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Carbonate Compensation Depth: Relation to Carbonate Solubility in Ocean Waters

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Abstract. In situ calcium carbonate saturation measurements suggest that the intermediate water masses of the central Pacific Ocean are close to saturation with respect to both calcite and local carbonate sediment. The carbonate compensation depth, located at about 3700 meters in this area, appears to represent a depth above which waters are essentially saturated with respect to calcite and below which waters deviate toward undersaturation with respect to calcite.

The variability of carbonate content in marine sediments was first observed almost a century ago by Murray and Renard (1), who reported the lack of carbonate-rich sediments in the deepest part of the oceans. Studies in subsequent years (2) have confirmed the observation of the *Challenger* expedition and showed that the transition zone between carbonate-rich and carbonate-poor sediments may be sharp. As the source of most carbonate material is at the ocean surface (tests and skeletons of marine plankton) and as its removal at depth is due to dissolution, this transition zone defines a horizon where the carbonate supply is compensated by the rate of dissolution. The depth of this boundary,

usually referred to as the carbonate compensation depth, is not constant in the oceans as, by definition, it is related to surface productivity and the chemistry of deep ocean waters—both of which are variable. Investigation of the factors controlling calcium carbonate dissolution in the oceans is essential because carbonate deposition on the ocean floor is a major sink of carbon and hence an important factor in the mass balance of carbon on the earth.

The carbonate compensation depth was originally explained as the boundary line between supersaturated and undersaturated ocean waters (1). It was argued that below the compensation depth, seawater is undersaturated with

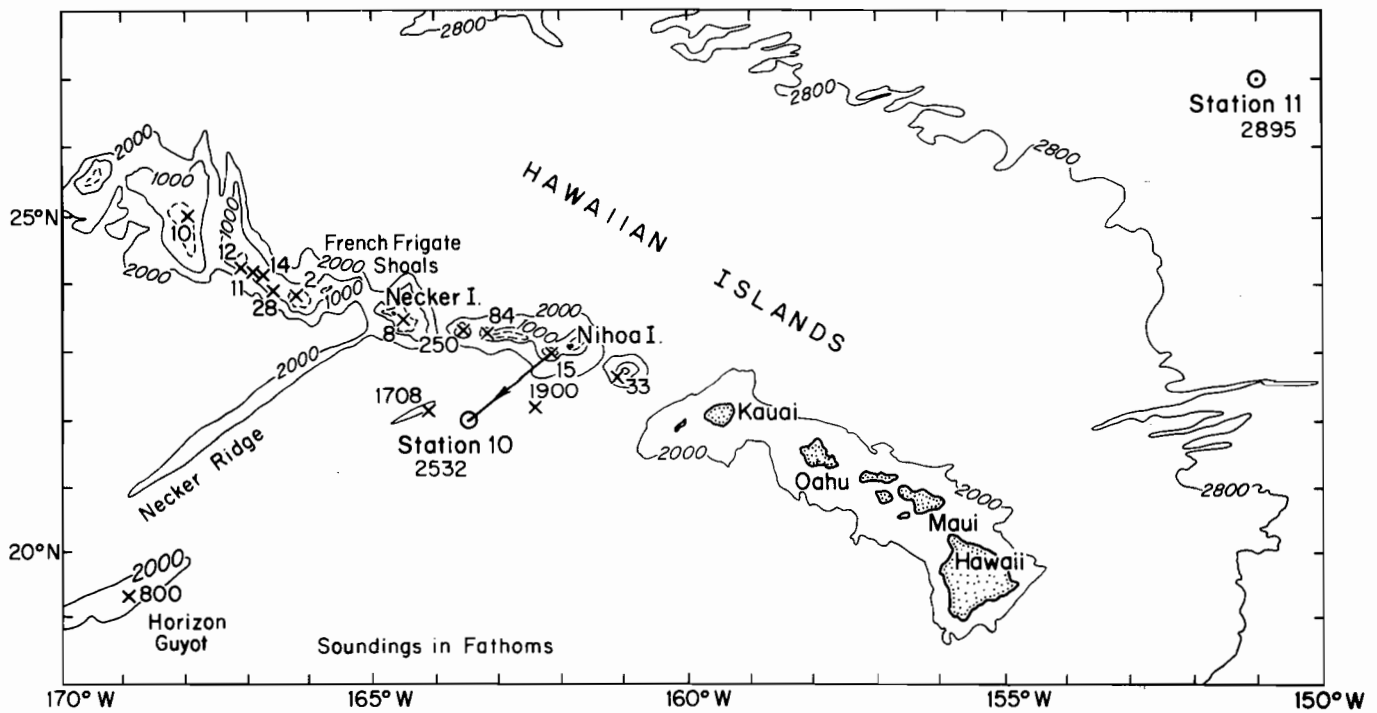


Fig. 1. Map of the study area. The maximum water depths are 4700 m in station 10 and 5300 m in station 11 (1 fathom \cong 1.8 m). Sediments were sampled along the slope marked by an arrow pointing to station 10. Topographical details irrelevant to this report have been omitted from the map.

respect to calcite (the least soluble form of CaCO_3) and all carbonate material reaching these waters dissolves. However, recent estimates (3) of carbonate saturation in the oceans, derived from laboratory analyses of sampled waters at atmospheric pressure, suggest that the carbonate saturation depth is much shallower than the carbonate compensation depth. These estimates, which assume precise knowledge of many thermodynamic constants at the in situ conditions, conflict with direct satrometer measurements previously reported (4). Here we present new data, which relate carbonate saturation in the water column to the carbonate compensation depth in the central Pacific Ocean.

The study was conducted in two adjacent areas (Fig. 1), one south of the Hawaiian Islands chain and the other about 1300 km northeast of the islands. Bottom depths were measured as 4700 m (station 10) and 5300 m (station 11). The carbonate compensation depth was investigated by sampling the sediment surface along a slope (marked as an arrow pointing to station 10 in Fig. 1), and later analyzing for CaCO_3 content. The latter was determined by weighing dry, washed sediment samples before and after treatment with 1N HCl.

Direct determinations of CaCO_3 solubility in central Pacific waters were con-

ducted with an in situ carbonate satrometer developed in our laboratory (5). Measurements were made by exposing different CaCO_3 minerals to ambient seawater at depth and monitoring the pH shifts due to the chemical reaction. This information, along with other parameters of the waters, was then used to calculate the degree of saturation

(6), defined as the ratio $IP/K'sp$ —where IP is the product of the concentrations of total dissolved calcium (Ca^{2+}) and carbonate (CO_3^{2-}) ions and $K'sp$ is the apparent solubility product of the carbonate mineral (7)—at the depth of measurement (8). The satrometer experiments reported here were conducted with three CaCO_3 forms:

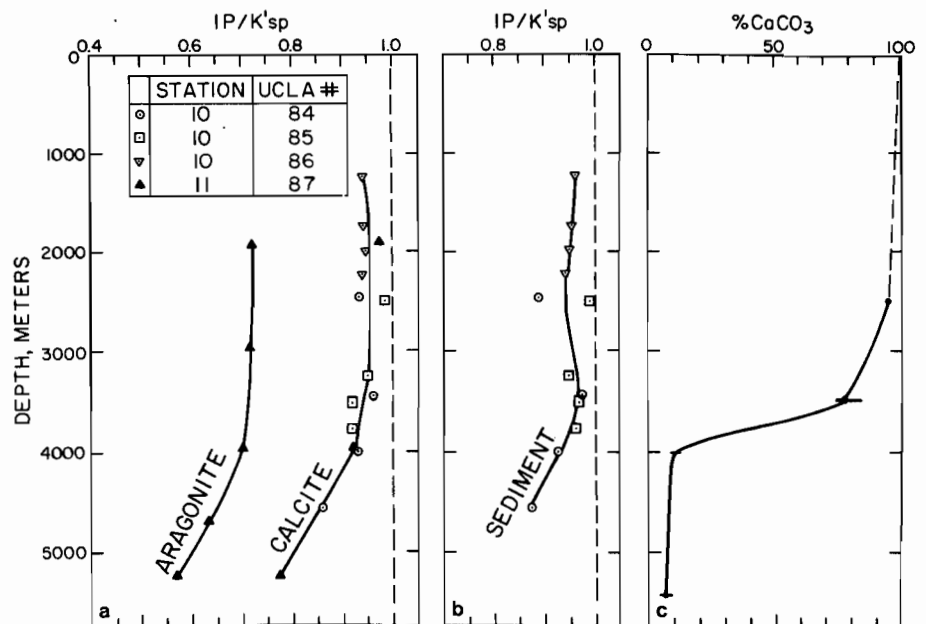


Fig. 2. Profiles of the degree of saturation of seawater with respect to (a) standard calcite and aragonite and (b) local sediment (all separated by sieving to the size range 0.35 to 0.50 mm) compared to (c) the carbonate content in adjacent sediment. The degree of saturation is given by $IP/K'sp$ (see text for definition).

standard calcite, aragonite (9), and carbonate sediments sampled from the slope adjacent to station 10 (Fig. 1). The sediments were raised from a depth of 2000 m and sieved to the size range 32 to 42 mesh (0.35 to 0.50 mm) before use in the saturometer cell. X-ray diffraction analyses revealed no traces of aragonite in the calcite standard, whereas calcite traces were present in the standard aragonite. The sediment separate used in experiments was found to be pure calcite; however, traces of aragonite were found in the finest fraction of the sediment.

The data (Fig. 2) show a correlation between the degree of carbonate saturation of seawater and the carbonate content of the sediments at the same depth. The results of the in situ carbonate measurements suggest that the intermediate waters of the central Pacific, between approximately 1000 and 3500 m, are close to saturation ($IP/K'sp \approx 0.95$) with respect to calcite (10). At about 3750 m, the degree of saturation profile exhibits a break and deviates toward undersaturation. Measurement of seawater saturation with respect to the local sediments duplicates that with respect to standard optical calcite, except that deviation toward undersaturation seems to start at a somewhat shallower depth. However, the significance of this difference cannot be assessed because of the scatter in the data and the small number of replicate measurements.

The profile of seawater saturation with respect to aragonite parallels that

with respect to calcite, but is shifted toward undersaturation, because aragonite is more soluble than calcite (7). Hence, there is good consistency between the experiments conducted with calcite, aragonite, and local sediments. Further, the data from station 11 correlate well with the data from station 10, which suggests similar carbonate solubility reactions along the two profiles.

The data reported here reveal that the zone between high and low carbonate content in the sediments coincides with the break in the calcite-seawater saturation profile (Fig. 2). This observation is in accord with data on carbonate dissolution rates in the central Pacific obtained by measuring the weight loss of carbonate material suspended for several months on mooring lines (11). Dissolution rates of both optical grade calcite and foraminiferal ooze were found to increase rapidly below approximately 3700 m.

Conceivably, the carbonate compensation depth may be depressed with respect to the break in the calcite saturation profile in areas with high productivity, that is, a high sedimentation rate of biogenic $CaCO_3$. We believe that further studies are essential before this can be proved.

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8. The ratio $IP/K'sp = 1$ signifies saturation with respect to the carbonate minerals, whereas ratios smaller or larger than unity signify undersaturation or supersaturation, respectively.
9. Materials were obtained from Ward's (Monterey, California). The calcite was an optical grade mineral from Chihuahua, Mexico, and the aragonite was from Farka, Switzerland. The minerals were crushed, sieved to the size range 32 to 42 mesh (0.35 to 0.50 mm), washed, and then dried overnight in an oven at 105°C.
10. Laboratory experiments seem to indicate that the slight undersaturation observed may be due to the presence of traces of a high-solubility phase in the carbonate material used, and does not represent the characteristics of the bulk solid.
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