

## Deep-Sea In Situ Calcium Carbonate Saturation<sup>1</sup>

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We used an in situ oceanographic system to measure the degree of saturation ( $IP/K_{sp}$ ) of calcium carbonate. Results of two profiles measured in the eastern Pacific Ocean off southern California are described and compared with data obtained by conventional chemical techniques. From this preliminary study it appears that the waters investigated become undersaturated with calcite at a depth of approximately 400 meters and remain so to a depth of about 1600 meters, where they move towards saturation. Below 2500 meters they appear to become undersaturated again and probably remain so to the depth of the ocean floor.

Two approaches have been used to study calcium carbonate saturation in the oceans: chemical analysis of sampled water and in situ solubility tests. Accurate determination of the in situ carbonate saturation by analyzing a sample at atmospheric pressure depends on precise knowledge of many thermodynamic constants that are used to calculate the in situ conditions. These include the apparent dissociation constant of carbonic acid and boric acid at in situ conditions and the apparent solubility product of the carbonate species at depth. On the other hand, the accuracy of the in situ solubility approach depends on the accuracy with which one can estimate the amount of  $CaCO_3$  that has dissolved or precipitated at the desired location.

*Li et al.* [1969] have studied the degree of  $CaCO_3$  saturation in the oceans by measuring total dissolved  $CO_2$  and partial pressure of  $CO_2$  of sampled waters. They estimated that their measurements were accurate to within 0.5% for  $T(CO_2)$  and to within 1% for  $pCO_2$ , and that the estimated error for the calculated degree of saturation  $IP/K_{sp}$  was 10%. *Hawley and Pytkowicz* [1969] calculated the degree of saturation of calcite in the Pacific Ocean by using pH-alkalinity data from *Ob* cruise 3 [IGY World Data Center A, 1961] and *Vityaz* cruises 26 and 29 [NODC, 1958, 1959]. They

give no estimate of errors in the calculated results. A comparison of their results with those of *Li et al.* [1969] shows marked differences. For example, *Hawley and Pytkowicz* have calculated that the crossover level from supersaturation to undersaturation with respect to calcite is approximately between 100 and 500 meters in the North Pacific. However, *Li et al.* [1969] have shown that this crossover level should be at approximately 1000 meters.

A more direct approach for studying the carbonate saturation in the ocean was undertaken by *Peterson* [1966] and *Berger* [1967]. *Peterson* suspended calcite spheres at various depths in the central Pacific and after 4 months measured the loss of weight. *Berger's* [1967] approach was similar, except that he used foraminiferal ooze rather than pure optical calcite. The major obstacle in these experiments is the difficulty in assessing the precise weight changes in the specimens. This was especially true in *Peterson's* experiments, in which the spheres at shallow depths lost less than 100  $\mu g$  during the experiment. Treatment of the spheres after recovery included washing with calcite saturated distilled water and further rinsing with distilled water, which may have resulted in solution of a fine precipitate of magnesium-rich calcite that may have formed in the upper water column. This might explain why none of the spheres increased in weight.

There are at least two aspects to the problem of measuring  $CaCO_3$  saturation in the ocean: (1) mapping of the ocean for the ionic product

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$[Ca^{++}][CO_3^{=}]$  that should control solution or precipitation of calcium carbonate, and (2) the behavior of different calcium carbonate minerals in the water column. Whereas (2) can be studied in the laboratory, (1) must be investigated either by sampling or by direct experiments in the oceans. The direct approach is probably more desirable, because it eliminates errors due to sample changes after collection. Carbonate saturography [Weyl, 1961; Ben-Yaakov and Kaplan, 1969] is especially attractive owing to its high sensitivity and potential precision. This paper summarizes some preliminary results obtained with an in situ carbonate saturograph to a depth of 3200 meters in the eastern Pacific Ocean.

#### EXPERIMENTAL

The in situ carbonate saturograph is a special adaptation of an oceanographic in situ instrument designed at UCLA [Ben-Yaakov, 1970]. It is built around a high-pressure pH glass electrode [Ben-Yaakov and Kaplan, 1968a] in a construction that facilitates pH measurement before and after a sample of sea water is equilibrated with solid  $CaCO_3$  grains (Figure 1).

A plexiglass cup is attached to the clamp holding the pH assembly [Ben-Yaakov, 1967] so that the glass bulb (pH electrode) sits in the center of the cup. The cell (cup) is filled with carbonate grains and connected through a hose to a pump and to a solenoid operated valve. When the pump and valve are on, sea water is pumped through the cell as shown in the figure, and since the flow is faster than time for equilibrium the pH electrode registers the pH of the sea water. In laboratory tests the pH so determined has been found to be within 0.05 pH unit of the original pH of the sea water. The operation of the pump and the valve is controlled by a repeat cycle timer which cycles between 5 min on and 15 min off. During the off period, the trapped sea water reacts with the carbonate, thereby moving toward equilibrium with the solid phase. Depending on the degree of saturation of sea water, carbonate may precipitate or dissolve, shifting the pH of the sea water toward higher or lower values, respectively. Hence, the pH electrode indicates the degree of saturation of the original solution. If the reaction reaches equilibrium, one can use the initial and final values of the

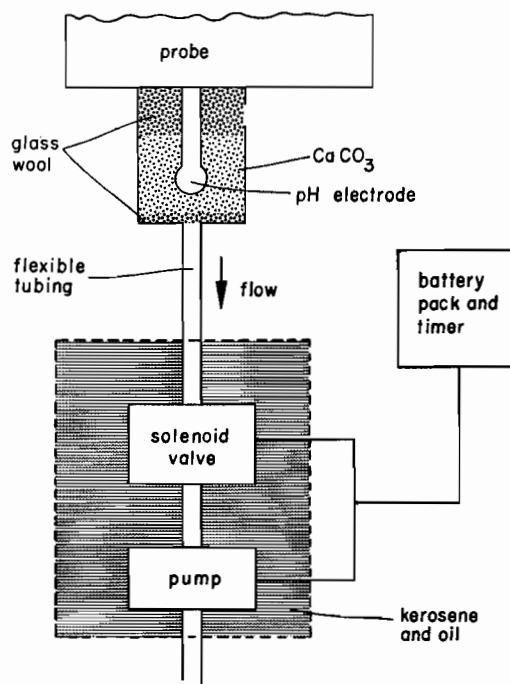


Fig. 1. Block diagram of the in situ carbonate saturograph.

pH for the exact calculation of the degree of saturation [Ben-Yaakov and Kaplan, 1969].

The pump and the solenoid operated valve are encased in a pressure equilibrated housing approximately 10 inches in diameter and 5 inches in height. The housing is filled with a mixture of kerosene and mineral oil (3:1) and equilibrated to the ambient hydrostatic pressure through a rubber disk. The pump is a commercial magnetically coupled centrifugal pump (IP675 W. W. Grainger, Inc.) in which the original ac motor has been replaced with a 12-volt dc motor of the type used for automobile windshield wipers. The valve is stainless steel and operated by a 12-volt electromagnet.

The pump and valve assembly are powered by a 12-volt NiCd battery pack (wet cells) through a repeat cycle timer (A. W. Hydon type 5300) with three cams and a 1-hour basic cycle. The three switches are normally connected in parallel, and the cams are adjusted to obtain a 20-min cycle (60/3). During its cycle, each switch is on for about 5 min, during which time both the valve and pump are operating. The timer is driven by a 6-volt dc

motor with no speed regulation, powered from the same battery pack after passing through a 6-volt voltage regulator (Fairchild,  $\mu A723$ ). Under these conditions, the expected speed variation is  $\pm 10\%$ .

The output of the glass electrode and the signals from the temperature and pressure sensors are converted to a proportional frequency signal [Ben-Yaakov and Kaplan, 1968b, c] and then recorded digitally in situ by a magnetic tape recording unit [Ben-Yaakov, 1968]. The system also records auxiliary parameters that are later used to correct for electronic drift, such as drift of the pH electrode electrometer.

The magnetic tapes are processed by a PDP-8/L computer in which a Focal (Digital Equipment Co., 1968) program is used to perform all the calculations [Ben-Yaakov, 1970].

Data from a printout of the computer output is shown in Table 1. The calculation steps include the correction of the raw data for electronic drift and take into account the calibration data of the various sensors. Information from the buffer test on board ship is used to

correct the pH values for asymmetry potential changes.

The output printout (Table 1) includes the running time (starting from the beginning of the experiment), depth, temperature, millivolt output of the pH electrode (corrected for electronic drifts), pH, Eh (corrected for temperature dependence of Ag/AgCl electrode potential), pump marker (4000 when pump is on), and battery voltage. The marker channel is used in the satrometer experiments to indicate when the cell is being flushed.

All in situ satrometer experiments were performed with crushed calcite that had been thoroughly washed, then dried in the oven at 105°C. Three different grain-size fractions were used: 32-40, 40-60, and <40 mesh; no difference in response was observed for the three groups. The smaller size was originally used to decrease unwanted cell flushing due to vertical movement of the assembly. The larger size has been used after a solenoid valve, opened only at the time of flushing, was installed at the cell output to eliminate the erroneous flushing. The larger size grains are advantageous because they

TABLE 1. A Sample of a Print-Out of Calculated Data

T(M)	D(M)	TEMP	PH(MV)	PH	EH	PUMP	B:
45.0	267.2	8.933	-373.70	8.037	474.62	2029.0	24.100
46.0	265.0	8.933	-372.46	8.015	472.46	2028.0	24.083
47.0	269.6	8.938	-372.60	8.018	471.62	2029.0	24.070
48.0	271.9	8.938	-372.30	8.012	471.12	2029.0	24.060
50.0	271.9	8.949	-377.80	8.110	469.61	4056.0	24.040
51.0	274.2	8.933	-378.06	8.115	470.06	4057.0	24.033
52.0	278.7	8.955	-378.04	8.114	469.47	4056.0	24.027
53.0	276.5	8.944	-378.10	8.116	469.21	4058.0	24.010
54.0	278.7	8.949	-374.64	8.054	468.97	2029.0	24.007
55.0	281.0	8.944	-372.99	8.024	468.74	2029.0	23.984
56.0	281.0	8.960	-372.04	8.007	468.46	2029.0	23.987
57.0	283.3	8.955	-373.09	8.026	468.23	2029.0	23.964
58.0	285.6	8.955	-371.34	7.995	466.77	2028.0	23.967
59.0	283.3	8.949	-371.04	7.989	466.77	2029.0	23.957
60.0	285.6	8.949	-370.99	7.988	467.04	2029.0	23.944
61.0	283.4	8.944	-370.20	7.975	467.31	2029.0	23.970
62.0	285.7	8.944	-371.00	7.989	467.51	2028.0	23.920
63.0	285.7	8.944	-369.70	7.966	467.61	2029.0	23.910
64.0	288.0	8.933	-369.30	7.959	467.22	2028.0	23.900
65.0	285.7	8.944	-369.60	7.964	467.41	2028.0	23.890
66.0	285.6	8.944	-369.04	7.954	467.28	2028.0	23.877
67.0	288.0	8.938	-369.64	7.965	467.28	2028.0	23.877
68.0	288.0	8.949	-368.64	7.947	466.87	2029.0	23.867
69.0	290.2	8.955	-368.59	7.945	465.83	2029.0	23.854
70.0	290.2	8.955	-374.39	8.049	466.23	2047.0	23.854
71.9	290.3	8.949	-377.94	8.113	465.87	4056.0	23.827
72.9	292.5	8.955	-378.08	8.115	464.33	4056.0	23.814
73.9	292.5	8.949	-378.48	8.122	462.04	4057.0	23.814

TABLE 2. Location and Dates of Oceanographic Stations

Station	Date	Location
1	Nov. 19, 1969	118°28'12"W, 33°48'18"N
2	Nov. 21, 1969	118°39'23"W, 33°55'N
3	Nov. 26, 1969	118°39'23"W, 33°55'N
4	Dec. 4, 1969	118°39'23"W, 33°55'N
5	Dec. 5, 1969	118°39'23"W, 33°55'N
6	Dec. 11, 1969	118°35'30"W, 33°58'N
7	Dec. 12, 1969	118°35'30"W, 33°58'N
9	Dec. 31, 1969	118°35'30"W, 33°58'N
10	Jan. 2, 1970	118°37'40"W, 33°49'49"N
11	Jan. 16, 1970	120°23'W, 32°35'N
12	Jan. 16, 1970	120°23'W, 32°35'N
13	Jan. 17, 1970	120°28'30"W, 32°31'N
14	Jan. 17, 1970	120°28'30"W, 32°31'48"N

offer less resistance to the flow and hence increase the flushing efficiency. Simulated laboratory experiments have shown that during the period of pump flushing, 2.5–3 liters of water pass through the cell, enough to wash out the waters from the preceding cycle of equilibration.

In most of the experiments a flushing-equilibration cycle of approximately 20 min was used. The pump and valve were on for 5 min, and for the rest of the time the trapped waters were left to react with the carbonate. In some of the earlier experiments a 1-hour cycle time was used.

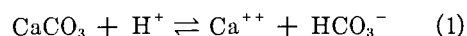
### RESULTS

Studies have been made in the Santa Monica Basin of southern California and on the continental slope off southern California. Table 2 summarizes the locations and dates of the established station. We tried to make all the measurements in a given area at the same location. However, because the sea was rough in many instances, the vessels drifted considerably, particularly in the area off the shelf, where the range radius was approximately 20 nautical miles.

We have used the computer output data to plot the change of the *pH* electrode output potential during the saturometer cycle. This was accomplished by another Focal program that uses the teletypewriter as a plotter. These are plots of millivolt output (horizontal) versus time (vertical). The scale sensitivity (millivolt/division) can be different for each plot and is indicated on each figure. The time scale is in minutes, and each point corresponds to a meas-

urement made during a cycle of the stepping relay. Positive millivolt changes are shown by displacement of values to the right on the plot.

From the equation of calcium carbonate equilibrium with sea water written as



an increase in *pH* signifies solution of  $\text{CaCO}_3$ , and a decrease indicates precipitation. The relationship between change in *pH* and electrode potential (millivolt) shift is given by

$$E = E_0 + \frac{RT}{F} 2.303 \log \frac{a_{\text{H}_{\text{sw}}}^+}{a_{\text{H}_{\text{int}}}^+} \quad (2)$$

Hence, an increase of  $a_{\text{H}_{\text{sw}}}^+$  that is a decrease in *pH* of sea water (carbonate precipitation) will positively shift electrode potential. A detailed discussion of the relationship between *pH* shift and degree of carbonate saturation ( $IP/K_{\text{sp}}'$ ) has been given elsewhere [Ben-Yaakov and Kaplan, 1969].

This study emphasizes qualitative rather than quantitative data, because usually equilibrium had not been reached, and the initial *pH* values are in slight error. However, the carbonate saturometer experiment should accurately determine the crossover point between super- and undersaturation because it corresponds to the transition between positive and negative millivolt shifts.

### SANTA MONICA BASIN

Figure 2a gives the result of measurements in surface water and clearly shows that the output of the *pH* electrode became more positive when the sea water was reacting with the carbonate, corresponding to a decrease in the *pH*. This means that  $\text{CaCO}_3$  was precipitating out of solution or that the surface sea water was supersaturated with calcite grains. Although equilibrium had apparently not been achieved, the final equilibrium potential can be estimated by extrapolation to be approximately 18 mv. This corresponds to a saturation ratio  $IP/K_{\text{sp}}'$  of approximately 2.2.

The effect of unwanted flushing due to the movement of the assembly can be seen in Figure 2a at 148.5 min. In this experiment the solenoid valve had not yet been installed. Although the sea was relatively calm (probably sea state 2) the small vessel was rolling and pulling the assembly up and down. The short

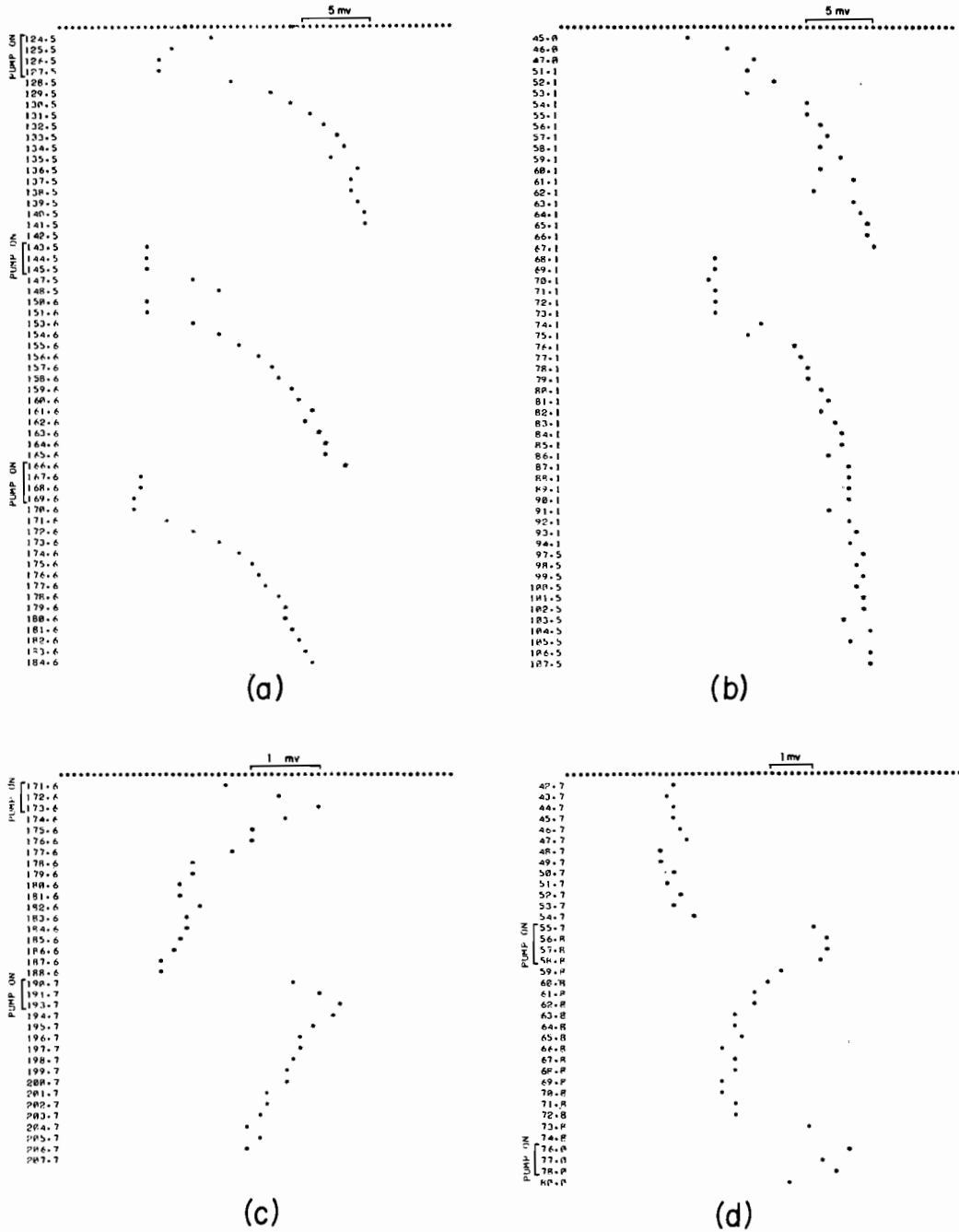


Fig. 2. In situ carbonate saturation: (a) Santa Monica Basin, station 10, surface; (b) Santa Monica Basin, station 3, depth: 100 meters; (c) Santa Monica Basin, station 10, depth: 400 meters; (d) Eastern Pacific off southern California, station 2, depth: 900 meters.

TABLE 3. Results of In Situ Carbonate Saturometry along a Profile in Santa Monica Basin

Depth, meters	Station	Temp., °C	pH	$\Delta$ , mv	$IP/K_{sp}'$
1	9	13.6 ± 0.1	8.18 ± 0.05	> +18.0	> 2.18
1	10	14.2 ± 0.1		> +13.0	> 1.76
100 ± 10	3	11.3 ± 0.1	8.15 ± 0.05	> +12.0	> 1.69
250 ± 20	9	8.5 ± 0.1	7.80 ± 0.05	< -2.2	< 0.91
400 ± 30	9	7.3 ± 0.1	7.75 ± 0.05	< -1.9	< 0.92
400 ± 30	10	7.2 ± 0.1		< -1.1	< 0.95

jump toward the sea water base line at 148.5 min indicates that the cell was flushed and the calcite was washed with the surrounding water. This phenomenon has been experienced in many stations, and when heavy rolling was encountered it rendered the data useless. The situation improved dramatically after the solenoid valve was added to the system.

Figure 2b depicts the results of measurements at 100 meters. The experiment was performed with a 1-hour cycle. Equilibrium was nearly complete in approximately 25 min, which is close to the equilibration rate that has been observed during laboratory tests. The sea water at this point was also supersaturated with calcite, as the millivolt shift was again positive. However, the experiment at 250 meters (Figure 2c) shows undersaturation. The total millivolt shift at this depth is small, approximately 2 mv, but it is a negative shift, indicating that the pH increased as a result of the carbonate-sea water interaction, which implies that the calcium carbonate was dissolving. At a depth of 400 meters the data again show undersaturation.

Figure 2c also illustrates the sensitivity of the system. Note that the scale is 0.1 mv/dot, and the total resultant shift is approximately 2 mv. The plot demonstrates that a shift of 0.5 mv can readily be detected because the range of the base line noise is smaller than 0.5 mv, which is equivalent to a pH change of  $\sim 0.01$ , or an  $IP/K_{sp}' \sim 0.01$ .

Table 3 summarizes the results of Santa Monica Basin saturometer measurements. It appears that the saturation level for calcite in this area is between 100 and 250 meters, probably about 200 meters in depth.

Except for the point at 100 meters, none of the experiments had reached equilibrium because of insufficient time and also because of

unwanted flushing during ship movement. The calculated saturation ratios, therefore, are only approximate: a minimum for the case of supersaturation and a maximum boundary for undersaturation. It is evident from the results that the waters in Santa Monica Basin are approaching saturation at a depth of approximately 200 meters and are very close to saturation from 250 to 400 meters. At the surface the sea water is clearly supersaturated with calcite, and the ratio  $IP/K_{sp}'$  is probably larger than 2.2.

#### EAST PACIFIC OCEAN OFF SOUTHERN CALIFORNIA

We made measurements about 210 km off the coast of southern California over the continental slope. Maximum ocean depth was approximately 4000 meters and measurements were taken to below 3000 meters. Results of saturometer profiles for this area are summarized in Table 4 (for locations of oceanographic stations, see Table 2).

The saturation ratio  $IP/K_{sp}'$ , with respect to calcite, shows supersaturation in two layers: at the surface and at a depth of about 2000 meters. The upper layer water is supersaturated with respect to calcite to approximately 450 meters, where the saturation ratio approaches one. The layer between this point and approximately 1800 meters seems to contain undersaturated waters. At 1800 meters, however, the saturation ratio once again appears to approach unity, and the waters below this point to approximately 2500 meters are probably slightly supersaturated. The last measured crossover is around 2700 meters, below which the ocean is undersaturated.

In general, the saturometer experiments did not reach equilibrium and the computed ratios ( $IP/K_{sp}'$ ) therefore represent the limits of supersaturation or undersaturation. True values

TABLE 4. Results of In Situ Carbonate Saturation Measurements in the Eastern Pacific off Southern California

Depth, meters	Station	Temp., °C	pH	$\Delta$ , mv	$IP/K_{sp}'$
1	12	15.1 ± 0.1	8.30 ± 0.05	> +10	> 1.51
1	13	15.3 ± 0.1	8.32 ± 0.05	> +11	> 1.64
1	14	15.3 ± 0.1	8.28 ± 0.05	> +7	> 1.37
1380 ± 20	12	8.5 ± 0.1	7.80 ± 0.05	> +1.2	> 1.05
400 ± 20	13	7.9 ± 0.1	7.75 ± 0.05	> +2	> 1.09
750 ± 50	11	5.5 ± 0.1	7.65 ± 0.05	< -5.2	< 0.79
900 ± 50	12	5.0 ± 0.1	7.66 ± 0.05	< -6	< 0.76
900 ± 50	13	4.7 ± 0.1	7.68 ± 0.05	< -6	< 0.76
1800 ± 50	13	3.0 ± 0.2	7.75 ± 0.05	0	1
1820 ± 50	14	2.8 ± 0.2	7.71 ± 0.05	> +1.8	> 1.08
2700 ± 80	13	2.3 ± 0.2	7.81 ± 0.05	< -1.6	< 0.93
3160 ± 80	14	2.1 ± 0.2	7.73 ± 0.05	< -3	< 0.87

of supersaturation should be greater than the calculated ratio, whereas true values of undersaturation should be lower. The experiments at 950 and 900 meters, however, had apparently reached or at least were very close to equilibrium at the end of each cycle. This can be evaluated by examining the shift of the pH

potential during the experiment. Figure 2d is a reproduction of a computer generated plot for the 900 meters point of station 12. The potential at the end of the first complete cycle (55.7 to 73.8 min) seems to have reached a steady level.

#### DISCUSSION AND CONCLUSIONS

Figure 3 depicts profiles for the degree of saturation in the Santa Monica Basin and in the eastern Pacific Ocean. The crossover level from supersaturation to undersaturation appears to be approximately 200 meters in Santa Monica Basin and 450 meters over the continental slope. Because the pH and temperature profiles in the two areas (Tables 3 and 4) were found to be similar down to 400 meters, the dissimilarity in  $IP/K_{sp}'$  is probably due to a difference in total  $CO_2$ . We emphasize that the determined pH values may be slightly in error because they are based on the assumption that the pH measured during flushing was the pH of the surrounding sea water.

The degree of saturation at any given depth is a function of total  $CO_2$ , pH, and the solubility of calcite at the in situ conditions. The solubility of calcite should increase with depth, as a result of increasing pressure and decreasing temperature [McIntyre, 1965; Hawley and Pytkowicz, 1969], or the ratio  $IP/K_{sp}'$  should decrease with depth if pH and  $T(CO_2)$  remain constant. For a given  $T(CO_2)$  a decrease in pH will reduce the concentration of  $CO_3^{2-}$  and hence the ratio  $IP/K_{sp}'$ . This ratio, however, is linearly proportional to  $T(CO_2)$  for a constant pH and  $K_{sp}'$ .

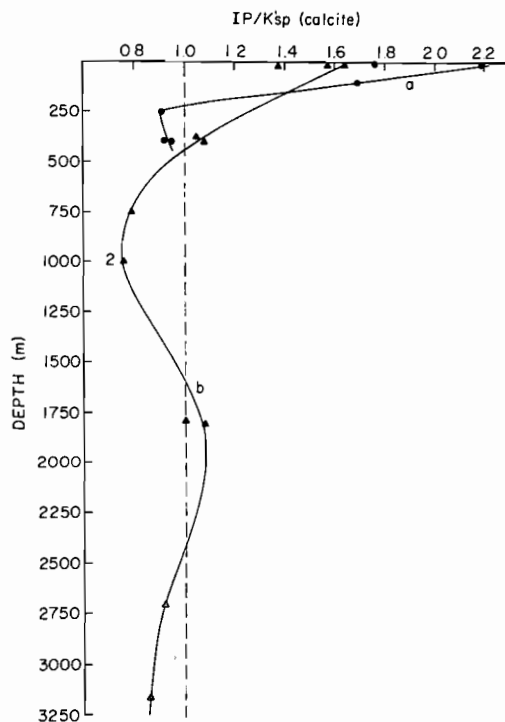


Fig. 3. Profiles of the degree of saturation ( $IP/K_{sp}'$ ) of sea water with respect to calcite in Santa Monica Basin (a) and eastern Pacific Ocean (b).

In the ocean, all three controlling parameters (depth,  $T(\text{CO}_2)$ , and  $p\text{H}$  change in a vertical column) and the saturation ratio at a given point depend on the balance between them. Total  $\text{CO}_2$  generally increases slightly with depth [Li, 1967] in the first 2000 meters owing to oxidation of organic debris and solution of  $\text{CaCO}_3$  (in undersaturated waters). The  $p\text{H}$  profile, however, passes through a minimum around the oxygen minimum zone (750 meters in our experiment; Table 4) and then slightly increases with depth. The  $p\text{H}$  increase, added to the total  $\text{CO}_2$  increase, is apparently enough to shift the ratio  $IP/K_{sp}$  above one at about 2000 meters despite the higher pressure and lower temperature in this layer compared with the overlying water.

Below 3000 meters total  $\text{CO}_2$  usually decreases [Li, 1967] possibly because of mixing of ocean currents or vertical diffusion. The  $p\text{H}$  passes a local maximum at depth [Park, 1966] and again decreases down to the bottom. Hence, below about 3000 meters an increase in depth is accompanied by an increase in pressure, a decrease in temperature, a decrease in  $p\text{H}$ , and a decrease in total  $\text{CO}_2$ . Since all these processes decrease  $IP/K_{sp}$ , the ocean should be undersaturated from approximately 3000 meters down to the bottom.

The shape of the degree of  $\text{CaCO}_3$  saturation profile is not constant over the entire ocean but is a function of the geographical area [Lyakhin, 1967], especially in the upper layer, where  $p\text{H}$  and  $T(\text{CO}_2)$  are strongly affected by surface productivity [Ben-Yaakov and Kaplan, 1968b; Li, 1967; Park, 1969]. Accurate comparison between independent determinations of the degree of saturation can therefore be accomplished only if the measurements were taken in the same area and possibly in the same season. However, the variability of the profile at depth may be less pronounced along a given latitude owing to homogenization of deep water.

Li [1967], Lyakhin [1967], and Hawley and Pytkowicz [1969] have recently calculated saturation profiles along the Pacific. Li's calculations are based on  $p\text{CO}_2$  and  $T(\text{CO}_2)$  measurements on sampled waters, whereas Lyakhin's calculation are based on  $p\text{H}$ -alkalinity measurements made by Russian oceanographic investigators. Hawley and Pytkowicz's calculations are also based in part on Russian measurements.

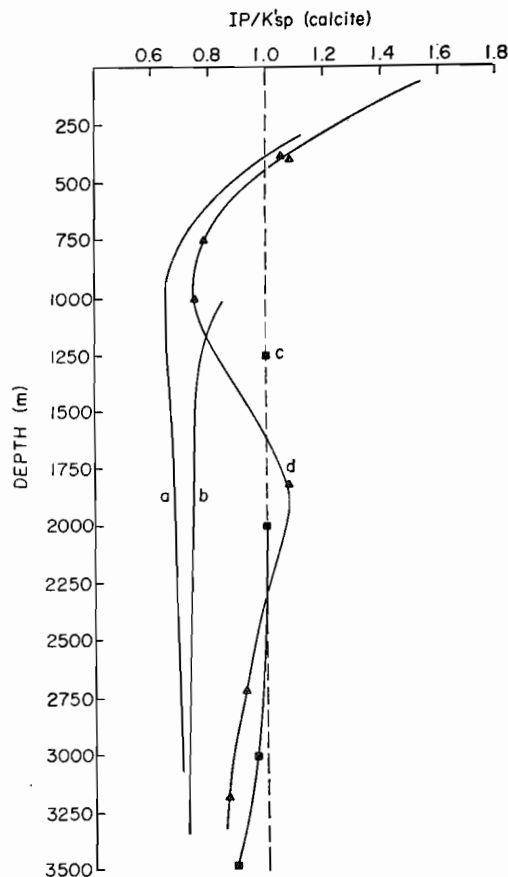


Fig. 4. Comparison of calcite saturation profile around latitude  $30^\circ\text{N}$  in the Pacific obtained by: (a) Lyakhin [1967], eastern region of northern subtropical area; (b) Hawley and Pytkowicz [1969],  $170^\circ\text{W}$ ,  $32^\circ\text{E}$ ; (c) Li [1969], northwest Pacific; (d) this work.

The plots in Figure 4 can be used to compare these profiles of calcium carbonate saturation with those obtained in this study. All data are for stations around  $30^\circ\text{N}$  latitude in the Pacific. However, the profiles of Li *et al.* [1969] and of Hawley and Pytkowicz [1969] are for the western Pacific ( $\sim 170^\circ\text{W}$ ), whereas our data and Lyakhin's [1967] data are for the eastern Pacific ( $\sim 120^\circ\text{W}$ ). We have not plotted the upper part of the profile from Li *et al.*, because there is too much scatter in their published data and it is difficult to estimate the average line. The scatter is probably due to the fact that Li *et al.* did not obtain complete profiles at any single station, and the horizontal distances



between two consecutive points are often large, in the range of hundreds of miles.

Our data and Lyakhin's profile correspond to roughly the same region in the Pacific, which can perhaps justify a comparison of the results in the upper layer. The first crossover points between supersaturation to undersaturation are around 400 meters for both sets of data. The two profiles agree well only at the uppermost layer, whereas at depths below 1000 meters Lyakhin's saturation ratio ( $IP/K_{sp}$ ) is consistently smaller than ours by about 0.2. At greater depth there is reasonable agreement between the data of Lyakhin and those of Hawley and Pytkowicz. This is not surprising because both calculations are based on the same field measurements. Differences between the results of these two laboratories arise partially from Hawley and Pytkowicz's use of their recently determined value for the pressure dependence of the solubility of calcite at low temperatures. Another factor that might contribute to differences is that the two profiles do not correspond to the same region. For deep water our data and those of Li et al. agree better. These two profiles suggest that the Pacific at 30°N is close to saturation between 1000 and 3000 meters and probably consistently undersaturated below 3000 meters. On the other hand, the data of Hawley and Pytkowicz [1969] and Lyakhin [1967] suggest that for the same latitude the Pacific is undersaturated from about 750 meters down to the bottom. It should be emphasized that the data of Li et al. show a consistently lower crossover level all over the Pacific than that calculated by Hawley and Pytkowicz. Our measurements for the eastern Pacific tend to support the findings of Li et al. We therefore support the conclusion that the change in degree of saturation for calcite from saturation to undersaturation may account for the decrease of  $\text{CaCO}_3$  content in the ocean sediments observed at water depths greater than 3000 meters in the Pacific.

The results of our preliminary field experiments demonstrate the feasibility of using the in situ carbonate saturometer as a tool for studying carbonate saturation in the ocean. Further in situ studies in different regions of the oceans using calcite and other carbonate species are needed.

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