model." From this model the observed spread of Pb-U ratios from U-Pb systems of the same original age is attributed to Pb loss or U gain during an episodic event. The second, known as "the continuous diffusion model," has been developed in various forms by Nicolaysen (*7*), Tilton (*8*), Wasserburg (*9*), and Wetherill (*10*). From this model the linear spread of Pb-U ratios on a concordia plot is interpreted as a function of continuous Pb loss by diffusion; the diffusion loss pattern on a concordia plot being nearly linear over much of its range.

The first application of the episodic loss interpretation to U-Pb isotope relations in cogenetic zircons was that of Silver and Deutsch (*1*). This mechanism has been advocated by Silver (*2*) as the most appropriate explanation for discordant Pb-U ages in numerous cogenetic Precambrian zircon suites from the southwestern United States.

Under the experimental hydrothermal conditions the metamict Ceylon zircon has undergone a significant and systematic Pb loss and also a possible minor loss of U. The Pb-U ratios show a systematic correlation with the duration of the experimental conditions, and, on a concordia plot, they form a linear array passing through the original zircon point and the origin (Fig. 2). These isotopic disturbances have been induced by a modern hydrothermal episode. A geological event reproducing the magnitude of the various experimental conditions would produce major episodic Pb losses from the natural metamict zircon and a pattern similar to that shown in Fig. 2. It can be argued that, since such effects are not observed in this zircon, the material has not been exposed to conditions of comparable severity in that it has become significantly metamict (for example, in the last 200 to 300 million years). This suggests that detailed examinations of the state of isotopic disturbance compared with the degree of metamictization in zircons may provide useful limiting data on the thermal history of the mineral.

The decrease in rate of Pb loss as the duration of the experimental conditions increases suggests that a second significant reaction or process may be interfering with or inhibiting the Pb-loss mechanism. From investigations of natural zircons we believe this may be related to the recrystallization process. An experimental study of the relation of Pb loss to recrystallization is proceeding as part of this current laboratory program.

In conclusion, a metamict zircon has undergone systematic episodic Pb loss with possible minor loss of U during a series of hydrothermal experiments in 2 molal NaCl at 500°C and 1000 bars fluid pressure for various durations. From this one sample of zircon and this one set of experiments it is impossible to generalize for all zircon U-Pb isotope systems. However, from the experimental evidence alone, episodic Pb loss is confirmed as a significant process and is supported as a possible explanation for many discordant U-Pb isotope relations observed in natural zircon suites.

R. T. PIDGEON*
JAMES R. O'NEIL†
LEON T. SILVER

Division of Geological Sciences,
California Institute of Technology,
Pasadena 91109

References and Notes

1. L. T. Silver and S. Deutsch, *J. Geol.* **71**, 721 (1963).
2. L. T. Silver, in *Radioactive Dating* (International Atomic Energy Agency, Vienna, 1963), p. 279; ———, in *Nuclear Geophysics* (National Academy of Sciences–National Research Council Publication 1075, 1963), p. 34; ——— and S. Deutsch, *Ann. N.Y. Acad. Sci.* **91**, 279 (1961).
3. H. D. Holland and G. Gottfried, *Acta Cryst.* **8**, 291 (1955).
4. G. R. Tilton, G. L. Davis, G. W. Wetherill, L. T. Aldrich, *Trans. Amer. Geophys. Union* **38**, 360 (1957); G. R. Tilton, C. Patterson, H. Brown, M. Inghram, R. Hayden, D. Hess, E. S. Larsen, Jr., *Bull. Geol. Soc. Amer.* **66**, 1131 (1955).
5. L. T. Silver, C. R. McKinney, S. Deutsch, J. Bolinger, *J. Geol.* **71**, 196 (1963).
6. G. W. Wetherill, *Trans. Amer. Geophys. Union* **37**, 320 (1956).
7. L. O. Nicolaysen, *Geochim. Cosmochim. Acta* **11**, 41 (1957).
8. G. R. Tilton, *J. Geophys. Res.* **65**, 2933 (1960).
9. G. J. Wasserburg, *ibid.* **68**, 4823 (1963).
10. G. W. Wetherill, *ibid.*, p. 2957.

11. Support for this work is derived from AEC research contract AT(04-3)-427 (Calt. -427-5); from NSF grant GP 5486; and from funds provided by the Division of Geological Sciences, California Institute of Technology (contr. No. 1416).

* Present address: Mineralogical Institute, Swiss Federal Institute of Technology, Zurich, Switzerland.

† Present address: Isotope Geology Branch, U.S. Geological Survey, Denver, Colorado.

11 July 1966

■

Deep-Sea pH

Abstract. *In the northeastern Pacific Ocean, north of 22°N and east of 180°W, a deep-sea* pH *maximum of 7.9 exists near 4000 meters. The effect of hydrostatic pressure on the dissociation constants of carbonic acid in sea water appears to be important in its formation.*

What controls the *p*H of the ocean has been a topic of discussion in recent years. Sillen (*1*), Garrels (*2*), and Mackenzie and Garrels (*3*) stress that the reactions between silicate minerals and sea water are of great importance in maintaining the *p*H of sea water near 8. The *p*H is also altered by reactions occurring in the oceanic carbon dioxide system (*4*), and it can be influenced biologically by production and consumption of carbon dioxide or of organic acids and bases (*5*).

Until now, however, there have been few reliable *in situ p*H data for the oceanic environment, especially for the deep-sea water. Scarcity of reliable data has been attributed to the contamination of water samples by brass water-sampling bottles (Nansen bottles) used in the past (*6*). Recently, the brass contamination has been minimized by coating the inside of the bottles with Teflon. A better method is to measure *p*H directly *in situ*, as attempted by Manheim (*7*), down to a depth of 16 m. However, no application of his method has been reported for deep-sea *p*H measurements. All *in situ p*H data for the ocean, including data for this report, are from shipboard analysis.

During a recent cruise of R. V. *Yaquina* of Oregon State University, April–July 1966, I measured approximately 3000 *p*H values for sea water in the northeastern Pacific Ocean by the method described in the manual of Strickland and Parsons (*8*). The area covered was between 22° and 57°N and 135° and 180°W (*9*). In this area depth profiles of the *in situ p*H possess two maxima and one minimum (Fig. 1). A deep-sea *p*H maximum over such a broad area in the Pacific has not been reported previously.

In general, the first *p*H maximum (8.2 to 8.3) exists intermittently near the surface within the first 100 m. The second maximum, of about 7.9, frequently exists near 4000 m. The *p*H minimum, with a value of 7.5 to 7.7, has a wide depth range of 200 to 1200 m; it generally exists at the depth of oxygen minimum (Fig. 1). The near-surface pH maximum exists as a result of the air-sea carbon dioxide exchange, changes in the water temperature, and biological activity.

A pH minimum at the oxygen-minimum depth strongly suggests a biogenic origin (*4*); it is formed mainly by the biochemical oxidation of living and dead organic matter, including the respiration of marine organisms, in sea water. My calculation of the expected pH at the oxygen-minimum layer from depletion of the oxygen concentration alone, assuming an initial pH of 8.2 before consumption of oxygen, gives a value of 7.5 (*10*). The calculated value is not far from the measured value of 7.60.

In my opinion, the deep-sea pH maximum is formed primarily by the effect of the hydrostatic pressure on the dissociation constants of carbonic acid (*11*). These constants increase with an increase in pressure; and consequently a decrease in pH results. The central part of Fig. 1 illustrates the calculated pH decrease with an increase in pressure (depth) as given by Buch and Gripenberg (*11*). The calculated slope of the decrease below 3500 m is essentially the same as the measured slope.

Theoretically, the deep-sea maximum can exist at great depth if the pressure effect of pH dominates over all other effects (that is, changes in temperature and calcium carbonate dissolution). Indeed, such conditions prevail in the depths of the northeastern Pacific Ocean. At depths of 3000 to 6000 m, the sea-water temperature varies very little, between 1.5° and 1.7°C. In the same depth range, the specific alkalinity (alkalinity/chlorinity) is essentially invariant, with a value of 0.132 to 0.133 meq liter^{-1} mil^{-1} (*12*). However, the slight increase in oxygen concentration with depth below the deep-sea pH maximum should favor an increase in pH because the extent of apparent oxygen utilization decreases with depth. Yet the *in situ* pH shows a decreasing trend with depth below 3500 m. I cannot explain this contradiction at present, although the discrepancy might be due to the effect of sediments.

Ivanenkov (*6*) reports a pH decrease of about 0.05 unit with the increase in depth near the bottom over red clay with low organic matter; the decrease depends on the character of sediment. The major portion of the northeastern Pacific Ocean that I studied is covered with red clay, according to Sverdrup *et al.* (*4*, p. 975). At present I cannot ascertain how far above the sea floor this effect alters the pH of sea water. In addition, if the decrease in pH observed by Ivanenkov is due to the oxidation of organic matter, then the decrease in pH should accompany a decrease in oxygen.

The deep-sea pH maximum might be taken as a boundary separating the vertical oceanic domain into two parts: one layer influenced biochemically and the other physicochemically. My suggestion is based on the fact that, above the maximum, biochemical mechanisms influence the pH strongly. Good correlation between the vertical profiles of oxygen and pH and their relatively sharp gradients with depth above the maximum support my suggestion (Fig. 1). Conversely, beneath the maximum, the biochemical mechanisms have little influence on pH, but the physicochemical mechanisms, such as effect of pressure on dissociation constants of carbonic acid, become important. In order to understand the formation and significance of the deep-sea pH maximum, direct measurements of the effects of pressure (depth) and sediments on pH should be made.

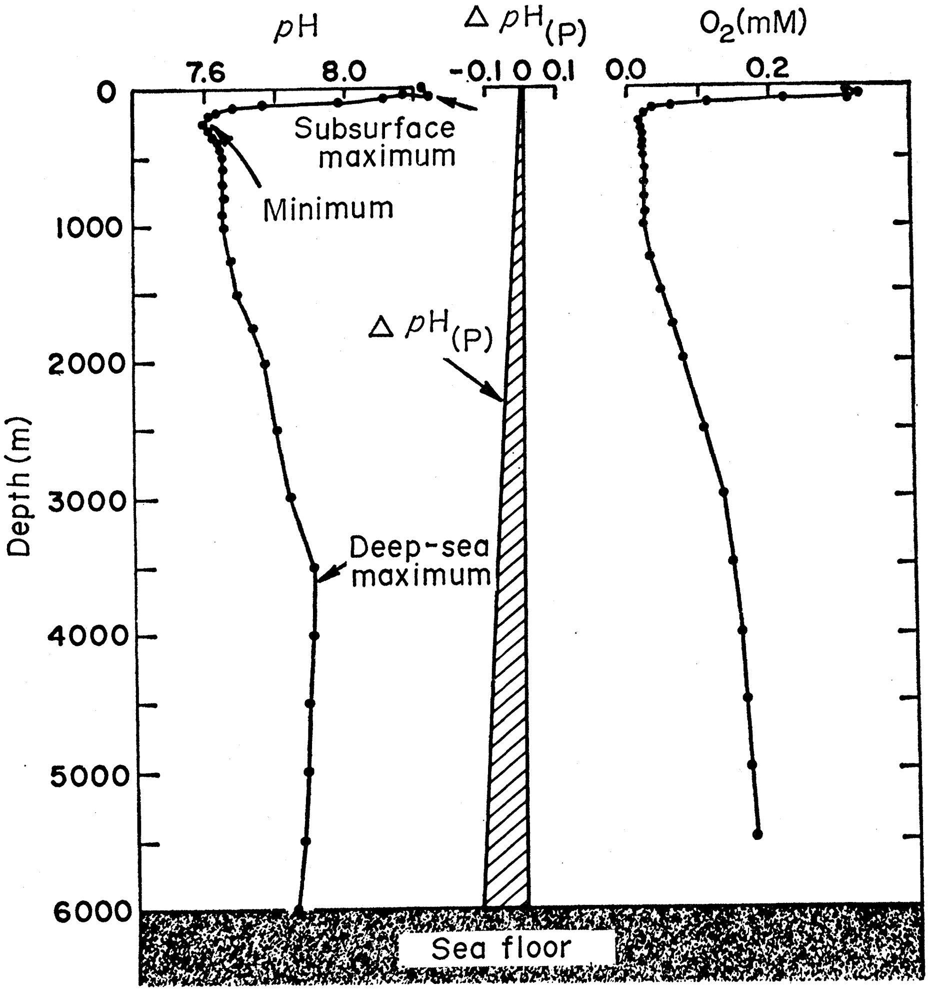

Fig. 1. Vertical profiles of pH and dissolved oxygen at 53°46′N, 158°36′W on 7 July 1966; ΔpH(p) denotes the calculated effect of the hydrostatic pressure, after Buch and Gripenberg (*11*), on sea-water pH. Theoretically, apparent oxygen utilization (not shown) is correlated more strongly with the pH profile than with the oxygen profile. Its profile is almost inversely proportional to the oxygen profile shown here.

KILHO PARK

Department of Oceanography,
Oregon State University,
Corvallis 97331

References and Notes

1. L. G. Sillen, in *Oceanography*, M. Sears, Ed. (AAAS, Washington, D.C., 1961), pp. 549–581.
2. R. M. Garrels, *Science* **148**, 69 (1965).
3. F. T. Mackenzie and R. M. Garrels, *ibid.* **150**, 57 (1965).
4. H. U. Sverdrup, M. W. Johnson, R. H. Fleming, *The Oceans* (Prentice-Hall, New York, 1942), pp. 195 and 209–210.
5. K. E. Chave of Lehigh University, personal communication.
6. V. N. Ivanenkov, "Carbonate system," in *Chemistry of the Pacific Ocean* (Nauka, Moscow, 1966), pp. 57–81, reports that the influence of the metallic water samplers (Nansen

bottles) on the *p*H of the deep-sea water was as great as +0.05 unit.

7. F. Manheim, *Stockholm Contrib. Geol.* **8**, 27 (1961).
8. J. D. H. Strickland and T. R. Parsons, *A Manual of Seawater Analysis* (Fisheries Research Board of Canada, Bull. No. 125, Ottawa, 1965), pp. 31–33.
9. S. Borden, Ed., *Cruise Report YALOC 66* (Oregon State Univ. Oceanogr. Tech. Rep. 77, Corvallis, 1966), pp. 1–18.
10. H. W. Harvey, *The Chemistry and Fertility of Sea-Waters* (Cambridge Univ. Press, Cambridge, 1960), pp. 5–6 and 153–182. A stoichiometric model of biochemical oxidation of organic matter in the ocean is described by F. A. Richards in *Chemical Oceanography,* J. P. Riley and G. Skirrow, Eds. (Academic Press, London, 1965), vol. 1, p. 624. He shows that 138 molecules of oxygen are required to release 106 molecules of carbon dioxide from the organic matter. I have used his ratio of oxygen to carbon dioxide (138 : 106) in my calculation of *p*H expected for the oxygen minimum zone.
11. K. Buch and S. Gripenberg, *J. Cons. Perm. Int. Explor. Mer* **7**, 233 (1932); R. M. Pytkowicz, *Deep-Sea Res.* **10**, 633 (1963). At present, C. Culberson, D. R. Kester, and R. M. Pytkowicz of this laboratory are measuring the effect of pressure on the dissociation constants of carbonic and boric acids in sea water.
12. Specific alkalinity increases when carbonate minerals dissolve into sea water and it decreases with the carbonate precipitation.

13. Supported by NSF grants GP-2232, GP-2876, and GP-5317, and by ONR contract Nonr 1286(10). I thank J. Lyman, F. T. Manheim, and D. Kester for their criticisms of the manuscript and S. J. Neshyba and J. G. Pattullo for field assistance.

22 September 1966 ■

Calcite: Rates of Dissolution in a Vertical Profile in the Central Pacific

Abstract. *Rate of dissoluton of calcium carbonate (calcite) was determined for a vertical profile 5000 meters deep in the central Pacific by measuring the loss of weight of optical calcite spheres arrayed on a mooring. Waters of the Pacific are undersaturated in all but the upper several hundred meters. A sharp increase in the rate of dissolution occurs at a depth of about 3700 meters, which corresponds closely to the depth below which calcite has been dissolved from the sediments.*

Distribution of calcium carbonate in sediments of the oceans far from land is clearly related to depth of water. Sediments in deep water, such as the typical floor of the central Pacific, contain virtually no calcium carbonate; sediments from shallow water, such as on rises, guyots, and seamounts, contain abundant calcium carbonate in the form of remains of small plants and animals that grow in surface waters and settle to the bottom. Both aragonite and calcite dissolve in deep ocean water, and the boundary between depths in which sediments contain much and little calcium carbonate is surprisingly sharp (*1*). The image of "snow-capped" peaks and a "snow line" at a water depth of about 4000 to 5000 m is probably not far from the truth.

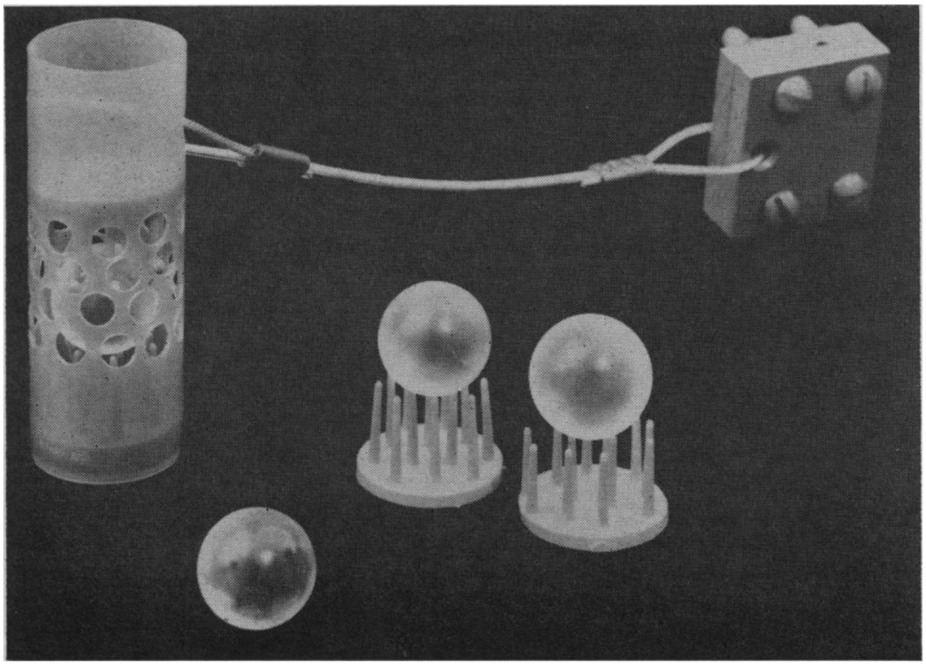

Fig. 1. Examples of spheres of optical calcite used to measure directly, by weight loss, the rate of dissolution of calcite in the central Pacific. One of the cages and wire clamps shows how the spheres were held.

Murray and Renard (*2*), on the basis of studies of samples taken on the voyage of H.M.S. *Challenger* almost a century ago, recognized the importance of dissolution of calcium carbonate from sediments on deep bottoms, as many others have since then (*3*).

Theoretical calculations of the state of saturation in complex and concentrated electrolytes at high pressures are very extended arguments. Ideally, they involve proper assignments of individual ion activity coefficients, accurate determinations of pressure and temperature effects on activity coefficients and equilibrium solubility constants, and the measurements of *p*H *in situ*. Many of these data are not available, but the most recent attempts to make these calculations (*4*, *5*) yielded results that compare favorably with the direct determination reported here.

Because the calcium carbonate in sediments beneath the deep oceans is actively dissolving, in order to understand the distribution of calcium carbonate in oceanic sediments it is necessary to know the rates at which this dissolution takes place. Therefore I attempted a direct measurement of these rates.

Measurement was made by exposing spheres, cut from optical calcite, to conditions of the open ocean and determining directly the rate of dissolution by weight loss. Despite additional work (*6*), a spherical shape was chosen because the probability of knocking off corners and chips was lessened and the surface area could be easily expressed. Weight of the spheres ranged from 2.5 to 15 g; they were cut from single-cleavage rhombs, ground to a smooth surface texture, gently etched in dilute HCl to remove disordered and sheared material at the surface, rinsed, dried thoroughly, and weighed on a model 1800 Sartorius microbalance. The error in determining final weight loss is assigned as ± 20 μg, although the balance is capable of considerably greater precision over short time intervals. The spheres were placed inside a polyethylene cage so constructed as to allow uninhibited circulation of sea water about the spheres, which were held coordinated between six polyethylene fingers (Fig. 1). After etching, the spheres were handled only with tygon-tipped forceps. The surface of each sphere consisted of very small abrasion pits of rhombohedral cleavage, prior to