

Calcium carbonate saturation in northeastern Pacific: *in situ* determination and geochemical implications

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(Received 19 March 1973; in revised form 11 September 1973; accepted 20 September 1973)

Abstract—*In situ* measurements by calcite and aragonite saturometry in the intermediate waters of the northeastern Pacific, indicate that these waters are close to saturation with respect to calcite. It is proposed that the carbonate compensation depth in this region is mainly controlled by the degree of carbonate saturation of ocean waters. If this suggestion is correct, then the carbonate compensation depth can be shown to be directly related to the alkalinity and nutrient cycles in the oceans. Three independent factors seem to control the depth of carbonate compensation: bottom topography, nutrient recycling rate (oceanic mixing) and a dependency factor relating biogenic CaCO_3 production to nutrient availability.

INTRODUCTION

EARLIER results of *in situ* calcite saturometry in the deep ocean (BEN-YAAKOV and KAPLAN, 1971) left some questions open concerning their reliability and interpretation. As calcium carbonate from a single source (optical grade calcite) had been used in the experiments, there was not the assurance that the past history of the mineral (WEYL, 1967) had not influenced the data. Thus, they may not have been representative of seawater-carbonate reactions at depth. Furthermore, their interpretation depended upon the pH value measured during the flushing period (BEN-YAAKOV, 1970) and it could not be positively proven that this was representative of the original pH of the waters at the point of measurement. For these reasons, the preliminary work was qualitative, rather than quantitative (BEN-YAAKOV and KAPLAN, 1971, 1972).

Our present purpose was to verify the earlier measurements by (a) repeating them with two carbonate minerals, calcite and aragonite and (b) by concurrently measuring the *in situ* pH using a separate glass electrode.

EXPERIMENTAL

The *in situ* carbonate saturometer is a special adaptation of an oceanographic *in situ* instrumentation system developed in our laboratory (BEN-YAAKOV, 1970; BEN-YAAKOV and KAPLAN, 1971). It contains a high pressure pH glass electrode (BEN-YAAKOV and KAPLAN, 1968) which is placed in a Plexiglas® cell packed with solid CaCO_3 grains. An *in situ* pump is turned on for 3–5 min periods every 20 min to flush the cell with the surrounding seawater. The potential of the glass electrode is recorded once every minute with other pertinent data, such as the *in situ* temperature and hydrostatic pressure, required to calculate the pH in the carbonate cell during the flushing and equilibrium periods. The pH (or potential) difference before and at equilibrium with the CaCO_3 is then used to determine the degree of saturation of the original seawater with respect to the given carbonate (BEN-YAAKOV and KAPLAN, 1969).

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In the present configuration of the *in situ* carbonate saturometer, an extra pH electrode was added to monitor the pH of the surrounding seawater continuously. Although in simulated laboratory experiments, flushing rate was fast enough to allow the pH in the cell to be nearly identical to the original pH of the waters, there was not positive proof that this was also the case under *in situ* conditions. However, the data of the modified *in situ* saturometer (Fig. 1) indicate that the pH values measured by the

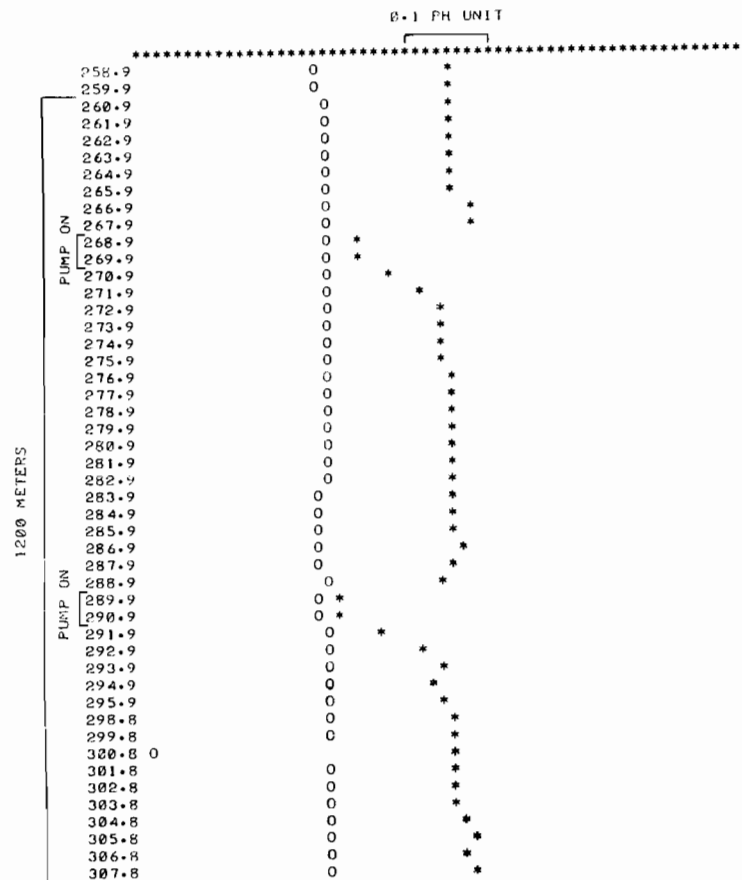


Fig. 1. *In situ* pH calculated from the readings of the saturometer (*) and pH monitoring (O) glass electrodes. Vertical scale corresponds to running time (min). The pH reading of the saturometer electrode during pumping should correspond to the pH reading of the independent pH electrode. Deviation during pumping reflects the accumulative error due to calibration, standardization, temperature effects and non-ideality of the glass membrane response.

two electrodes—during the flushing cycle—differ by no more than 0.03 pH unit. The difference seems to be fairly consistent and probably represents a systematic error. It also appears that the present data support our original non-reproducibility estimate of the *in situ* pH measurement: ± 0.02 pH unit. Very accurate determination of the original pH of the seawater is not required here, because the calculation of the degree of saturation is fairly insensitive to large errors in pH (BEN-YAAKOV and KAPLAN, 1969). It is also relatively insensitive to errors in temperature, hydrostatic pressure and the accuracy of

the apparent constants of the carbonate and borate systems, but it is sensitive, however, to errors in the determination of the mV shift due to the carbonate reaction. The precision of the instrumentation system is within ± 0.1 mV and the accuracy is within ± 0.5 mV. It is estimated that the maximum error in the ratio IP/K'_{sp} due to the instrumentation is about ± 0.01 . However, the actual accuracy of the estimated value of IP/K'_{sp} depends to a large extent on the reversibility and kinetics of the chemical reaction between the carbonate and the seawater. In particular, the saturometer measurements are accurate only if true equilibrium is reached in 20 min. This question can probably be best answered by examining the variation of the potential of the saturometer electrode with time as discussed below.

The potential of the saturometer electrode is expected to reflect only the pH changes within the carbonate cell, but spurious potentials may result if metallic materials are placed in the vicinity of the cell. Thus, large error signals were generated when a stainless steel hose connected the *in situ* pump to the cell. This error signal was synchronous with the pumping cycle and, therefore, inseparable from the saturometer signal. Its source is probably a metal-solution potential between the surfaces of the stainless steel hose and the seawater. The magnitude of these erroneous signals may be very large as judged by running the instrument with an empty saturometer cell (Table 1). It should be emphasized that all the present as well as the earlier data (BEN-YAAKOV and KAPLAN, 1971) were obtained with an all-plastic construction.

The calcite and aragonite minerals used in the present study were obtained from Ward's (Monterey, California). The calcite was an optical grade material (Iceland Spar) reported to have come from Chihuahua, Mexico, and the aragonite from Furka,

Table 1. Results of *in situ* saturometry experiments in Santa Monica Basin. Data from Sta. 32 are inaccurate due to metal-solution potentials (see text). Station locations are given in Table 2.

| Depth (m) | Carbonate mineral | Station | Temp. (°C) | pH | Shift (mV) | $IP/K'_{sp}\dagger$ |
|-----------|---------------------------|---------|------------|------|------------|---------------------|
| 100† | Cell empty | 32 | 9.61 | | +8.50 | — |
| 400 | | 41 | 7.25 | | 0.0 | — |
| 1 | Calcite (32-42 mesh) | 44 | 15.1 | 8.17 | +15.00 | 1.92* |
| 200 | | 44 | 9.0 | 7.75 | +1.84 | 1.08* |
| 300 | | 44 | 8.2 | 7.69 | +0.67 | 1.03 |
| 400 | | 44 | 7.1 | 7.65 | -1.67 | 0.93 |
| 1 | | 43 | 14.7 | 8.21 | +7.66 | 1.40 |
| 100 | Aragonite (32-42 mesh) | 46 | 9.5 | 7.89 | +3.33 | 1.16 |
| 200 | | 43 | 8.4 | 7.86 | +1.33 | 1.06 |
| 200 | | 46 | 8.9 | 7.76 | +1.00 | 1.04 |
| 300 | | 43 | 8.4 | 7.77 | -1.33 | 0.94 |
| 300 | | 46 | 8.3 | 7.68 | -2.66 | 0.89 |
| 400 | | 43 | 7.5 | 7.71 | -5.66 | 0.78 |
| 400 | | 46 | 7.6 | 7.63 | -5.99 | 0.77 |

*Values obtained by extrapolation to equilibrium by fitting the saturometer curve to an exponential function.

†Measurements made with stainless steel hose and cell insert. All other measurements made with Tygon® and Plexiglas® hardware.

‡ IP is the ionic product of Ca^{2+} and CO_3^{2-} (concentration) and K'_{sp} in the apparent dissociation of the $CaCO_3$ mineral at the *in situ* conditions.

Switzerland. An X-ray diffraction scan of the aragonite showed no traces of calcite. Both of the carbonate materials were crushed and sieved to the size range 32–42 mesh. The grains were then thoroughly washed in distilled water and dried overnight in the oven at 105°C.

RESULTS

Experiments were conducted in Santa Monica Basin and in the open ocean coast of Southern California (Table 2). The measurements were made in the same location at different times in order to compare the calcite and aragonite profiles and to estimate the reproducibility of the *in situ* carbonate saturometer.

Table 2. Location of oceanographic stations.

| Station | Date | Location | | Area |
|---------|---------------|----------|----------|-------------------------------|
| 32 | July 31, 1970 | 33°56'N | 118°42'W | North Santa Monica Basin |
| 41 | Feb. 11, 1971 | 33°56'N | 118°42'W | North Santa Monica Basin |
| 43 | May 27, 1971 | 33°56'N | 118°42'W | North Santa Monica Basin |
| 44 | May 28, 1971 | 33°56'N | 118°42'W | North Santa Monica Basin |
| 46 | June 11, 1971 | 33°56'N | 118°42'W | North Santa Monica Basin |
| 47 | June 19, 1971 | 32°31'N | 120°28'W | 180 miles West of San Diego |
| 48 | June 19, 1971 | 32°18'N | 120°25'W | 180 miles West of San Diego |
| 49 | June 19, 1971 | 32°06'N | 120°22'W | 180 miles West of San Diego |
| 60 | July 13, 1972 | 33°49'N | 121°47'W | 80 miles SW of Pt. Conception |

The mV shift required for IP/K'_{sp} determination (BEN-YAAKOV and KAPLAN, 1969) was obtained from the saturometer plots (Figs. 2 and 3). Figure 2 shows that at the surface point of Sta. 44, the output potential of the saturometer electrode became more positive, as the carbonate reacted with the trapped seawater, which is equivalent to a decrease in pH. This implies that carbonate had precipitated (BEN-YAAKOV and KAPLAN, 1969) and, therefore, that the original seawater was supersaturated with respect to calcite as expected. It appears, however, that equilibrium has not been reached, since the output potential of the glass electrode has not reached a stable value. Figure 3 is an example of a case in which equilibrium has apparently been reached, since the potential of the glass electrode has leveled off before the following pumping period was initiated. An equilibration time of 20 min is long enough for most undersaturation conditions, but too short in the supersaturation cases, particularly when calcite was used.

Equilibrium values for the saturometer experiments in which steady state was apparently not achieved, were estimated by fitting the saturometer curve to an exponential function and extrapolating it to infinity. All the saturometer curves were found to follow the function:

$$V(t) = V_{\infty} (e^{-t/T} - 1), \quad (1)$$

where $V(t)$ is the output potential shift of the saturometer electrode, V_{∞} is the shift at equilibrium, t is time and T is a constant. The time constant (T) was in the range 2–15 min. Using a non-linear least squares fitting, V_{∞} was estimated for data points where the reaction had not reached completion.

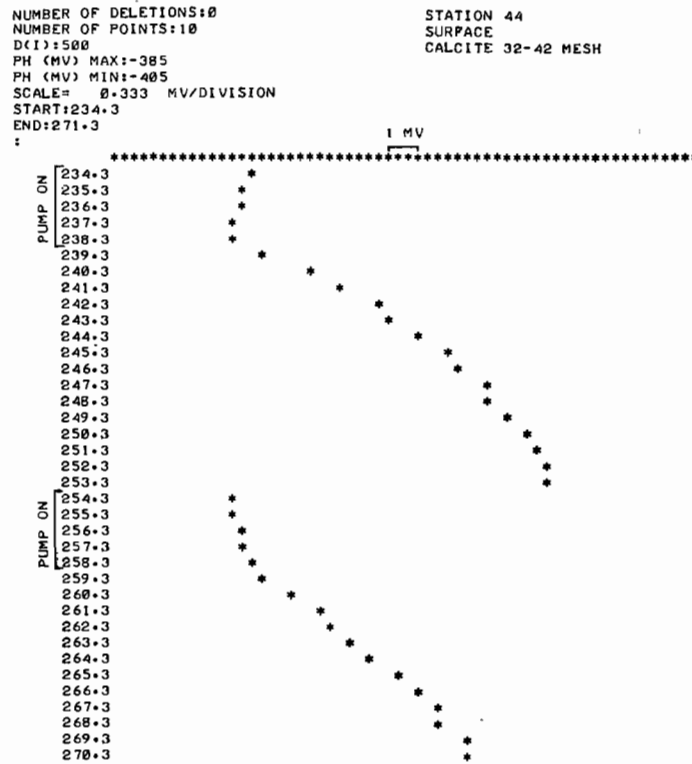


Fig. 2. Output of the saturometer electrode (horizontal axis) versus running time (min) for the surface point of Sta. 44 (Santa Monica Basin). Carbonate mineral: calcite (32-42 mesh).

Repeated experiments at the same location on different dates produced, in general, very close results. The ratios IP/K'_{sp} for Stas. 43 and 46 (Table 1), for example, differ by about 0.05. However, part of the difference may be attributed to non-stability of the upper layers and the actual reproducibility of the saturometer is probably better than the above value. This can be inferred by examining the results of the 400 m points of Stas. 43 and 46, which differ by no more than 0.02. The water layer at this depth is probably fairly stable and the difference between the readings should be attributed mainly to the limited reproducibility of the *in situ* carbonate saturometer. The present data are in good agreement with the measurements taken a year earlier in Santa Monica Basin. The present estimate of IP/K'_{sp} for calcite at 400 m is 0.93 (Table 3), whereas the previous one was 0.95 (BEN-YAAKOV and KAPLAN, 1971).

The measurements in the northeastern Pacific (Table 3) confirm, in general, those made previously (BEN-YAAKOV and KAPLAN, 1971) although there are not enough points to give the fine details of the saturation profile. The data for aragonite saturometry (Table 3) yield IP/K'_{sp} values consistently lower than those with calcite of the same location, as might be expected, because the apparent solubility product (K'_{sp}) of aragonite is larger than that of calcite (MACINTYRE, 1965).

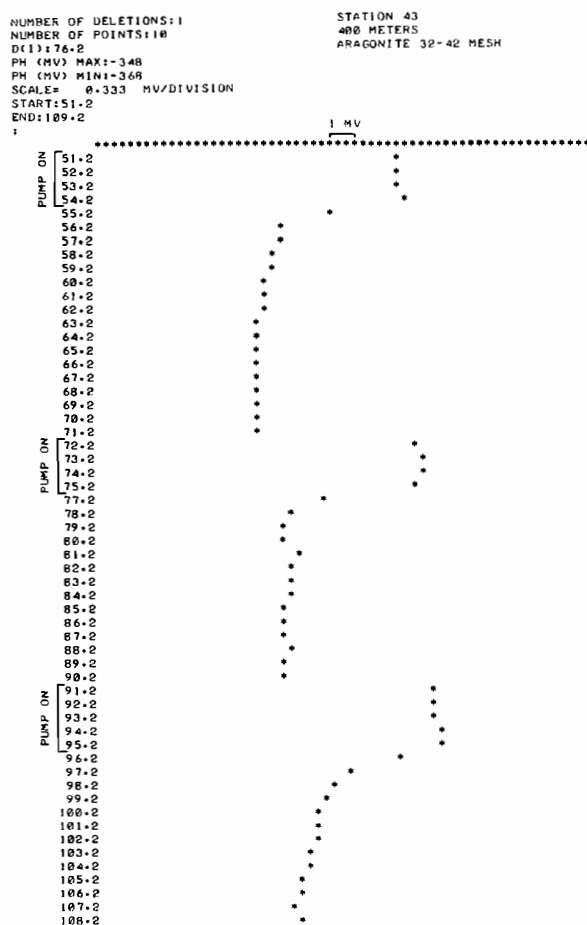


Fig. 3. Output of the saturometer electrode (horizontal axis) versus running time (min) at the 400 m depth level of Sta. 43 (Santa Monica Basin). Carbonate mineral: aragonite (32-42 mesh).

DISCUSSION

As pointed out by BEN-YAAKOV and KAPLAN (1971), the data of *in situ* calcium carbonate saturometry suggest that the intermediate waters of the northeastern Pacific are close to saturation with respect to calcite. This conclusion conflicts with those of other investigators (HAWLEY and PYTKOWICZ, 1969; CULBERSON, 1972), based on analyses of water samples under shipboard conditions. The *in situ* saturometer measurements sharply disagree with the values calculated from shipboard analysis, the latter being consistently displaced toward undersaturation (Fig. 4). In fact, by this method, the degree of saturation of calcite is smaller than the saturometer values for aragonite, even though aragonite is about 1.5 times more soluble than calcite (MACINTYRE, 1965).

Despite the large differences between the two independent determinations of IP/K'_{sp} , there is good agreement between the *in situ* pH measured by us and those estimated by Culberson from the YALOC-69 data (Fig. 5). This is not surprising, because the *in situ* pH is calculated by considering the temperature and pressure effects on the apparent dissociation constant of the carbonate and borate system (K_1' , K_2' ,

Table 3. Results of *in situ* saturometry experiments in the northeastern Pacific. Station locations are given in Table 2.

| Depth (m) | Carbonate mineral | Station | Temp. (°C) | pH | Shift (mV) | $IP/K'_{sp} \dagger$ |
|-----------|-------------------|---------|------------|------|------------|----------------------|
| 145 | | 48 | 9.2 | 7.87 | +4.06 | 1.19 |
| 646 | | 48 | 4.8 | 7.53 | -4.89 | 0.80 |
| 1208 | | 48 | 3.4 | 7.57 | -1.79 | 0.92 |
| 2000 | | 60 | 2.1 | 7.70 | -0.97 | 0.96 |
| 2202 | Calcite | 48 | 2.0 | 7.66 | -0.60 | 0.97 |
| 3000 | (32-42 mesh) | 60 | 1.7 | 7.77 | -1.48 | 0.94 |
| 3000 | | 60 | 1.7 | 7.76 | -0.84 | 0.96 |
| 3443 | | 48 | 1.7 | 7.69 | -1.30 | 0.94 |
| 3535 | | 60 | 1.6 | 7.76 | -1.79 | 0.92 |
| 87 | | 47 | 11.1 | 7.99 | +3.92 | 1.19 |
| 544 | | 47 | 5.7 | 7.54 | -8.90 | 0.67 |
| 698 | | 47 | 4.8 | 7.56 | -8.74 | 0.67 |
| 1005 | Aragonite | 47 | 3.9 | 7.61 | -8.43 | 0.68 |
| 1234 | (32-42 mesh) | 47 | 3.4 | 7.64 | -5.57 | 0.78 |
| 2106 | | 47 | 2.1 | 7.75 | -5.57 | 0.78 |
| 2792 | | 49 | 1.8 | 7.77 | -6.34 | 0.75* |

*All values except IP/K'_{sp} for 2792 m were extrapolated to equilibrium by fitting the saturometer curve to an exponential function.

† IP is the ionic product of Ca^{2+} and CO_3^{2-} (concentration) and K'_{sp} in the apparent dissociation of the $CaCO_3$ mineral at the *in situ* conditions.

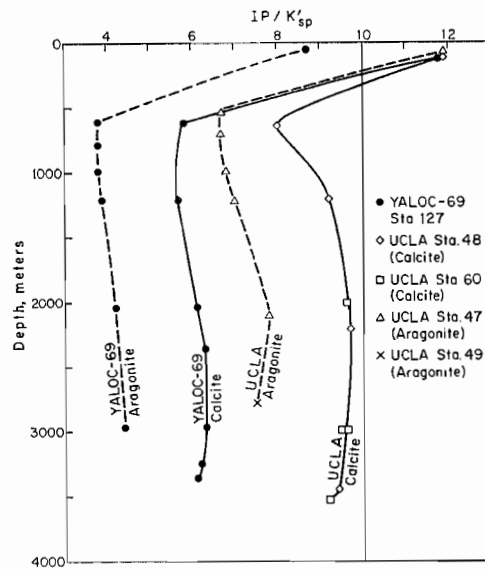


Fig. 4. Calcite and aragonite saturation in northeastern Pacific as measured by the *in situ* saturometer (UCLA) and calculated by CULBERSON (1972) for YALOC-69 data (CULBERSON and PYTKOWICZ, 1970).

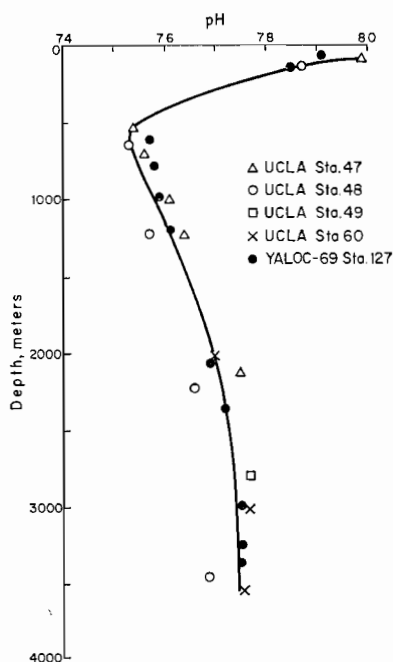


Fig. 5. *In situ* pH in northeastern Pacific as measured by the *in situ* probe (UCLA) and calculated by the method of CULBERSON (1972) from the YALOC-69 data (CULBERSON and PYTKOWICZ, 1970).

K_B'), which were determined by pH measurements at atmospheric (LYMAN, 1957) and high pressure (CULBERSON and PYTKOWICZ, 1968). Hence, the agreement between the directly and indirectly measured *in situ* pH values only reflects the fact that the mathematical relationship described by the apparent constants (LYMAN, 1957; SKIRROW, 1965), are useful in predicting the *in situ* pH. This does not necessarily imply, however, that these mathematical relationships will also accurately predict *in situ* concentration of the carbonate ion (CO_3^{2-}), which is used in calculating IP/K'_{sp} . In fact, some doubt has been cast (TAKAHASHI, WEISS, CULBERSON, EDMOND, HAMMOND, WONG, LI and BAINBRIDGE, 1970; BERNER and WILDE, 1972) on the accuracy of the accepted value of K_2' (LYMAN, 1957; SKIRROW, 1965). If K_2' is in error, the calculated (CO_3^{2-}) will be in error in about the same proportion, because the two are related by:

$$(\text{CO}_3^{2-}) = CA \frac{K_2'}{a\text{H}^+ + 2K_2'}, \quad (2)$$

where CA is carbonate alkalinity (a nearly conservative parameter), and $a\text{H}^+$ is defined by:

$$a\text{H}^+ = 10^{-\text{pH}}. \quad (3)$$

BERNER and WILDE (1972) assumed that K_2' reported by LYMAN (1957) is too small by about 30%. If their deductions are confirmed, then the calculated (CO_3^{2-}) concentration will be about 30% larger, which would considerably improve the agreement between the *in situ* determined IP/K'_{sp} and the calculated ratio. However, the calculated IP/K'_{sp} values are also dependent on K'_{sp} , and there are some indications that the most generally accepted K'_{sp} values (MACINTYRE, 1965) may also be in error.

The K'_{sp} values for calcite reported by MACINTYRE (1965) are probably too large by at least 6% (BEN-YAAKOV and GOLDHABER, 1973). If so, the calculated IP/K'_{sp} would be too small by the same percentage. This, by itself, will slightly improve the agreement between the measured and calculated *in situ* IP/K'_{sp} . However, the values of K'_{sp} as determined by MACINTYRE (1965) are dependent on K_2' (BEN-YAAKOV and GOLDHABER, 1973). This would tend partially to cancel out the improvement between the results of the two studies due to the possible error in K_2' .

In the foregoing discussion, it was implicitly assumed that calcite-seawater reactions are thermodynamically well-behaved. However, the reaction is irreversible and the observed apparent solubility product of calcite in supersaturated seawater is greater than that observed in undersaturated conditions, probably due to precipitation of a magnesium calcite phase (WEYL, 1967; BEN-YAAKOV, 1970). The question arises then, whether the discrepancy between the *in situ* saturometer measurements and the calculated values are due to this effect. The above effect may be applicable for the data points of supersaturated waters measured by *in situ* saturometry, but we do not believe that it is a valid argument for undersaturation data. Repeated *in situ* saturometer experiments have demonstrated that the results are independent of whether a given (undersaturated) point has been approached from a supersaturated or undersaturated water layer. Evidently, the flow rate during the flushing period is sufficient to remove any coating that may have built up in supersaturated waters (WEYL, 1967; PYTKOWICZ, 1972). Furthermore, if a newly-formed carbonate coating interferes with measurements in undersaturated water, then the IP/K'_{sp} values determined by the saturometer should be lower than the calculated ones, because the coating was shown to be more soluble than calcite (WEYL, 1967; BEN-YAAKOV, 1970). Such a tendency is indeed observed in supersaturated waters, but our measured values show IP/K'_{sp} to be greater—and not smaller, as might have been expected—than the calculated ones (Fig. 4). It would appear that the postulated coating effect cannot be invoked, to explain the disagreement. However, as pointed out by BEN-YAAKOV and KAPLAN (1972), there is a possibility that this effect may have introduced some error in the determination of K'_{sp} (MACINTYRE, 1965) and the pressure coefficient of K'_{sp} (PYTKOWICZ and FOWLER, 1967; HAWLEY and PYTKOWICZ, 1969).

Another possibility that should be considered, perhaps, is that the *in situ* saturometer results do not represent equilibrium conditions. However, there is no reason to believe that carbonate dissolution is carried on in two stages, a fast and a very slow step. It is hard to believe, for example, that the saturometer curve (Fig. 3) does not indicate that an equilibrium state has been reached. Furthermore, the experimental results of MACINTYRE (1965), WEYL (1967) and BEN-YAAKOV (1970) suggest that carbonate-seawater reactions are fast with a time constant in the order of 10 min, depending, of course, on the solid-to-solution ratio which is maximized in the *in situ* saturometer (BEN-YAAKOV and KAPLAN, 1972). Furthermore, if arguments of 'very slow reaction rates' are invoked, then they equally apply to the accuracy of available K'_{sp} data (MACINTYRE, 1965) and its pressure coefficients (PYTKOWICZ and FOWLER, 1967; HAWLEY and PYTKOWICZ, 1969) which are used for calculating the *in situ* IP/K'_{sp} from surface analyzed data.

Taking our results at their face value, the present study suggests that the intermediate waters of northeastern Pacific are close to saturation with respect to calcite. This is in agreement with the conclusions of LI, TAKAHASHI and BROECKER (1969), and

the basic premise of the seawater composition models proposed by SILLÉN (1961), MACKENZIE and GARRELS (1966a) and HOLLAND (1972), which suggest that on a *gross* scale, the oceans are close to saturation with respect to solid CaCO_3 .

The present saturometer data is confined to the northeastern Pacific area and does not represent the oceans as a whole. Hence, application of these data to explain the mechanism that controls carbonate compensation depths must await further *in situ* saturometer studies in different parts of the world oceans. If, indeed, the intermediate layers of ocean water are closer to saturation with respect to carbonate than previously predicted (BERNER, 1965; PYTKOWICZ and FOWLER, 1967; HAWLEY and PYTKOWICZ, 1969; CULBERSON, 1972), the carbonate compensation depth at any one location on the ocean floor could be dependent on the degree of carbonate saturation of the overlying seawater at that location. The question as to a linear or non-linear dependency of rate of carbonate dissolution on deviation from saturation as raised by BERNER (1971) and MORSE and BERNER (1972) cannot be answered with the information presently available.

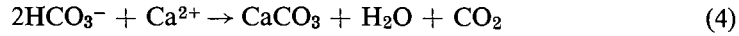
As there is evidence that the carbonate compensation depth was maintained at about the present level during the last several hundred thousand years (BROECKER and BROECKER, in press), the degree of carbonate saturation of the oceans must have been constant for that period. Possible mechanisms that may have contributed to a fixed carbonate compensation depth are considered in the next section.

A QUALITATIVE MODEL FOR THE CARBONATE COMPENSATION DEPTH

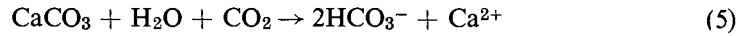
As pointed out by BROECKER (1971) and by BROECKER and BROECKER (in press), the depth of the carbonate compensation horizon is fixed, on the gross scale, by the requirement that the total flux of carbonate lost to the sediment be balanced against its input to the oceans. Furthermore, negative feedback mechanisms within the oceans (LI, TAKAHASHI and BROECKER, 1969; BROECKER, 1971; BROECKER and BROECKER, in press) tend to suppress excursion of the carbonate compensation depth from its present levels. The question arises, however, as to whether the present compensation depth (approximately 4000 m) is a result of a fortuitous combination of the magnitude of carbonate input to the oceans, production rate of CaCO_3 , oceanic mixing rates and other related parameters (BROECKER and BROECKER, in press) or whether the depth of the compensation level is relatively insensitive to the magnitude of these parameters. The compensation depth has probably oscillated during recent geologic time, but surprisingly, the deviations from the present level were apparently relatively small. BROECKER and BROECKER (in press) have concluded, for example, that 5 million years ago the compensation level in the South Pacific was within 150 m of its present depth. It seems unlikely that the same depth was maintained due to sheer luck (WEYL, 1966) which hold all the controlling parameters in the right proportion so as to keep the compensation depth at exactly the same value. Alternatively, it may be considered that the depth of carbonate compensation is relatively insensitive to the recognized controlling parameters. In order to resolve this question, the dependency between the compensation depth and the controlling parameters must first be understood. In the following sections, an attempt is made to evaluate some of these interrelations.

It has been customary (REVELLE and FAIRBRIDGE, 1957; PYTKOWICZ, 1968; BROECKER, 1971; BROECKER and BROECKER, in press) to study the controls of carbonate

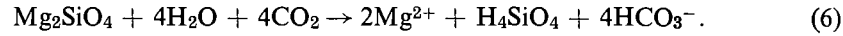
compensation in the oceans in terms of the carbon cycle. The carbon input to the ocean is mainly in the form of bicarbonate (GARRELS and MACKENZIE, 1972), whereas the main sink is calcium carbonate burial, that is, the carbon leaving the oceans is mainly in the form of carbonate (CO_3^{2-}). Transfer through the ocean is not smooth and involves chemical and biological reactions. Calcium carbonate formation should release CO_2 :



and the gas phase (CO_2) must leave the ocean to the atmosphere and be fed back to the ocean through the weathering process, e.g.:



or:



A simpler approach would be to consider the problem in terms of the alkalinity cycle rather than the carbon cycle. Most of the seawater alkalinity is in the form of carbonate alkalinity (SKIRROW, 1965), as the contributions of borate and silica do not amount to more than a few tenths per cent. Therefore, carbonate alkalinity is to a first approximation a conservative tracer, and since its residence time is in the order of 300,000 a, its input to the ocean must be closely balanced by its output when averaged over a period of hundreds of thousands of years. Although a relatively minor constituent (*ca.* 2 mequiv kg^{-1}), carbonate alkalinity must be assumed to have remained about constant during the last half-billion years (HOLLAND, 1972), because relatively large variations in alkalinity would have drastically changed the composition of seawater.

The main paths of the alkalinity cycles pertinent to the present discussion (Fig. 6) include an input flux from the land (F_{12}), biogenic CaCO_3 production (F_{23}), inorganic

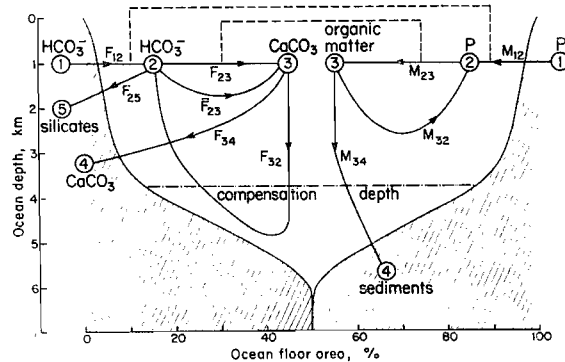


Fig. 6. Schematic presentation of the alkalinity (left) and nutrients (right) in the oceans. 'P' represents nutrients. The broken lines suggest coupling between the alkalinity and nutrients fluxes. See text for detailed discussion of the pathways. The relationship between % ocean floor area and ocean depth after SVERDRUP, JOHNSON and FLEMING (1942).

precipitation (\bar{F}_{23}), carbonate burial (F_{34}), CaCO_3 dissolution (F_{32}) and losses due to silicate reactions (F_{25}) either by reverse weathering reactions or precipitation of authigenic silicate minerals (GARRELS, 1965; HOLLAND, 1965; MACKENZIE and GARRELS, 1966b; SIEVER, 1968; BROECKER, 1971) e.g.:



The main driving force of the alkalinity cycle is biogenic production of CaCO_3 (F_{23}) which is far more important than inorganic precipitation (\bar{F}_{23}). This organic path, however, heavily depends upon the availability of nutrients (BROECKER, 1971; BROECKER and BROECKER, in press) and hence, the alkalinity cycle is intimately dependent on the nutrients cycle. This cycle by itself (Fig. 6) is composed of several pathways, those pertinent to the present discussion being input from land (M_{12}), fixation into organic matter (M_{23}), retrieval by oxidation of organic matter (M_{32}) and burial (M_{34}).

Total alkalinity lost to the sediment can be related to the path fluxes of the alkalinity cycle by making the simplifying assumption that CaCO_3 production is evenly distributed over the ocean surface and that the carbonate compensation level is, to a first approximation, at a constant depth. Under these assumptions, and for a balanced input and output, the following relation must hold:

$$F_{12} = (F_{23} + \bar{F}_{23}) A_s/A + F_{25}, \quad (8)$$

where A is the total area of the ocean floor, A_s is the area of seafloor above the carbonate compensation depth and (F) are normalized fluxes (equivalents per unit time). The last relationship implicitly assumes that CaCO_3 dissolution in the water column is negligibly small when compared to dissolution on the ocean floor (POND, PYTKOWICZ and HAWLEY, 1971; BERGER and PIPER, 1972).

The alkalinity cycle can be linked to the nutrients cycle by assuming that biogenic CaCO_3 production is, to a first approximation, linearly proportional to the availability of nutrients; namely:

$$F_{23} \approx K(M_{12} + M_{32}), \quad (9)$$

where K is a constant for a given ecological condition. By combining the last two equations, the ratio of the area below (A_u) and above (A_s), the carbonate compensation level can be expressed as a function of the various fluxes:

$$\frac{A_u}{A_s} \simeq \frac{K(M_{12} + M_{32}) + \bar{F}_{23}}{F_{12} - F_{25}} - 1. \quad (10)$$

GARRELS and MACKENZIE (1972) presented evidence that the streams of the past had the same weight percentage composition of dissolved species as those of today. If this conjecture is accepted, then M_{12} , F_{12} and F_{25} must be linearly related to one another. Making this assumption and considering that inorganic precipitation of CaCO_3 (\bar{F}_{23}) is negligible, the following relationship is obtained:

$$A_u/A_s \simeq K \cdot [K_1 + K_2 M_{32}/F_{12}] - 1, \quad (11)$$

where K_1 and K_2 are constants and K , as before, relates biogenic CaCO_3 production to nutrient supply.

As pointed out by BROECKER (1971), only about 1% of the nutrients sinking to the deep ocean are preserved in the sediments ($M_{32} = 100M_{34}$) and therefore, if $M_{34} = M_{12}$ at steady state, $M_{32} \approx 100M_{12}$ and the last equation can be further simplified to:

$$A_u/A_s \simeq K \cdot K_2 M_{32}/F_{12} - 1. \quad (12)$$

For the present oceans, $A_u/A_s \approx 4$ (LI, TAKAHASHI and BROECKER, 1969; BROECKER and BROECKER, in press), and, under the assumptions made here, this ratio is controlled by three parameters: alkalinity influx to the ocean (F_{12}), nutrients recycling (M_{32}), and the

dependency between biogenic CaCO_3 production and nutrient availability (K). The most variable parameter of the three is (F_{12}) because alkalinity input to the ocean is probably dependent on climatic and tectonic conditions on Earth. However, despite these random controls, the ratio A_u/A_s should have stayed fairly constant, because M_{32} is partially dependent on (F_{12}). To a first approximation, the nutrient reflux (M_{32}) can be expressed as:

$$M_{32} \simeq V \cdot P, \quad (13)$$

where V is the rate of vertical mixing and P is nutrient concentration of the deep ocean. The latter should be proportional to M_{12} and, therefore, to F_{12} and equation (12) can be rewritten as:

$$A_u/A_s \simeq K_3 \cdot K \cdot V - 1, \quad (14)$$

where K_3 is a constant. Hence, under the present assumptions, mixing rates (V), and biological processes (K) in the oceans are the only independent controls on the ratio of ocean floor areas above and below the carbonate compensation level. The actual depth of this level will be determined, of course, by the distribution of ocean floor areas as a function of depth.

It seems reasonable to assume that within a time span of a few hundreds of thousands of years, and perhaps a few million years, the two independent parameters controlling A_u/A_s have stayed approximately constant. The present relationship between sea floor area and depth is such that below 4 km a small change in depth will result in a correspondingly large change in sea floor area represented (see Fig. 6). Thus, if the ratio A_u/A_s changes by 10%, the equivalent change in the carbonate compensation depth will only be about 100 m, and the shift will probably not be recognized in the sediment record.

CONCLUSIONS

The data of this study suggest that the intermediate waters of the northeastern Pacific are close to saturation with respect to calcite. This result is in conflict with the conclusion derived from shipboard analysis of ocean waters. Due to the complexity of applying corrections to surface-derived data for calculating *in situ* effects, it is impossible at present to reconcile the differences between the two approaches. Joint studies of *in situ* determination and surface analysis may shed some light on the reasons for the discrepancy. If our data prove to be compatible with surface shipboard analyses, and we are shown to be correct, it must then be considered that the compensation depth is more directly related to the state of saturation of carbonate in the ocean than is presently accepted. Using this as an *a priori* assumption, one can derive a functional relationship between the compensation depth and the alkalinity and nutrient cycles in the oceans. The analysis presented here suggests that three independent factors control the carbonate compensation depth: bottom topography, nutrient recycling rate (oceanic mixing) and the dependency of biogenic CaCO_3 production on nutrient availability. Although somewhat different in approach, the present analysis is in accord with that presented by BROECKER and BROECKER (in press).

Acknowledgements—We wish to thank P. GREENE and D. FRIEDMAN for assistance in construction and testing of the instrumentation. We further wish to thank the Los Angeles Sanitation Department and the Scripps Institution of Oceanography for making research vessels available to us for equipment tests and field measurements. The National Science Foundation is gratefully acknowledged for making this study possible by awarding us Grant No. GA-34104.

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