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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.

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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.

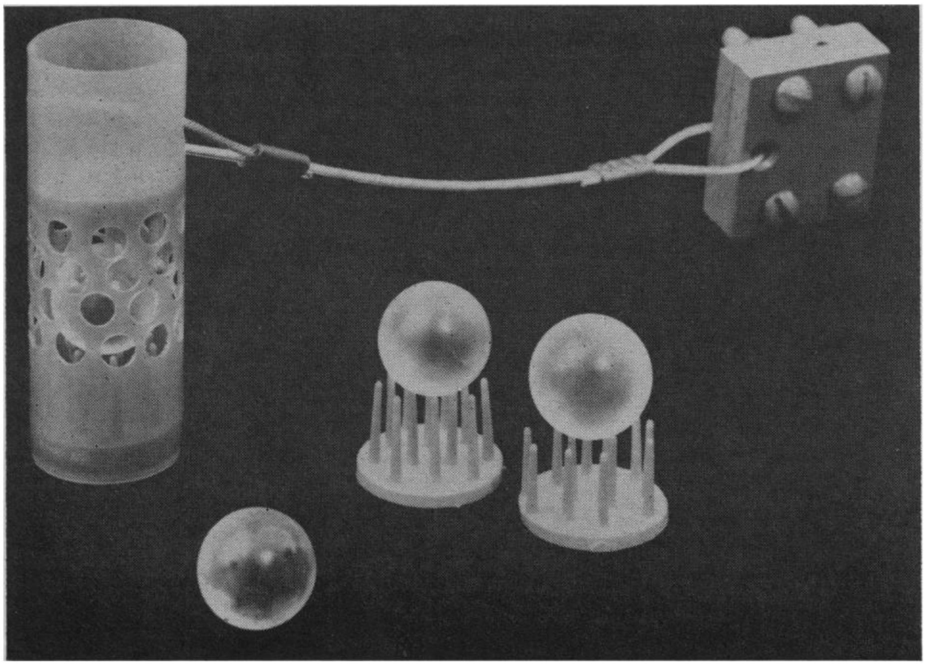

Fig. 1. Examples of spheres of optical calcite used to measure directly, by weight loss, the rate of dissolution of calcite in the central Pacific. One of the cages and wire clamps shows how the spheres were held.

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 pH *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 etching in HCl, that were distorted by the etching. These surface irregularities were not considered in calculations of surface area.

Seventy-one spheres were arrayed, from bottom to top of the ocean, to form a vertical profile. They were placed on a taut-wire mooring, in 5000 m of water, at intervals of 70 m (site at 18°49′N, 168°31′W; 1100 km southwest of Honolulu). The site was flat and sediment-covered and had no large seamounts within at least 16 km; it was about 30 km south of Horizon Guyot. The sequence of spheres on the wire was random with respect to size of spheres and position in the weighing sequence.

The entire mooring, except the anchor, was recovered intact after a little more than 4 months, and the complete profile of samples was also recovered. All spheres except one were in perfect condition; that one had a gooseneck barnacle growing on it, and serious etching was visible under the attachment. This point has been omitted from the study.

Immediately upon recovery, the spheres were thoroughly rinsed, while still in their cages, in distilled water that, for 4 months, had been in contact with the same calcite of which the spheres were made; they were then quickly rinsed in pure distilled water and allowed to air dry. When they were returned to the laboratory the spheres were thoroughly desiccated, removed from their cages, and weighed again.

Weight loss, per square centimeter of surface area of the sphere, is shown in Fig. 2. Circles show a running average of five samples. Hydrocasts were also taken at the start and finish of the experiment and will be considered in a more extended treatment than this initial report.

Throughout the water column, from several hundred meters down to 3700 m, the spheres showed a consistent small loss of weight. This can be attributed only to dissolution and shows that most of the column of sea water is undersaturated with respect to calcite (and hence also for aragonite). Evidence for undersaturation at relatively shallow depths is corroborated by the fact that foraminifera collected on this same cruise, from the top of Horizon Guyot (1600 m water depth), just 30 km north of the mooring, show clear evidence of dissolution (*7*). The only samples that showed virtually no weight loss were from the upper several hundred meters. These were in surface waters generally demonstrated to be supersaturated (*4, 8*). No increase in weight was noted for any sphere.

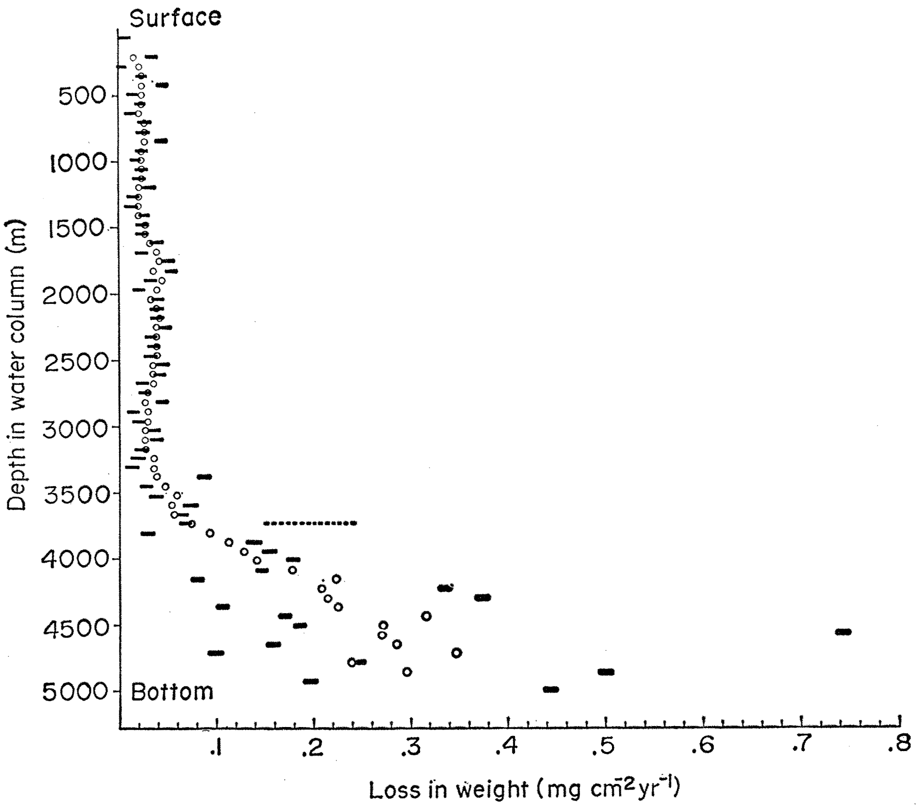

Fig. 2. Vertical profile of rate of dissolution of calcium carbonate in a 5000-m water column. Bars show rates of dissolution for individual calcite spheres (length of bars represents uncertainty due to assigned weighing errors). Circles show rates of dissolution averaged over five adjacent spheres. Dashed line shows the level of abrupt increase in rate.

The most conspicuous feature of the profile is the abrupt increase in loss of weight for spheres below 3700 m, which can only mean a very important increase in the rate of dissolution below this depth. The scatter of points about the general trend is greater under conditions of faster dissolution. This probably results from the individuality of the crystals, in terms of defects and compositional variations, becoming apparent as the result of a process proceeding rapidly enough to make these differences show up. I doubt if any of this scatter is oceanographically meaningful, but replicate specimens should be examined.

Plots of calcium carbonate versus depth for certain regions of the ocean (*1*) show that almost complete removal of the calcium carbonate takes place over only a narrow range of depth, and that the first significant removal commonly occurs at about 3600 to 4000 m. This is remarkably close to the depth (3700 m) at which the rate of dissolution, measured from the profile, sharply increases.

The change in calcium carbonate content of the sediments, commonly known in the past as the "carbonate compensation depth," is due to a sharply increased rate of dissolution rather than to a change from supersaturation to undersaturation, or to a gradual overtaking of precipitation by compensating dissolution. Also, the depth of principal change in the calcium carbonate content is related to effects in the main mass of sea water rather than to some effects deriving from the sediments themselves or to processes of bottom life. The level of principal change is apparently strongly linked to a well-defined oceanographic level and, as such, is not easily shifted up and down in a truly compensatory sense.

The rate of dissolution at depths is appreciable, amounting to the ability to dissolve, on the order of 1 μ per year, from large single crystals. Thus, some foraminifera should not be noticeably affected during their quick descent (several days), but slowly settling foraminifera and nanoplankton should be largely dissolved even during the time needed to settle through only a short column of this deeper water (*1*). Dissolution probably does not take place as fast at the bottom as it does at a comparable level in open water, because of decreased circulation in and just above the sediment. The "bottom" sample of this profile may not have been lying exactly on the bottom; it was on a tether to allow it to hang past the anchor and the weak-link assemblies.

The relation of rate of dissolution to degrees of undersaturation is not clear. One intuitively feels that the greater the departure of the ion activity product, in the undersaturated sense, from the equilibrium solubility product, the greater will be the rate of the dissolving. This is surely true, in a gross sense, but there seems no assurance that the rate of solution will be related in a simple way to the degree of undersaturation, as this departure becomes small. Masking and coating and exchanging by molecules and ions may be important rate-determining effects under these conditions.

However, the main mass of sea water is undersaturated, with the exception of the upper several hundred meters, and there is an abrupt increase in rate of dissolution at a level reasonably related to the level of principal change of calcium carbonate content in the sediments.

Interpretations of the presence and absence of calcium carbonate in sediments that consider only possible variations in surface productivity and do not entertain the possibility that some predetermining level, such as that described in this report, might be subject to vertical migration, are surely now suspect and must be reviewed.

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Isotopic Composition and Origin of the Red Sea and Salton Sea Geothermal Brines

Abstract. *Deuterium and oxygen-18 measurements show that the Red Sea and Salton Sea brines are the results of a single process, the leaching of sediments by surface water circulating downward to a geothermal reservoir. The Salton Sea brine is derived from local precipitation but the Red Sea brine originates 1000 kilometers south of its basin, on the shallow sill which controls the circulation of the Red Sea. On this sill sea water penetrates a thick evaporite sequence to a depth of 2000 meters, and, driven by its increased density relative to sea water, flows northward to emerge in the brine-filled deeps.*

Two remarkable occurrences of hot saline waters with salinities almost ten times that of sea water have recently been discovered in extensively faulted tectonic troughs containing thick stratigraphic sequences and igneous intrusions. The Salton Sea geothermal brine (*1, 2*) was found 1400 m down in the sediment fill of the Salton trough, the landward extension of the Gulf of California; the extrapolated bottom hole temperature of the discovery well is 340°C (*2*). The Red Sea brine (*3*), found at a depth of 2000 m of water in the median rift at the bottom of the Red 56°C, but it is a true geothermal brine Sea, has temperatures of only 44° to considerably hotter than the surrounding bottom water of 22°C. Speculation concerning the origin of the Red Sea brine has been widespread; among the proposed processes are: local solution of exposed salt on the sea floor (*3*), evaporation in coastal lagoons with density flow of brine to the depths (*4*), release of ancient interstitial sea water (connate water) from sediments by heat and tectonic activity (*5–7*), leaching of evaporites in underlying strata (*7*), and extensive evaporation over the entire Red Sea basin in some early stage (*8*). The much hotter Salton Sea brine, which is also much more enriched in heavy metals and trace elements, is a more difficult problem; it was originally suggested that this brine is a pure magmatic water rising from a magma chamber at depth (*9*).

It is clearly fundamental for the development of our knowledge of geothermal systems to know whether these two brines, which occur in such similar geological settings, originate by quite different discrete events such as most of the processes which have been suggested, or whether they represent minor variations of basically similar dynamic circulation and concentration pattern. The multiplicity of working hypotheses cited above reflects the fact that the chemical composition of the brines does not uniquely specify their origin (*10*). They have some similarities to certain oil field brines (*11*) generally considered to be connate or to have dissolved salts from evaporites, but these in turn have compositions somewhat similar to that postulated for magmatic water (*1*); unfortunately, no known examples of actual connate or magmatic water exist for comparison. In this report I compare the concentrations of the isotopic water molecules HDO and H_2O^{18} in the brines and in other waters in the same area, and show that both brines formed by the same process—extraction of salts from sediments by downward circulating surface waters—and that the specific source waters are uniquely identified by natural isotopic labeling resulting from isotopic fractionation in the atmosphere and the sea.

Figure 1 is a deuterium versus oxygen-18 diagram showing the isotopic data measured on surface and subsurface waters of the Salton Sea geothermal region (*12*). The solid line with slope 8 and intercept 10 is the isotopic relationship established for worldwide precipitation (*13*); this relationship, the result of the several isotopic fractionation effects in the ocean-atmosphere water cycle, labels fresh waters on the earth's surface unaffected by excessive evaporation. Evaporation of fresh waters produces an isotopic enrichment with a slope of about 5 because of kinetic effects in liquid-vapor molecular exchange (*14, 15*); the Salton Sea water is related to the water of Lake Mead in this way but is unrelated to the subsurface geothermal waters which are derived from local precipitation.

The relationship of the geothermal waters in Fig. 1 is a striking example of the "oxygen isotope shift," the increase in oxygen-18 content of local surface water with constant deuterium content, observed in seven of the world's major geothermal systems (*16*). Isotope exchange with carbonates and