturation.⁷² Salinity is a rough index of the length of time water has remained at or near the surface, because the basic way in which water becomes saline is through evaporation, and the higher the salinity the longer the water has been in a position where it could evaporate. Therefore if the length of time that the water remains in a state of supersaturation is a factor, salinity may be an indirect index of the precipitation of calcium carbonate.

These possible explanations of the relation of the calcium carbonate content of marine sediments to salinity are offered as working hypotheses in an attempt

to account for the closer relation of the calcium carbonate content of the sediments to the salinity of the water than is indicated by the solubility of calcium carbonate in sea water.

GEOLOGIC APPLICATION OF RELATIONSHIPS

The sediments the geologist encounters in the field leave clues about the conditions under which they were deposited. The proper interpretation of these clues depends largely upon knowledge of the conditions under which sediments now accumulate. As Bigelow⁷³ mentions repeatedly, our knowledge of the processes and conditions that prevail in the ocean is handicapped greatly by paucity of observations. The field is so big and the science is so young that many problems are far from being solved satisfactorily. The problem of deposition of sediments is no exception to this statement. The conditions of deposition of calcium carbonate have probably been investigated as fully as any other problem of sedimentation, but, as is evident from this paper, much is yet to be learned about the manner in which calcium carbonate is deposited in sediments. Consequently it is hazardous at this time to reason backward from the calcium carbonate content of ancient sediments and infer the conditions under which the sediments were deposited. However, to illustrate the possibilities afforded by studies of the calcium carbonate content of ancient sediments, two subjects—the deposition of red clay and inferences about past climates—may be discussed briefly here.

FORMATION OF RED CLAY

Wattenberg⁷⁴ states that below a depth of 500 meters in the south Atlantic the saturation of the water with calcium carbonate ranges between 90 and 100 percent. The degree of saturation of the water in these parts of the ocean is influenced strongly by the temperature and by the production of carbon dioxide, either by decomposition of organisms after death or by the metabolic processes of living organisms. The lower temperature and the higher carbon dioxide content of the deep water increase the solubility of the water for calcium carbonate, with the result that the degree of saturation of the water becomes less. If the degree of saturation decreases, there is a greater tendency for particles of calcium carbonate to be dissolved as they fall through the water, and the quantity of calcium carbonate deposited in the sediments becomes smaller. Conversely, if the temperature of the water were increased or if the rate of formation of carbon dioxide were lessened, the saturation of the water with calcium carbonate would be increased and the calcium carbonate content of the sediments should become larger.

⁷¹ Cf. Johnstone, J., *An introduction to oceanography*, 2d ed., pp. 256–303, Liverpool, 1928.

⁷² Gee, H., *Calcium equilibrium in the sea*, V, Preliminary experiments on precipitation by removal of carbon dioxide under aseptic conditions: *Scripps Inst. Oceanography Tech. ser.*, vol. 3, no. 7, p. 183, 1932. Moberg, E. G., Greenberg, D. M., Revelle, R., and Allen, E. C., *The buffer mechanism of sea water*: *Scripps Inst. Oceanography Tech. ser.*, vol. 3, no. 11, p. 247, 252, 1934.

⁷³ Bigelow, H. B., *Oceanography*, New York, Houghton Mifflin Co., 1931.

⁷⁴ Wattenberg, H., *Kalziumkarbonat- und Kohlensäuregehalt des Meereswassers*: *Wiss. Ergeb. Deutschen Atlantischen Exped. Meteor*, 1925–27, Band 8, Teil 2, p. 222, 1933.

According to data presented by Wattenberg⁷⁵ for temperatures ranging between 0° and 10° C., an increase of 3° would decrease the solubility of calcium carbonate in the water about 10 percent—that is, the degree of saturation would increase about 10 percent. If all the water before the temperature was raised was more than 90 percent saturated, which according to Wattenberg⁷⁶ now holds for the subsurface water of the south Atlantic, and presumably for other oceans as well, an increase of 10 percent in the degree of saturation would cause the water everywhere to be more than 100 percent saturated. Particles of calcium carbonate therefore would not dissolve as they fell to the sea floor, with the result that calcareous sediments instead of red clay would be deposited in the ocean. Although Wattenberg's data may be subject to correction, they certainly indicate the order of magnitude. The absence or scarcity of red clay among ancient sediments might therefore be explained by the greater degree of saturation of the deep water in the ocean in the past than at present. The increase in degree of saturation of the water could have been caused by an increase in temperature, but it could also have been caused by the water remaining at the same temperature long enough to become saturated by solution of calcareous particles as they fell to the sea floor, or by a decrease in carbon dioxide content of the water.

The cold water that now occupies the lower part of the ocean is derived largely from polar regions. It is probable that if the polar ice caps were removed the water at the bottom of the ocean would become warmer, the capacity of the water to hold calcium carbonate in solution would become less, and there would be a tendency for the sediments to have a greater content of calcium carbonate.

If it is assumed that essentially all the water from the surface to the bottom was saturated with calcium carbonate at the end of the Pliocene epoch, the advent of the ice age would have lowered the temperature of most of the ocean, and the degree of saturation of the water, particularly of the subsurface layers, would have become less. The sediments deposited during Pleistocene time in general should therefore contain relatively little calcium carbonate.

At the end of the Pleistocene epoch, or perhaps even during the warm interglacial intervals, the temperature of the ocean would gradually rise and the calcium carbonate content of the sediments accordingly should increase. That is, the calcium carbonate content of sediments such as *Globigerina* ooze would diminish progressively downward from the surface of the deposits until a zone of pre-Pleistocene (or interglacial) sediments was reached. Such a downward diminution of

calcium carbonate is reported by Pratje⁷⁷ and Iselin⁷⁸ in *Globigerina* oozes in the Atlantic. These authors regard this downward decrease in carbonate as due to progressive upward leaching of the calcium carbonate; but the phenomenon is perhaps explained more plausibly by the progressive increase in saturation of the overlying water since Pleistocene time.

The same condition would result also if the water remained at the same temperature for considerable time. If the temperature remained constant for a sufficiently long period, the water would eventually become saturated, because of solution of calcareous particles falling through the water, with the result that the calcium carbonate content of the sediments would become relatively high. Presumably red clay would not be deposited under such conditions until the overlying water again became undersaturated with calcium carbonate. A general lowering of the temperature of the deeper layers of water seems the simplest way to decrease the degree of saturation of the water, but increased production of carbon dioxide by any cause would have the same effect.

It is evident from this discussion that the depth at which red clay now forms in the sea is influenced strongly by the degree of undersaturation of the water with calcium carbonate, and that in other geologic periods the depths at which it could form would probably be different from the present depths.

RELATION OF CALCIUM CARBONATE CONTENT OF ANCIENT SEDIMENTS TO CLIMATE

The average salinity of the surface of the ocean is about 35 parts per thousand. The sediments in regions in which the surface salinity is greater than 35 parts in general contain considerable calcium carbonate, and the sediments in areas in which the salinity is less than 35 parts, particularly in areas in which it is less than 34 parts, contain relatively little calcium carbonate. (See table 1.) That is, the sediments in areas in which the salinity is above the average are likely to be rich in calcium carbonate, and those in areas in which the salinity is below the average are likely to be poor in calcium carbonate.

This relationship is subject to many exceptions. The calcium carbonate content of sediments is influenced by several factors in addition to salinity, particularly by the proportion of terrigenous constituents, which in many areas masks the effects of other factors; for even though the rate of deposition of calcium carbonate is constant, the sediments off the mouths of large rivers contain little calcium car-

⁷⁵ Wattenberg, H., op. cit., p. 207.

⁷⁶ Idem, p. 222.

⁷⁷ Pratje, O., *Geologische Tiefseeforschungen auf der Deutschen Atlantischen Expedition: Deutsch. geol. Gesell. Zeitschr., Monatsber., Band 79, p. 203, 1927.*

⁷⁸ Iselin, C. O., Recent work on the dynamic oceanography of the North Atlantic: *Am. Geophys. Union Trans. 10th Ann. Meeting, pp. 88-89, Nat. Research Council, 1930.*

bonate compared with the sediments off arid coasts. Consequently it is not safe to generalize backward and infer that if a sediment contains little calcium carbonate it necessarily was deposited in water of sub-normal salinity, or that if it contains much calcium carbonate it was deposited in water having a salinity greater than normal. The data presented in this paper indicate, however, that there is a significant chance that the calcium carbonate content of some sediments reflects the climate, particularly with respect to rainfall, at the time the sediments were deposited.

Therefore, some alternations between limestone and calcareous shale or between calcareous shale and non-calcareous shale may represent fluctuations in climate. The more calcareous layers might have been deposited

during dry periods, which would favor the evaporation of water and tend to increase the salinity in the basin of deposition and which at the same time would decrease the quantity of detritus transported to the basin of deposition. The less calcareous layers might have been deposited during wet periods, in which the water had a low salinity and the quantity of detritus transported by rivers was large.

It would be presumptuous to advocate that alternations between limestone and shale should in general be interpreted in this way. However, the possibility should be mentioned that some alternations between limestone and shale or between calcareous and non-calcareous shale might have resulted largely from alternate changes in climate.