

# Chemical Erosion of Beach Rock and Exposed Reef Rock

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GEOLOGICAL SURVEY PROFESSIONAL PAPER 260-T



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By ROGER REVELLE *and* K. O. EMERY

BIKINI AND NEARBY ATOLLS, MARSHALL ISLANDS

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GEOLOGICAL SURVEY PROFESSIONAL PAPER 260-T

*A study of the solution of calcium  
carbonate in the intertidal zone*



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## BIKINI AND NEARBY ATOLLS, MARSHALL ISLANDS

### CHEMICAL EROSION OF BEACH ROCK AND EXPOSED REEF ROCK

By ROGER REVELLE<sup>1</sup> and K. O. EMERY<sup>2</sup>

#### ABSTRACT

Above the low-tide line the beach rock and reef rock of Bikini and nearby atolls have a highly irregular surface with numerous small depressions, many of which are separated only by knife-edge ridges. This and other geological evidence suggests that some process of solution is of great importance in removing limestone in the intertidal zone. Marked diurnal changes in the alkalinity-chlorinity ratio of the water in the depressions strongly indicate that intertidal solution of calcium carbonate does in fact occur, probably at a comparatively rapid rate. But computations based on the experimentally determined solubility product of calcium carbonate in sea water show an apparent supersaturation in the basin and reef water that ranges from 175 to 800 percent. Possible rationalizations of these opposing lines of evidence are that (1) solution may occur within the limestone of the basin floors or in the interstitial water of the algal mats which cover some of the floors; (2) solution may occur in the films of water left on the basin walls by the receding tide; or (3) much of the calcium may be complexed or hydrated, and the time involved in the formation and dissociation of complexes containing calcium is long relative to the time required to precipitate free calcium ions or to obtain them from solution of calcium carbonate. If this is true, solution can occur when the carbonate concentration or temperature, or both, are rapidly decreased even though the product of the concentrations of total calcium and carbonate remains above the equilibrium saturation value. Erosion of calcium carbonate in warm ocean water is very widespread but is confined to the intertidal zone, where marked diurnal changes in conditions occur. These facts, coupled with the slow attainment of calcium carbonate saturation equilibrium in the laboratory, support the hypotheses of slow complexing or slow hydration and dehydration.

In the intertidal basins, cooling at night and respiration by plants and animals cause a drop in temperature and pH and an increase in carbon dioxide content of the water, all of which favor solution. Precipitation of calcium carbonate during the daytime is facilitated by warming of the water and by the decrease in carbon dioxide and increase in pH corresponding to the excess of plant photosynthesis over respiration. In some of the basins the water shows a stable density stratification at night, with more extreme conditions for solution near the bottom.

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#### INTRODUCTION AND ACKNOWLEDGMENTS

Above the low-tide line the beach rock and reef rock of Bikini and nearby atolls have highly irregular surfaces with numerous small basin-shaped depressions (pl. 225), many of which are separated only by knife-edge ridges. The walls of some basins are overhanging so that their maximum diameters are below their rims. Very irregular basins are obviously the result of lateral coalescence of two or more smaller ones. Where two basin floors are at different levels, their junction may form a steplike structure and cause complete drainage of the higher basin. The floors of the basins are fairly flat, but the floors and especially the walls exhibit small sharp irregularities suggestive of corrosion rather than abrasion. Similar irregularities are present on the surfaces of melting ice, dissolving salt pans, and some meteorites. The basins seldom contain cobbles that might have served as tools to abrade potholes; moreover, some are floored by a thin mat of fragile foraminiferal sand held together by filamentous algae.

Erosion of limestone in the intertidal zone has been reported from the warm and temperate belts in many parts of the world (see, for example, MacFadyen, 1930; Kuenen, 1933; Fairbridge, 1952; and Guilcher, 1953). Solution basins in the upper parts of reef flats (pl. 226), nips (deep notches or undercuts) and caves at the base of sea cliffs in all kinds of calcareous rock from Pleistocene reef material to dense Paleozoic limestone, and nips around negroheads atop reef flats are common and widespread (pl. 227-229). The very existence of the broad and dead reef flat just below low-tide level indicates the efficacy of erosion of limestone in the intertidal zone. This erosion is as effective in sheltered lagoons as on exposed shores.

In some respects the irregular microtopography of the intertidal zone is similar to that of the karrenfelds on the elevated limestones of Guam and other high islands of the western Pacific. These karrenfelds have extremely jagged surfaces formed by vertical and

lateral corrosion of the limestone. Parts of the surfaces are exposed only to the air, and here solution must be brought about by films of rain water rather than by ground water. Unlike the intertidal basins, many of the steep-walled hollows in the karrenfelds are not closed basins capable of retaining water.

The geologic evidence for solution in the intertidal zone of warm tropical waters is in conflict with the results of laboratory studies of the solubility of calcium carbonate in sea water. The problem has been well stated by Kuenen (1950, p. 436):

Geological observations \* \* \* appear to establish beyond doubt the solvent action of tropical surface waters on reef limestone \* \* \*. Investigation of sea water from the surface in tropical seas has led chemists to the conclusion that it is always saturated or even supersaturated with lime. Hence they have concluded that solution of limestone is not possible. But it is exceedingly difficult to establish whether solution under natural conditions is really excluded.

He left the question essentially as it was in 1933 (p. 75) when he wrote that—

\* \* \* whether it is the greater range in temperature, the contact with the atmosphere, some influence of surface tension, the alternate wetting and drying, or some other unsuspected influence which was overlooked in the experimental work, I am unable to say.

Solution in the upper part of the intertidal zone has been attributed to rainwater or to fresh ground water by some workers (Wentworth, 1938; Hills, 1949), but this is not likely to be important where rainfall is slight and where ground water cannot reach basins and nips, as on negroheads. Other investigators have supposed that animals burrowing into or grazing upon the rocks and algae boring below the rock surface are chiefly responsible for intertidal erosion of limestone (Duerden, 1902, p. 326-332; Gardiner, 1931, p. 68; and Ginsburg, 1953, p. 61-68).

Emery (1946) demonstrated that in the relatively cool waters of La Jolla, Calif., basins in the sandstone along the shore form in part through solution by biochemically modified sea water. The calcium carbonate cement of the sandstone is dissolved during the nighttime, when the carbon dioxide content of the water in the pools is raised by animal and plant respiration. In the daytime carbon dioxide is removed by photosynthesis, and calcium carbonate is precipitated, probably as small loose crystals that wash out of the pool at the next high tide. Thus, by alternate solution of calcareous cement and flushing out of the precipitate, the calcium carbonate is removed. Growth of the pools is aided by sand-ingesting organisms, particularly snails of the genus *Littorina* (North, 1954, p. 190-194). At La Jolla the characteristics of intertidal rock surfaces

indicate that some chemical and organic erosion also occurs outside of pools.

The basins at Bikini differ in several ways from those at La Jolla. Obvious points of difference are their presence in limestone instead of in sandstone, the absence of *Littorina*, the lesser abundance of other conspicuous animals and of algae, the greater rainfall, and especially the higher temperature.

A brief investigation of the chemical and physical processes taking place in the solution basins at Bikini was carried out in 1946 during Operation Crossroads. Measurements of temperature, oxygen content, and hydrogen-ion concentration of the water in basins and on the reef flat were made during the scientific resurvey in 1947 and the Mid-Pacific Expedition in 1950. In an attempt to resolve uncertainties resulting from these researches, supplementary studies of 13 basins at Guam were carried out by Emery in 1952. These included field determinations of alkalinity, temperature, oxygen content, and hydrogen-ion concentration of the basin and reef waters.

The field work at Bikini in 1947 was done by T. S. Austin and T. Goreau; the investigations in 1950 were under the direction of R. F. Dill and R. Y. Morita. Their careful work under difficult conditions is gratefully acknowledged. E. D. Goldberg, Wilson Orr, and N. W. Rakestraw made valuable suggestions concerning the interpretation of the results, particularly with regard to the problems of complexing or hydration of calcium. We are indebted to R. W. Fairbridge for helpful discussions, for assembling many of the photographs in plates 226 to 229, and for invaluable assistance in reviewing the literature. The studies at Guam were carried out during geologic mapping in the islands of the western Pacific accomplished as a part of a joint program of the Corps of Engineers, U. S. Army, and the U. S. Geological Survey.

#### MEASUREMENTS OF DIURNAL VARIATIONS IN SOLUTION-BASIN AND REEF WATER

Measurements of temperature, oxygen content, and hydrogen-ion concentration in basins and on the reef flat at Bikini were made at intervals of 2 to 4 hours over several days, and water samples were collected for later chlorinity determinations.

Dissolved oxygen was determined by the Winkler method. Hydrogen-ion concentration was measured with a pH meter, using a glass electrode. The meter was carried to each basin in turn, and the pH determined on a freshly collected water sample.

Five basins in the beach rock near the southeastern end of Bikini island were studied in 1950. Three of

these were below mean-tide level and consequently were flooded much of the time. Basin 3 was near the high-tide line and was only occasionally flooded. Basin 4 was above high tide during the survey and was not reached by sea water. These two basins show a more extreme range of conditions than the others and serve

more easily to elucidate the processes taking place on the reef. Measurements from the two basins are shown in figure 233; selected data are given in table 1, as are data from the reef flat. Results very similar to these were obtained during the investigations of 1946 and 1947.

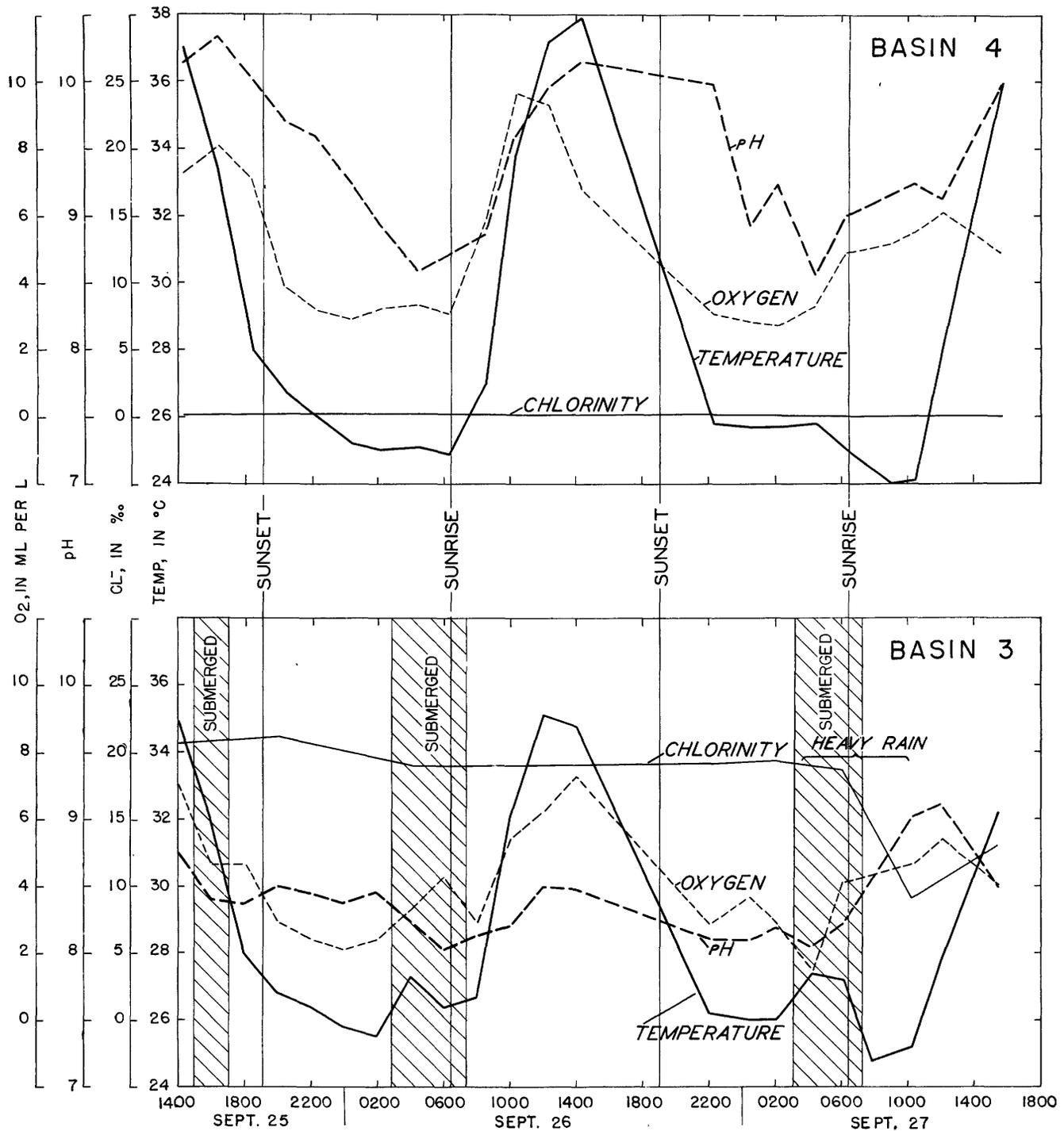


FIGURE 233.—Changes in water characteristics of two solution basins at Bikini island in 1950. Basin 4 contains fresh rainwater; basin 3 contains normal sea water.

The basic difference between the two basins was in the chlorinity of the water. Basin 4 contained nearly fresh water having a chlorinity of less than  $0.2\text{‰}$  (parts per thousand). Until the last morning, when a heavy rain diluted the water, the chlorinity in basin 3 was close to that of the sea water around the atoll, ranging between  $18.4$  and  $21.0\text{‰}$ . In both basins the water temperature increased during the day and decreased during the night, with a total range of  $13^\circ\text{C}$  in the brackish basin and  $9^\circ\text{C}$  in the saltier one.

Oxygen content and pH showed marked diurnal cycles. Computations from the data given in figure 233 indicate that oxygen in basin 3 varied from about 30 percent of saturation at night to 180 percent of saturation in the afternoon. Roughly the same range of percentage saturation, 50 to 190 percent, occurred in basin 4. On the reef flat the diurnal variation was much smaller, from 85 to 140 percent. The oxygen increase in the daytime was due to the excess of photosynthetic-oxygen production by marine algae living on the basin floors and within the water, over oxygen consumption by animal and plant respiration. A corresponding decrease in carbon dioxide content must have occurred. At night, when photosynthesis ceased, oxygen was removed by respiration, and carbon dioxide was liberated. These inferred changes in carbon dioxide

content are reflected in the observed cycle of pH, which was high during the day, when the carbon dioxide content was small, and low during the night, when the amount of carbon dioxide was relatively large.

Unfortunately, alkalinity was not determined in the field because it was believed that changes in the oxygen content would suffice to compute changes in carbon dioxide. Subsequent computations showed, however, that oxygen was being exchanged with the atmosphere so rapidly that the change in oxygen content was not a reliable measure of the change in carbon dioxide. Therefore, alkalinity of a few samples was measured nearly 2 years after the samples had been collected. Uncertainty in these results led to more complete field measurements of water in 13 basins and a reef flat at Guam in 1952 (Emery, in manuscript). In addition to measurements of temperature, oxygen content, and pH, water samples were filtered within a few hours after collection, and alkalinity was determined by the titration method of Wattenberg (1930). Representative data from the reef flat and from three basins of widely varying chlorinity (designated as brackish water, normal sea water, and hypersaline water) are given in table 1. A 24-hour series of observations of the normal sea-water basin (Guam 4) is illustrated in figure 234. The diurnal variations of alkalinity in the basins

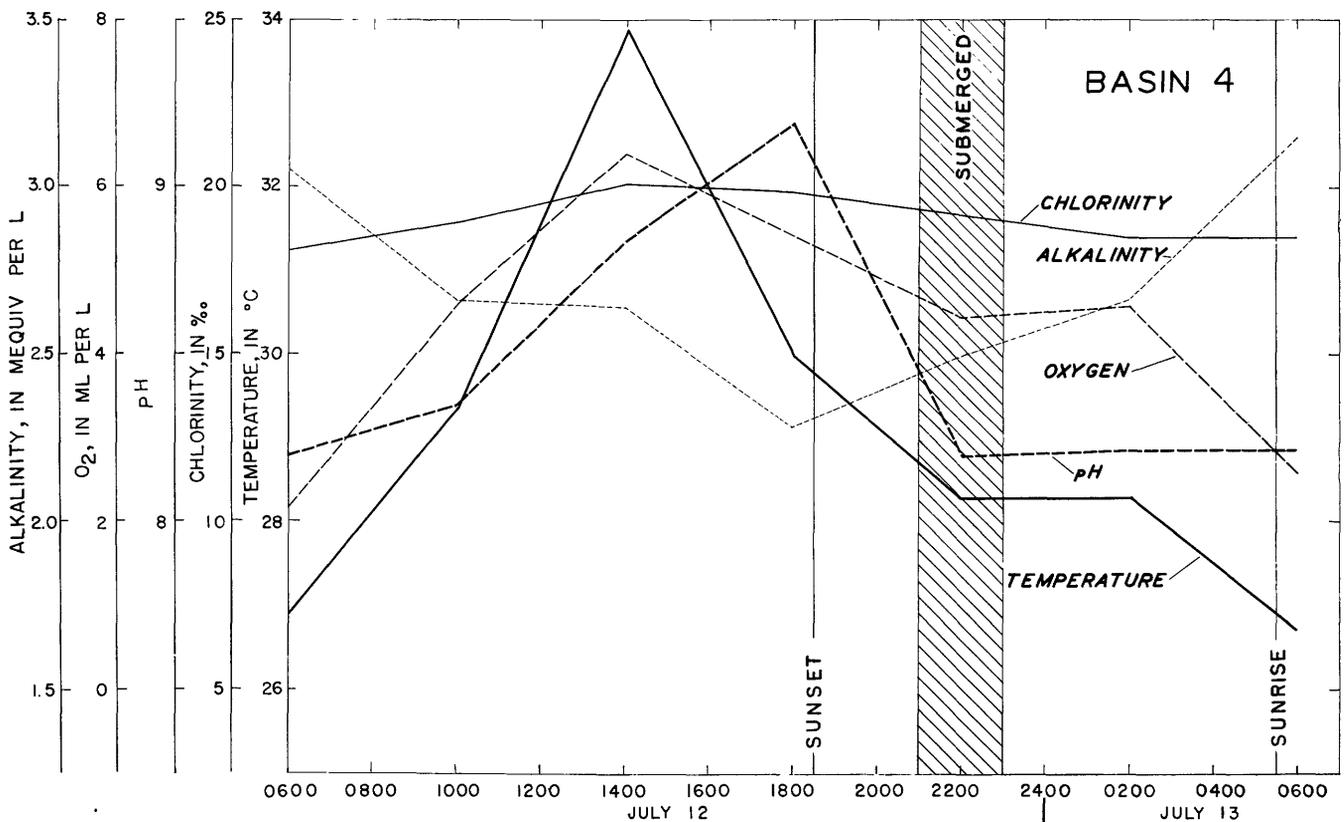


FIGURE 234.—Changes in water characteristics of normal sea-water basin 4 at Guam in 1952. Basin is 75 cm long, 50 cm wide, 10 cm deep.

were large and in any one basin were roughly inverse to the variation in pH.

RESULTS

In the eight solution basins at La Jolla investigated by Emery (1946), the carbonate concentration increased during the daytime as carbon dioxide and bicarbonate decreased; consequently, calcium carbonate was precipitated. This precipitation resulted in a proportionate decrease of the alkalinity. During the night the carbon dioxide content of the water increased; the alkalinity increased as calcium carbonate was dissolved. The water was apparently supersaturated with calcium carbonate in late afternoon but undersaturated at night. Computations based on Smith's (1941, p. 240) apparent solubility product for calcium carbonate (aragonite) show as much as 425 percent saturation in the daytime and only 45 percent saturation at night. A minor error in the previously published computations

of percentage saturation, kindly pointed out to us by R. N. Ginsburg, is corrected in table 1.

Similar computations, using Smith's solubility product, indicate that at a temperature of 25° C, a chlorinity of 19‰, and an alkalinity of 2.34 mequiv per l (milliequivalents per liter), typical values for the tropics, solution can take place only if the pH is below 7.74. None of the pH values for tropical-basin and reef water given in table 1 are less than 8.00. The water is apparently supersaturated with calcium carbonate at all times. The greatest excesses occur in the afternoon and the least just before dawn, but the degree of saturation, using Smith's apparent solubility product for aragonite, is never less than 175 percent and rises to more than 800 percent (table 1). Thus, tropical sea water is apparently incapable of dissolving calcium carbonate at any time. This conclusion is opposed both by the geological evidence and by the observed changes in alkalinity.

TABLE 1.—Summary of data for water from solution basins and reef flats

[Symbols: B, bottom; T, top; X, 400 ft from shore; Y, 1,400 ft from shore]

| Type of feature          | Date     | Local time | Sampled locality | Temp (°C) | Cl (‰) | pH    | Oxygen           |                    | Total CO <sub>2</sub> (mg per l) | Alkalinity (mequiv per l) | Alkalinity: chlorinity | Calcium carbonate (percent saturation) <sup>1</sup> |
|--------------------------|----------|------------|------------------|-----------|--------|-------|------------------|--------------------|----------------------------------|---------------------------|------------------------|---|
|                          |          |            |                  |           |        |       | Ml per l         | Percent saturation |                                  |                           |                        |   |
| <b>La Jolla</b>          |          |            |                  |           |        |       |                  |                    |                                  |                           |                        |   |
| Normal sea-water basin   | 1944     |            |                  |           |        |       |                  |                    |                                  |                           |                        |   |
|                          | Apr. 28  | 0500       | T                | 13.3      | 18.60  | 8.00  |                  |                    | 93.39                            | 2.298                     | 0.1234                 | 125   |
|                          | Apr. 28  | 1700       | T                | 24.8      | 22.07  | 9.00  |                  |                    | 44.07                            | 1.905                     | .0863                  | 425   |
|                          | May 6    | 0645       | T                | 15.9      | 18.98  | 7.62  |                  |                    | 107.28                           | 2.418                     | .1274                  | 46  |
| <b>Bikini</b>            |          |            |                  |           |        |       |                  |                    |                                  |                           |                        |   |
| Normal sea-water basin 3 | 1950     |            |                  |           |        |       |                  |                    |                                  |                           |                        |   |
|                          | Sept. 26 | 0615       | T                | 26.4      | 18.95  | 8.00  | 4.30             | 89                 |                                  | 2.302                     | 0.1215                 | 175   |
|                          | Sept. 26 | 1415       | T                | 34.8      | 19.10  | 8.50  | 7.30             | 178                |                                  |                           |                        |   |
| Fresh-water basin 4      | Sept. 27 | 0200       | T                | 26.0      | 19.34  | 8.20  | 2.95             | 61                 |                                  | 2.474                     | .1279                  | 265   |
|                          | Sept. 25 | 1420       | T                | 37.0      | .10    | 10.10 | 7.33             | 146                |                                  |                           |                        |   |
|                          | Sept. 26 | 0430       | T                | 25.1      | .19    | 8.60  | 3.38             | 57                 |                                  |                           |                        |   |
| Reef flat                | Sept. 26 | 1220       | T                | 37.0      | .11    | 9.95  | 9.35             | 187                |                                  |                           |                        |   |
|                          | Sept. 27 | 0430       | T                | 25.8      | .07    | 8.55  | 3.33             | 57                 |                                  |                           |                        |   |
|                          | Sept. 27 | 1500       | T                | 36.0      | .02    | 9.95  | 4.91             | 96                 |                                  |                           |                        |   |
|                          | Sept. 25 | 1435       |                  | 32.0      | 18.99  | 8.30  | 4.58             | 105                |                                  |                           |                        |   |
|                          | Sept. 26 | 0615       |                  | 26.4      | 18.95  | 8.00  | 4.30             | 89                 |                                  | 2.302                     | .1216                  | 175   |
|                          | Sept. 26 | 1200       |                  | 31.1      | 19.00? | 8.35  | 6.21             | 140                |                                  |                           |                        |   |
|                          | Sept. 27 | 0610       |                  | 27.2      | 18.58  | 8.20  | 4.08             | 85                 |                                  | 2.276                     | .1224                  | 245   |
|                          | Sept. 27 | 1545       |                  | 30.0      | 18.71  | 8.25  | 4.80             | 106                |                                  | 2.421                     | .1294                  | 325   |
| <b>Guam</b>              |          |            |                  |           |        |       |                  |                    |                                  |                           |                        |   |
| Hypersaline-water basin  | 1952     |            |                  |           |        |       |                  |                    |                                  |                           |                        |   |
|                          | July 12  | 0600       | T                | 26.7      | 22.75  | 8.41  | 2.29             | 50                 |                                  | 3.73                      | 0.164                  | 625   |
|                          | July 12  | 0600       | B                | 27.3      | 22.89  | 8.27  | H <sub>2</sub> S | 0                  |                                  | 5.60?                     | .244                   | 590   |
|                          | July 12  | 1800       | T                | 28.3      | 23.80  | 8.52  | 4.11             | 94                 |                                  | 3.86                      | .162                   | 785   |
|                          | July 12  | 1800       | B                | 29.9      | 23.61  | 8.50  | 3.15             | 74                 |                                  | 3.82                      | .162                   | 810   |
|                          | July 13  | 0600       | T                | 26.4      | 22.41  | 8.29  | 2.10             | 46                 |                                  | 3.61                      | .161                   | 495   |
|                          | July 13  | 0600       | B                | 27.2      | 22.89  | 8.20  | H <sub>2</sub> S | 0                  |                                  | 4.09                      | .179                   | 515   |
|                          | July 12  | 0600       | B                | 26.9      | 18.08  | 8.20  | 2.09             | 43                 |                                  | 3.05                      | .169                   | 330   |
|                          | July 12  | 1400       | B                | 33.9      | 20.10  | 8.84  | 6.41             | 143                |                                  | 2.64                      | .131                   | 805   |
|                          | July 24  | 1600       | B                | 37.2      | 18.85  | 9.39  | 11.56            | 294                |                                  | 2.03                      | .108                   | 770   |
| Brackish-water basin     | July 25  | 0400       | B                | 27.8      | 18.85? | 8.47  | 2.54             | 54                 |                                  | 2.91                      | .154                   | 480   |
|                          | July 24  | 1600       | B                | 27.8      | .32    | 9.10  | 5.23             | 91                 |                                  | .80                       | 2.50                   | 180   |
|                          | July 25  | 0400       | B                | 26.4      | .36    | 8.20  | 3.10             | 52                 |                                  | 3.21                      | 8.90                   | 250   |
| Reef flat <sup>3</sup>   | July 5   | 1840       | X                | 31.7      | 19.10  | 8.28  | 6.00             | 137                |                                  | 2.676                     | .140                   | 395   |
|                          | July 6   | 0610       | X                | 22.8      | 18.90  | 8.24  | 3.44             | 67                 |                                  | 2.676                     | .143                   | 345   |
|                          | July 5   | 1815       | Y                | 30.0      | 19.12  | 8.17  | 5.27             | 117                |                                  | 2.750                     | .144                   | 335   |
|                          | July 6   | 0545       | Y                | 28.8      | 19.50  | 8.24  | 3.36             | 73                 |                                  | 2.793                     | .143                   | 355   |

<sup>1</sup> Computed from Smith's (1941) apparent solubility product for aragonite.

<sup>2</sup> Analyses made nearly 2 years after collection of water samples.

<sup>3</sup> Reef flat 2,200 ft wide.

Reference to table 1 and figure 234 shows that in the brackish-water and normal sea-water (Guam 4) basins at Guam, and in the bottom of the hypersaline-water basin, the alkalinity increased at night and decreased in the daytime. These changes could have been caused by evaporation at night and dilution during the day, by solution of calcium carbonate at night and precipitation during the day, or possibly by other processes affecting the alkalinity. We are convinced that any other such processes were insignificant in the Guam and Bikini basins.

Under some circumstances the alkalinity may change because of solution or deposition of magnesium carbonate (Riviere, 1940, p. 41; Fairbridge, 1950, p. 385). This is probably not a significant factor at Bikini and Guam because magnesium carbonate is only a minor constituent of the rock. In localities where organic matter is rapidly decomposing, the alkalinity may be increased appreciably through production of salts of organic acids and, under extreme conditions, through reduction of sulfates to sulfides. In the clear and nearly colorless waters of the basins at Bikini and Guam, the concentration of organic material is undoubtedly too small to affect the alkalinity measurably. Hydrogen sulfide was noted in only one basin, and, as shown below, the amount was insufficient to account for more than a small fraction of the observed change in alkalinity.

Evaporation and dilution would have affected the chlorinity and the alkalinity in the same proportion. It is probable that the slight changes in alkalinity observed on the reef flats were due to these causes, because the alkalinity-chlorinity ratio was constant within the limits of experimental error. But table 1 shows that in the basins the alkalinity-chlorinity ratio was significantly lower in the daytime than at night, and therefore precipitation and solution, respectively, are indicated.

For the normal sea-water basin (Guam 4) the diurnal change of alkalinity on July 12 was 0.41 mequiv per l. This is not extreme either for this basin or for the other basins, even though it is very much larger than the changes observed in the reef water. The change in calcium computed from the change in alkalinity is illustrated in table 2. When this computed change in calcium concentration is corrected to a constant chlorinity, that of the reef water, it is found that 9 mg per l (milligrams per liter) of calcium was dissolved during the night and nearly 5 mg per l was precipitated during the day. If the calcium carbonate dissolved at night is derived entirely from solution of limestone, the rate of solution is such that about 33 years would be required to dissolve a layer of limestone 1 cm thick.

This should be considered a minimum time because much of the calcium carbonate added to the water at night must have originated from solution of calcareous organic remains or re-solution of the calcium carbonate precipitated during the day. The net rate of removal of limestone depends in part on the tidal renewal of water at night and in part on the rate at which calcium carbonate, precipitated as small particles during the day, can be washed out of the basin by the tidal flow.

TABLE 2.—Computed amounts of calcium carbonate dissolved and precipitated in a typical solution basin

|   | Normal sea-water basin (Guam 4) |        | Reef-flat water (Guam) |
|---|---------------------------------|--------|------------------------|
|   | 0600                            | 1400   | 1815                   |
| Cl.....%  | 18.08                           | 20.10  | 19.12                  |
| Ca balanced against weak bases, computed from measured alkalinity.....mg ions per l.            | 1.53                            | 1.32   | 1.38                   |
| Do.....mg per l.  | 61.1                            | 53.0   | 55.1                   |
| Ca balanced against weak bases, computed from alkalinity-chlorinity ratio in reef water.....do. | 52.1                            | 57.8   | 55.1                   |
| Ca dissolved.....do.  | 9.0                             | 0      | -----                  |
| Ca precipitated.....do.   | 0                               | 4.8    | -----                  |
| CaCO <sub>3</sub> dissolved.....do.   | 22.5                            | 0      | -----                  |
| CaCO <sub>3</sub> precipitated.....do.  | 0                               | 12.0   | -----                  |
| Volume of basin water.....cm <sup>3</sup>   | 36,000                          | 36,000 | -----                  |
| Area of basin floor.....cm <sup>2</sup>   | 3,900                           | 3,900  | -----                  |
| Thickness of CaCO <sub>3</sub> (assumed density 2.5) dissolved per 24 hr.....μ.                 | .83                             | -----  | -----                  |

In the bottom of the hypersaline-water basin at Guam, some of the nighttime increase in alkalinity evidently resulted from the reduction of sulfate to sulfide, a weak Brönsted base, during the latter part of the night after the free oxygen was depleted. Because of the relative inefficiency of anaerobic respiration, the rate of hydrogen sulfide production must have been lower than the rate of decrease of oxygen during the earlier part of the night. The total hydrogen sulfide produced was probably less than 1 ml per l (milliliters per liter). This corresponds to a change in alkalinity of only 0.05 mequiv per l whereas the observed changes in alkalinity were 0.3 and 1.8 mequiv per l. Thus, the larger part of the diurnal change in the alkalinity of the bottom water must have resulted from solution and precipitation of calcium carbonate.

The average alkalinity-chlorinity ratio of the reef-flat water at Guam is 10 percent higher than the value of 0.123 which is characteristic of surface water in the open sea. This difference probably means that the reef water contains a considerable admixture of island ground water which has dissolved calcium carbonate in its passage through the limestone. A mixture of 90 percent sea water with 10 percent brackish water having an alkalinity of 3 mequiv per l (similar to that in the brackish-water basin) would give the alkalinity-chlorinity ratio of about 0.142 found on the reef. Subsequent evaporation would raise the chlorinity to the

prevailing value in the open sea around Guam. Water of the normal sea-water basin (Guam 4) is frequently exchanged with water from the reef, and consequently their average alkalinity-chlorinity ratios are nearly the same. In the hypersaline-water basin at Guam the higher average alkalinity-chlorinity ratio indicates that under the extreme conditions in this isolated basin more calcium carbonate remains dissolved throughout the day than in the basin with normal sea water. In the brackish-water basin the very high alkalinity-chlorinity ratio accords with the well-known fact that calcium carbonate is easily dissolved by fresh water.

Some of the calcium which the high alkalinities indicate as being present in solution actually may be in colloidal form. The water was filtered before the alkalinity titrations were made, but finely divided colloidal particles might have been able to pass through the filter paper. However, the existence of such a suspension could not explain the changes in alkalinity between day and night.

#### CONCLUSIONS

Geologic evidence suggests that some process of solution is of great importance in removing limestone in the intertidal zone. This process is faster than solution by rainwater, as indicated by the existence of intertidal nips in water sheltered from wave action (pl. 227-229). That it is much faster than solution below the intertidal zone is shown by the fairly level surface of the reef flat at a depth less than 30 cm below normal low tide.

The diurnal changes in alkalinity-chlorinity ratios given in table 1 strongly indicate that intertidal solution of calcium carbonate does in fact take place, probably at such a rapid rate that it is an important factor in reducing islands and raised reefs to the monotonously uniform level of the reef flat. The problem remains as to how solution can occur even though, in comparison with published solubility products, the water is apparently always supersaturated with calcium carbonate.

Smith's value for the apparent solubility product,  $K'_{\text{CaCO}_3}$ , is based on laboratory measurements of the ion product in samples of sea water, collected over the Great Bahama Bank, which had been equilibrated with calcareous bottom mud from the bank for periods of 11 to 38 days. The mud contained large numbers of minute aragonite needles. Other work (Hindman, 1943; Wattenberg and Timmerman *in* Sverdrup, Johnson, and Fleming, 1942, p. 206), in which equilibrium was approached by dissolving or precipitating calcite, yields values of the apparent solubility prod-

uct for calcite about half as great as Smith's solubility product for aragonite. Revelle and Fleming (1934), in experiments in which aragonite was precipitated by passing air free of carbon dioxide through sea water for periods of several weeks, obtained an apparent solubility product for aragonite twice as large as Smith's value, but it is likely that the sea water was still supersaturated at the termination of their experiments. If solution and precipitation are determined by the apparent solubility product, the value of this product in the tropical basins must be at least twice that found by Revelle and Fleming, and 4 to 5 times Smith's value. Smith's apparent solubility product, when corrected for temperature and salinity, appears to be applicable to the La Jolla basins, and there is no evident reason why the solubility should be different in the tropics. Other explanations must be sought.

Clearly the diurnal cycles of oxygen, pH, and carbon dioxide reflect respiration by plants and animals, counterbalanced during the daytime by photosynthesis by plants. The greater range of the diurnal variations in the basin water, compared to the water of the reef flat or the open sea, is a result of the greater concentration of plant and animal tissue, relative to the amount of water, in the basins. Vertical gradients of chemical properties in the hypersaline-water basin indicate that more extreme conditions for carbonate solution or precipitation may exist at the bottom than within the main mass of water; this is in evident response to the bottom position of most organisms. In the hypersaline-water basin, bacterial respiration actually brings about anaerobic conditions near the bottom at night, with complete depletion of oxygen and production of hydrogen sulfide. Both sets of morning observations from this basin show a stable density gradient because the higher chlorinity near the bottom more than compensates for the slightly higher temperature. Evaporation during the daytime raises the density of the surface water so that overturning probably occurs in the late afternoon.

The presence of vertical gradients suggests that solution may occur under special local conditions. It may take place within the rock surface of the basin floors by organic acids liberated by boring algae, or by carbon dioxide produced in respiration beneath the algal mats that cover some of the floors. Measurements in 1953 by H. Rotschi while on the Capricorn Expedition of the Scripps Institution of Oceanography showed that the water beneath living algal masses on the reefs of Tahiti had a pH range of 6.0 to 8.7, much wider than in the overlying water. The diurnal changes of alkalinity given in table 1 demonstrate, however, that so-

lution and precipitation wherever they occur are reflected in changes of chemical composition of the main mass of basin water.

Solution may take place on the walls of the basins above the pool of standing water, as indicated by the highly irregular surfaces and the fact that the basins coalesce by lateral enlargement. Although it has not yet been tested, the suggestion is made that solution of calcium carbonate on the walls occurs in the film of water remaining on the rock during ebb tide. The ratio of plant and animal bulk to water bulk must be very large in such films; consequently the films should exhibit extreme ranges of pH which may permit the solution of limestone. Examination of these films should be most fruitful for understanding the development of solution basins and nips in the intertidal zone.

But the universal solution of intertidal limestone suggests that something other than localized processes is involved. Two facts are characteristic of the problem: in warm ocean water, solution is confined to the intertidal zone, where rapid and profound changes in the water conditions occur; and in the laboratory, several weeks are required for apparent equilibrium to be attained when calcium carbonate is being dissolved or precipitated in sea water (Hindman, 1943). These two facts suggest that the problem is one of reaction rates. If the calcium is involved in two simultaneous reactions—solution or precipitation of calcium carbonate, and formation of complexes with chloride or sulfate or of hydrates—and if these reactions have markedly different reaction rates, the observations could be reconciled with the laboratory equilibrium values for the apparent solubility of calcium carbonate. This would require that much of the calcium is normally in the complex or the hydrated form and that the time constant for the complexing reaction or for hydration is much longer than the time required for solution or precipitation.

Let it be supposed that at a particular time the water is supersaturated; that is, calcium is slowly proceeding from the complex or the hydrated form to simple ionic form and is being precipitated as it is freed from the complex or the hydrated state. Let a marked change in conditions suddenly occur, for example a decrease in temperature and a decrease in pH, with a corresponding decrease in carbonate-ion concentration. Calcium carbonate will be dissolved, even though the overall concentrations of carbonate and of calcium in both complex or hydrated and simple ionic form are still sufficiently high that the apparent ion product is above the equilibrium saturation value. Eventually, if the new conditions continue, solution will cease and precipitation will again occur. But, if while solution is

still proceeding, the temperature, pH, and carbonate-ion concentration are increased to the previously existing value, it is possible to restore the solution nearly to its original condition, provided the equilibrium constant for the complexing reaction or for hydration and the rates of complexing or hydration, solution, and precipitation vary sufficiently with temperature. A pseudo-equilibrium may thus tend to persist, when there is a diurnal oscillation of pH and temperature, around a point where the average product of total calcium and carbonate considerably exceeds the laboratory equilibrium value.

Complexing of a sufficiently high proportion of calcium with organic substances could conceivably reduce the calcium activity to a level so low that the product of calcium and carbonate concentrations, multiplied by the activity coefficients, would be less than the solubility product, particularly at night. However, this would require a far higher content of organic matter in the water (of the order of 1 g per l) than has been observed. Fox, Isaacs, and Corcoran (1952, p. 42), found a 0.25 to 35 mg per l range of concentration of colloidal organic matter in inshore surface-water samples. It is concluded that either slow complexing with chloride or sulfate or slow hydration and dehydration are more probable explanations of the nightly solution of calcium carbonate by the apparently supersaturated basin water. An excellent review of the problem of complex-ion formation is given by Young and Jones (1952).

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**APPENDIX—METHOD OF CALCULATION OF THE PERCENTAGE SATURATION OF CALCIUM CARBONATE**

The apparent percentage saturation of calcium carbonate is given by the ratio of the product of the calcium and the carbonate concentrations to the apparent solubility product. Thus

$$\text{percentage saturation} = \frac{[\text{Ca}^{++}] \times [\text{CO}_3^{--}] \times 100}{K'_{\text{CaCO}_3}}$$

For the usual range of temperature, chlorinity, and pH, the maximum changes of calcium, owing to solution or deposition produced by gains or losses of carbon dioxide, can amount to only about  $0.5 \times 10^{-3}$  g ions per l (gram ions per liter), or about 5 percent of the total calcium concentration. Under field conditions it is exceedingly difficult to measure the calcium directly with an accuracy of more than a few percent. Consequently the concentration of calcium was not determined experimentally but was estimated from the calcium-chlorinity ratio of sea water with the modification described below. In the open oceans the ratio of calcium to chlorinity is 0.02106 (Sverdrup, Johnson, and Fleming, 1942, p. 173), hence the concentration of calcium, expressed as gram ions per liter, is

$$[\text{Ca}^{++}] = \frac{0.02106 \text{ Cl} \times 1.025}{40}$$

if it is assumed that the concentration of calcium is governed by evaporation or dilution of sea water. This equation is accurate only when solution or precipitation of calcium carbonate has not occurred and when the sea water has not been diluted with fresh water in which the calcium-chlorinity ratio differs from that in the open sea.

Calcium totals about 400 mg per l (milligrams per liter) in ordinary sea water; of this amount, about 50 mg can be balanced against weak Brönsted bases, principally carbonate, bicarbonate, and borate. The concentration of weak bases, expressed in milliequivalents per liter (mequiv per l), is called the alkalinity. In water near the surface of the open sea the ratio between the alkalinity and the chloride concentration in grams per liter is 0.120; hence, the alkalinity-chlorinity ratio is about 0.123.

If it is assumed that measured changes in the alkalinity-chlorinity ratio correspond to changes in the calcium-chlorinity ratio, the concentration of the calcium is

$$[\text{Ca}^{++}] = \frac{0.02106 \text{ Cl} \times 1.025}{40} + \frac{([\text{A}] - 0.123 \text{ Cl}) \times 10^{-3}}{2}$$

The carbonate concentration can be determined by measurement of chlorinity, temperature, hydrogen-ion concentration, and either alkalinity or total carbon dioxide. Measurement

of total carbon dioxide content is impractical in the field, hence alkalinity was chosen for the study at Guam. The carbonate concentration in gram ions per liter was computed by means of the following equations adapted from Sverdrup, Johnson, and Fleming (1942, p. 198-200).

$$[\text{CO}_3^{--}] = \frac{[\text{A}_{\text{CO}_2}] \times K'_2 \times 10^{-3}}{[\text{H}^+] + 2K'_2}$$

where

$$[\text{A}_{\text{CO}_2}] = [\text{A}] - \left( \frac{K'_B \times [\Sigma \text{H}_3\text{BO}_3]}{K'_B + [\text{H}^+]} + [\text{H}^+] - \frac{K_W}{[\text{H}^+]} \right) \times 10^3$$

and

$$[\Sigma \text{H}_3\text{BO}_3] = 0.0221 \text{ Cl} \times 1.025 \times 10^{-3}$$

Values of  $K'_2$ ,  $K_W$ , and  $K'_B$  were taken from tables given by Harvey (1945).

For the basins within the normal range of chlorinity of sea water the apparent solubility constant of calcium carbonate was based upon Smith's (1941) value corrected, by Wattenberg's coefficients, for the observed chlorinity and temperature:

$$pK'_{\text{CaCO}_3} = 5.933 + 0.019(20.0 - \text{Cl}) + 0.012(30.0 - T)$$

For the brackish-water basin the apparently solubility was obtained by interpolation between Wattenberg's value of  $18 \times 10^{-8}$  at a chlorinity of 5 ‰ and the solubility for distilled water,  $0.5 \times 10^{-8}$  (Sverdrup, Johnson, and Fleming, 1942, p. 205, 207). A "virtual chlorinity" corresponding to the supposed ionic strength of the solution was estimated from the measured chlorinity and alkalinity.

The symbols used above are as follows:

$[\text{Ca}^{++}]$  = gram ions per liter of calcium

$[\text{CO}_3^{--}]$  = gram ions per liter of carbonate

$[\text{H}^+]$  = gram ions per liter of hydrogen =  $10^{-\text{pH}}$

$[\text{A}]$  = total alkalinity =  $([\text{HCO}_3^-] + 2[\text{CO}_3^{--}] + [\text{H}_2\text{BO}_3^-] + [\text{OH}^-] - [\text{H}^+]) \times 10^3$

$[\text{A}_{\text{CO}_2}]$  = carbonate alkalinity =  $([\text{HCO}_3^-] + 2[\text{CO}_3^{--}]) \times 10^3$

$K'_2$  = apparent second-dissociation constant for carbonic acid =  $10^{-\text{p}K'_2}$

$K_W$  = ion product for water =  $10^{-\text{p}K_W}$

$K'_B$  = apparent first-dissociation constant for boric acid =  $10^{-\text{p}K'_B}$

$K'_{\text{CaCO}_3}$  = apparent solubility product of calcium carbonate =  $10^{-\text{p}K'_{\text{CaCO}_3}}$

Cl = grams of chlorine and chlorine equivalent of bromine and iodine per kilogram of sea water, in parts per thousand

$T$  = temperature, in degrees centigrade.



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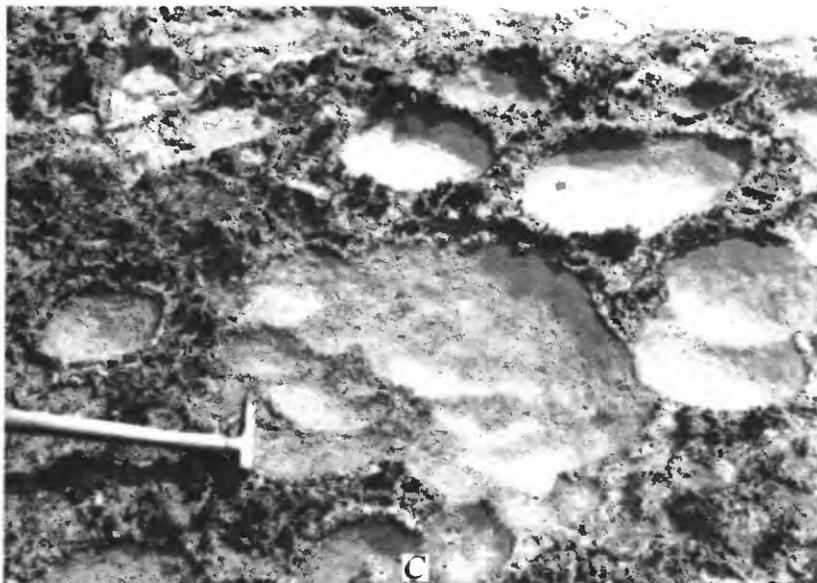
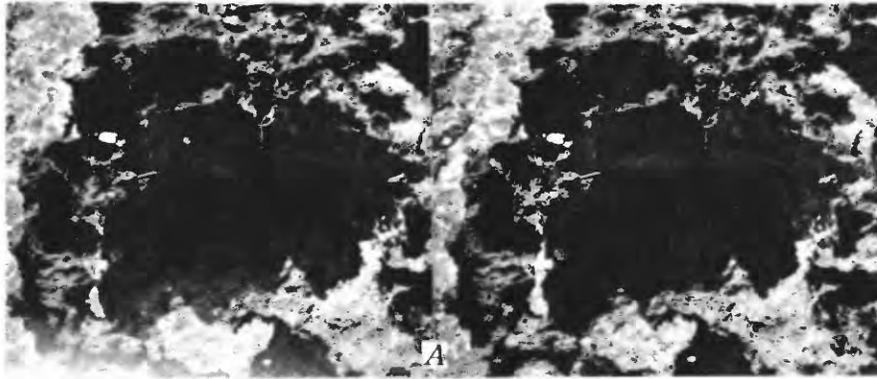
PLATES 225–229

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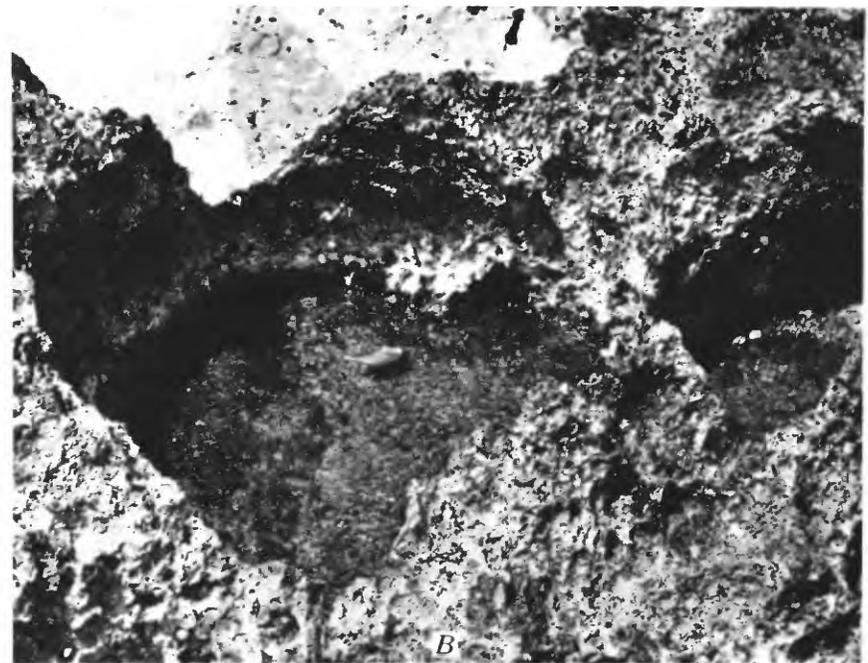
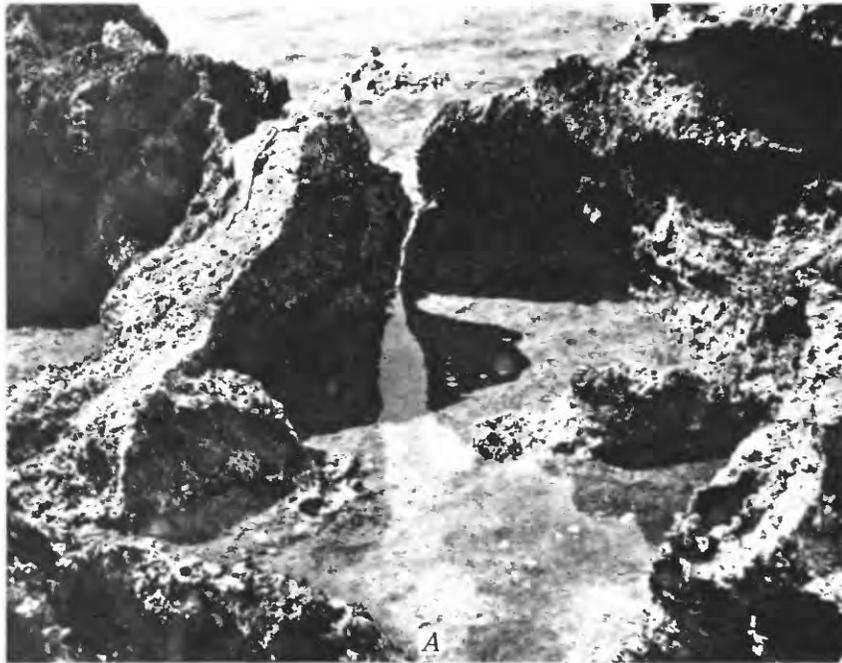
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PLATE 225

- A.* Stereopair of karren (lapies) etched in beach rock on upper part of shore ramp, about 4-5 feet above low-tide level. Bikini island. (Photograph by J. I. Tracey, Jr.)
- B.* Solution basins, now partly filled with sand, on highest part of shore ramp, about 5-6 feet above low-tide level. Bikini island. (Photograph by K. O. Emery.)
- C.* Solution basins, showing coalescence; note relatively smooth floors, and jagged surfaces between basins. Latoback island, Rongerik Atoll. (Photograph by J. I. Tracey, Jr.)



ETCHING AND SOLUTION BASINS IN THE INTERTIDAL BELT, BIKINI AND NEARBY ATOLLS



SOLUTION BASINS IN THE INTERTIDAL BELT, GUAM AND AUSTRALIA

PLATE 226

*A.* Solution basin 5, Toguan Bay, Guam. (Photograph by K. O. Emery.)

*B.* Solution basin 6, Gogna Cove, Guam. (Photograph by K. O. Emery.)

*C.* Marine solution basins, with rills and undercut runnels, etched in beach rock 5 feet above low-tide level. Western Australia, between Dongara and Geraldton. (Photograph by R. W. Fairbridge.)

*D.* Solution basin showing scalloped margins and undercuts and outlet channel following a joint plane. Western Australia, north of Murchison River. (Photograph by R. W. Fairbridge.)

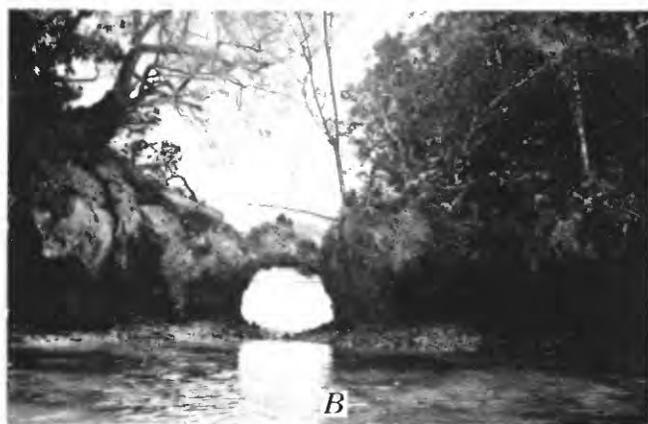
PLATE 227

- A.* Undercut cliffs of an isolated island of emergent Pleistocene coral limestone in the protected bay of Vavau; undercuts reach from low-tide level to about 5 feet above it. Tonga Group, Vavau. (Photograph by J. B. MacFall.)
- B.* Undercut cliff of limestone in intertidal zone, 6 feet high. Guam, near Inarajan. (Photograph by K. O. Emery.)

*C.* Undercut cliff of Pleistocene coral limestone, 6 feet high; note protection from mechanical erosion by offshore reef; maximum depth of notch corresponds approximately to mean sea level. Western Australia, Port Denison, near Dongara. (Photograph by R. W. Fairbridge.)



UNDERCUT SEA CLIFFS (NIPS), TONGA, GUAM, AND AUSTRALIA



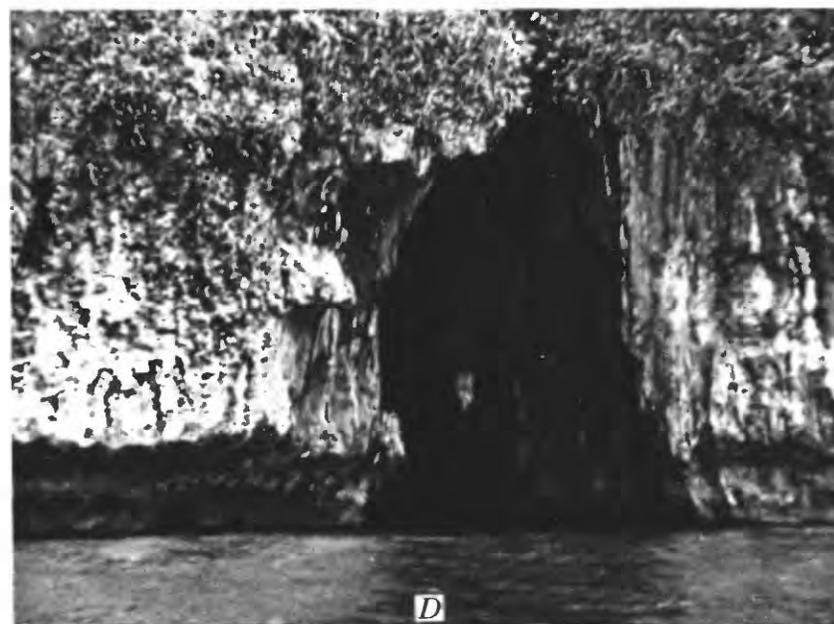
"MUSHROOM" ROCKS, REEF FLATS, AND UNDERCUT SEA CLIFFS (NIPS), FIJI

PLATE 228

- A.* Undercut cliff, showing remnants of horizontal reef platform approximately 10 feet above present reef flat. Passage between Ongea Levu and Yanuia. (Photograph by Edwin H. Bryan, Jr.)
- B.* Undercut islands nearly separated by progressive intertidal corrosion, leaving small natural bridge. Bay of Islands, Vanua Mbalavu. (Photograph by J. Edward Hoffmeister.)
- C.* Undercut cliff, with very deep notch that in places exceeds 20 feet in depth but is only 5-8 feet high; note extensive landslide due to collapse of undercut. North shore of Ongea Ndriki. (Photograph by Max Agassiz.)
- D.* Well developed "mushroom" rock (undercut stack) at low tide; top surface of undercut is 5-8 feet above reef flat. Mango. (Photograph by E. C. Andrews.)
- E.* Narrow protected bay with steep limestone cliffs undercut just as in exposed places. East shore of Ngillangillah. (Photograph by W. McM. Woodworth.)

PLATE 229

- A.* Undercut cliff, 10 feet high, in Pleistocene lagoon limestone; seen at low tide, tidal range being 3 feet; note horizontally eroded reef flat in protected lagoon. Western Australia, Middle Island, in Pelsart Lagoon, Houtman's Abrolhos islands. (Photograph by R. W. Fairbridge.)
- B.* Very deep notch, at least 20 feet deep and 5 feet high, in emergent Pleistocene coral limestone cliff. Shore is protected here by off-lying reefs and land. East Indies, west point of Waaf. (Photograph by Ph. H. Kuenen.)
- C.* Undercut cliffs and "mushroom" rocks, showing prominent overhang and horizontal top, which is the remnant of a former reef platform 10 feet above the present one. Red Sea, Farsan islands, east coast of Kamaran island. (Photograph by W. A. MacFadyen.)
- D.* Undercut cliffs leading into large sea cave (believed due to Pleistocene karst formation). Note that undercut extends into dark, protected waters of the cavern. Tonga islands, Vavau. (Photograph by Alan Jones.)



UNDERCUT SEA CLIFFS (NIPS), REEF FLAT, "MUSHROOM" ROCKS, AND SEA CAVE, AUSTRALIA, EAST INDIES, RED SEA, AND TONGA

