THE UNIVERSITY OF OKLAHOMA

GRADUATE COLLEGE

A GEOCHEMICAL ANALYSIS OF THE CARBON SYSTEM IN A MODERN TROPICAL LAGOON: DISCOVERY BAY, JAMAICA

A THESIS SUBMITTED TO THE GRADUATE FACULTY

in partial fulfillment of the

requirements for the degree of

MASTER OF SCIENCE

By

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1985

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ACKNOWLEDGEMENTS

I wish to acknowledge my major advisor, Dr. John D. Pigott, who provided me with both the idea for this study and his critique of this manuscript. Dr. P.K. Sutherland and Dr. Gordon Atkinson each provided their criticism and advice for the improvement of this study. Perhaps most helpful in the interpretation of my data were those who introduced me to the applications of the school's computer software, thereby allowing the numerous calculations and necessary manipulations of my data base. I wish to extend a special thanks to Karen Cochran for her helpful reviews of my early drafts and to my friends at The University of Oklahoma School of Geology and Geophysics who have made academia enjoyable. I also wish to thank my parents and numerous siblings for their support and encouragement throughout my years of education.

Funding for this study was provided by Sigma Xi Scientific Foundation, American Association of Petroleum Geologist's Grants-in-Aid program, and Chevron Corporation.

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ABSTRACT

The factors which alter the total CO_2 content of waters residing in Discovery Bay, Jamaica include photosynthesis, respiration, precipitation, dissolution, groundwater invasion, aerobic decay of organic matter, and gas exchange across the air-sea interface. Groundwater invasion of CO_2-charged meteoric waters can be accounted for by monitoring alkalinity and pH decreases associated with decreases in chlorinity. Disregarding the changes in alkalinity resulting from dilution, alkalinity changes represent the effects of precipitation and dissolution. Diurnal oxygen variations are used to estimate the organic metabolism and oxidation reactions occurring within the bay. The changes in total CO_2 resulting from gas exchange can be determined by subtracting the total CO_2 changes resulting from productivity, precipitation-dissolution, and groundwater invasion from the observed total CO_2 changes.

Based on the assumptions of a closed system and that the aforementioned factors fully define the pathways of CO_2 fluxes, several conclusions can be drawn regarding Discovery Bay. Both photosynthesis-respiration and dissolution-precipitation processes are linked to invasion-evasion, yet show no apparent link to each other. Although a net dissolution is observed within Discovery Bay, precipitation occurs as CO_2 evades from the bay waters. Diffusion across the air-sea interface is the result of an extremely high pCO_2 gradient. As CO_2 escapes to the atmosphere $CaCO_3$ precipitation is enhanced.

Saturation states of bay waters indicate undersaturation with respect to magnesium calcites < 7 mole % $MgCO_3$. Cursory x-ray diffraction of sediment samples around Discovery Bay may suggest a diagenetic neomorphism of biogenic high Mg calcite (i.e., > 13 mole % Mg calcite) to the less soluble low Mg calcite (3 mole % $MgCO_3$) with distance from the reef crest.

A GEOCHEMICAL ANALYSIS OF THE CARBON SYSTEM IN A MODERN TROPICAL LAGOON: DISCOVERY BAY, JAMAICA

CHAPTER I

INTRODUCTION

The chemistry of the carbon dioxide in natural marine waters has been investigated from a geological standpoint in order to better understand the role of dissolved carbon dioxide in reactions of carbonate minerals. Dissolved carbon dioxide also plays a critical role in many geologically significant processes such as pH buffering of natural waters, particularly seawater; it is also essential in many weathering reactions, including those which may be responsible for the "steady-state" composition of the sea (Garrels and Christ, 1965).

On a local scale, the sources of carbon dioxide in natural marine waters include organic respiration, aerobic decay of organic wastes, transfer of gas from the atmosphere, invasion of meteoric waters, and calcium

carbonate dissolution. Quantification of carbon dioxide fluxes between these interrelated sources provides the information necessary to document the carbon budget for the backreef lagoonal waters of Discovery Bay. Thus, perhaps the most challenging aspect of this research is to differentiate the CO2 sources and to quantify their affects on the carbon budget.

This paper addresses the problem of material-balance of the inorganic carbon within Discovery Bay, a modern tropical lagoon on the north coast of Jamaica. The conclusions reached regarding material-balances are based largely on chemical analyses which determine ionic compositions of the lagoon waters. Diurnal studies of several parameters of water samples provide information regarding rates of photosynthesis-respiration and precipitation-dissolution for the entire bay area. The parameters analyzed include pH and total alkalinity as master variables (Smith, 1973). Temperature, chloride activity, calcium activity, and magnesium activity are additional parameters which provide information regarding equilibria of carbonate minerals. Oxygen concentration is used to estimate changes in CO2 chemistry resulting from biomass metabolism.

The diurnal variations in pH, dissolved CO2, and carbonate saturation of natural marine waters have been documented by numerous authors (Smith, 1973; Schmalz and Swanson, 1969; Revelle and Emery, 1957). Conventional

wisdom suggests these diurnal cycles to be the result of changing rates of the opposing reactions, respiration and photosynthesis. Nonetheless, the complexities of Discovery Bay, including freshwater invasion of CO2-charged meteoric waters and high rates of CO2 evasion, mask the expected diurnal variations of the backreef lagoon.

CHAPTER II

GEOLOGIC SETTING

The island of Jamaica is located in the northwestern region of the Caribbean Sea. The major axis of the island is situated N70W, and it is roughly 230 kilometers in length and 90 kilometers in width, making Jamaica the third largest island in the Caribbean. Although the southern extension of Cuba lies only 150 kilometers to the north, Jamaica is separated from that island by the Cayman Trench which reaches depths of more than 7000 meters below sealevel. The western extension of Haiti lies some 200 kilometers to the east.

Jamaica displays a rugged topography on its eastern seaboard. Dominated by the Blue Mountains, which rise over 2000 meters, this region, or block, is the most mountainous of the island. The central and western regions barely reach 900 meters above sealevel and suggest a history of faulting and erosion. The dominant surface rock type of these regions is limestone within which a labyrinthine system of sinkholes, caves, and underground conduits exist as a result

of water drainage (Zans, 1951). For a more detailed explanation of the geologic history of Jamaica and an understanding of its evolution since the Cretaceous, Horsfield and Roobel (1974) and Malfiat and Dinkelman (1972) are recommended.

The coastlines of northern and southern Jamaica also differ. The southern coastline is marked by coastal plains composed of alluvial sands, gravels and loams. Patch reefs are the dominant reef structures and can extend several miles from shore. The northern coast, however, has a narrow shelf dominated by fringing reefs. These fringing reefs are often separated from the island by backreef lagoons (Woodley and Robinson, 1977).

The samples for this study were gathered from Discovery Bay, which is located on the north coast of Jamaica (Fig. 1). Approximately 55 kilometers east of Montego Bay, Discovery Bay is a circular body of water covering about 1.25 square kilometers and coning to 53 meters in depth (Fig. 2). Originally named Porto Seco by Christopher Columbus for its lack of running water, the bay is separated from the sea by fringing reefs. Owing to the convenience of Discovery Bay's marine laboratory and the considerable previous interdisciplinary studies performed at the bay, Discovery Bay provides an excellent location to study the chemistry of carbon dioxide as it applies to modern carbonate geology.

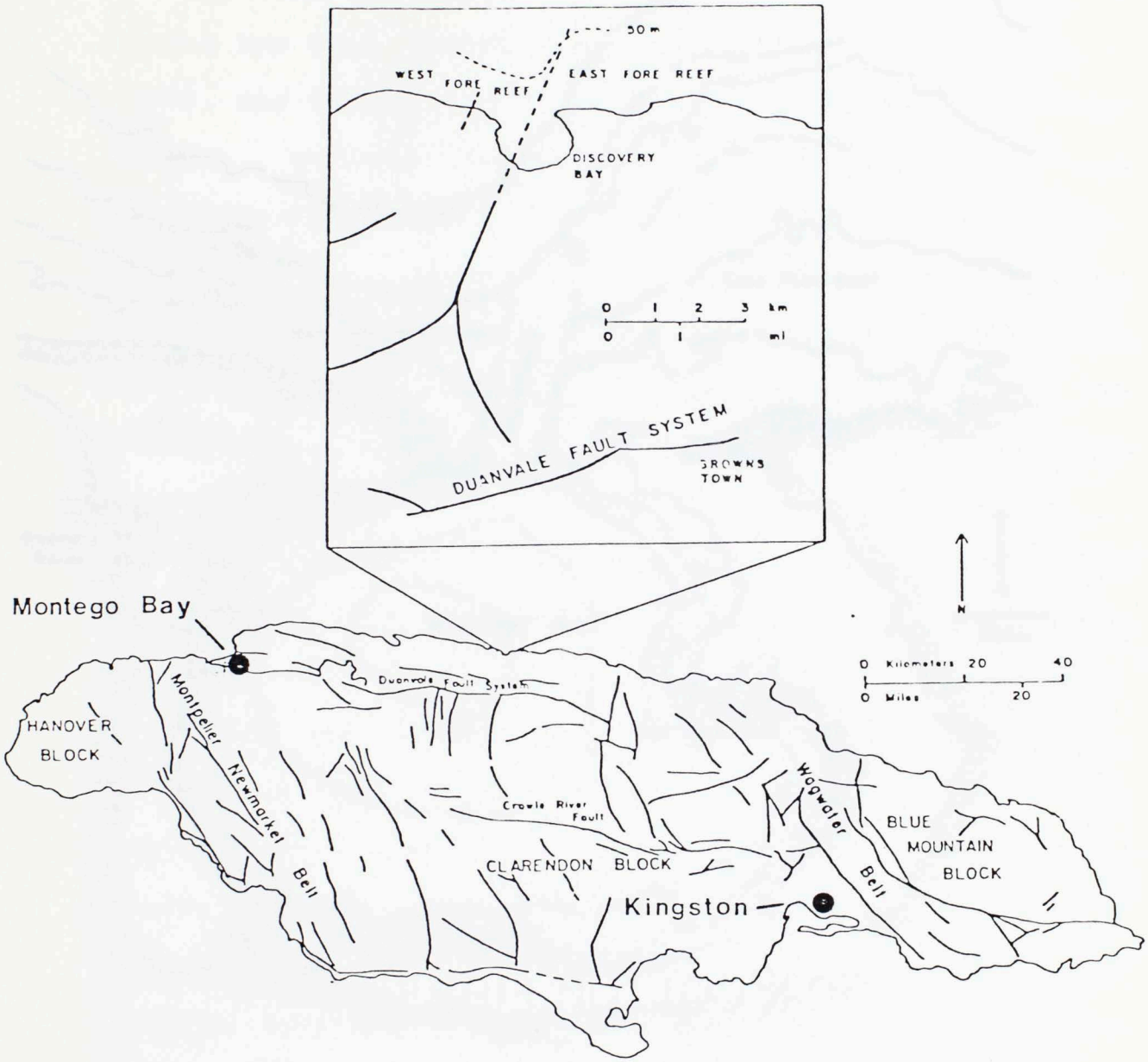


Figure 1: Structural map of Jamaica (from Wright, 1974). Inset shows location and faults of the Discovery Bay area. Dashed lines are inferred offshore traces of faults, including one separating the East and West Fore Reef areas.

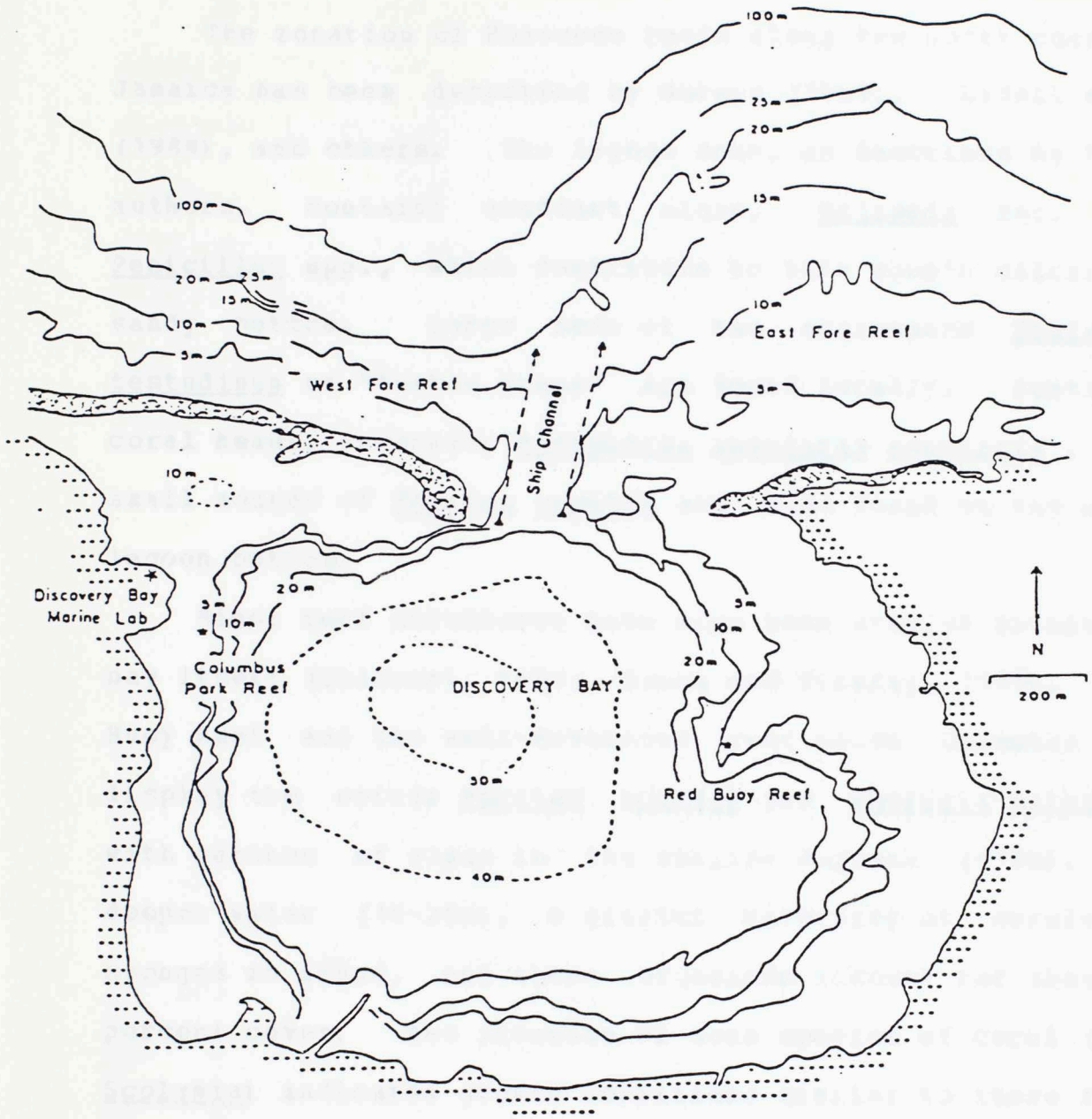


Figure 2: Bathymetry map of Discovery Bay (from Lidell, Ohlhorst, and Coates, 1984).

The zonation of Holocene reefs along the north coast of Jamaica has been described by Goreau (1959), Lidell et al (1984), and others. The lagoon zone, as described by these authors, contains abundant algae, Halimeda spp. and Penicillus spp., which contribute to this zone's calcareous sandy bottom. Large beds of the angiosperm Thalassia testudinum or "turtle grass" are found locally. Scattered coral heads, generally Montastrea annularis annularis , and small mounds of Porites porites are also found on the sandy lagoon bottom.

Minor reef structures have also been studied within the bay itself (Ohlhorst, 1980; Bonem and Stanley, 1977). Red Buoy Reef and the well-developed reef below Columbus Park display the corals Porites porites and Madracis mirabilis with patches of algae in the shallow regions (<10m). In deeper water (10-20m), a greater diversity of corals and sponges is found, and these organisms account for about 32 percent cover. The presence of some species of coral (e.g. Scolymia) indicates growth conditions similar to those found in the forereef, but at much greater depths.

The deepest regions, located in the center of Discovery Bay, are covered with fine carbonate sediments and are barren of biota. Although the shallower regions of Discovery Bay are subject to moderate wave energies during high winds, these basinal areas are sheltered and provide a sink for the finer grained sediments.

Physical and chemical parameters measured in previous studies (Ohlhorst, 1980; Jackson, 1972) have included seasonal temperatures, salinities, and oxygen saturations (Fig. 3). Studies regarding the influence of light, sediment, waves, and storms have been predominantly focussed toward learning more about the reef structures which protect the lagoon from the adjacent seawater (Goreau and Goreau, 1959; Woodley et al., 1981).

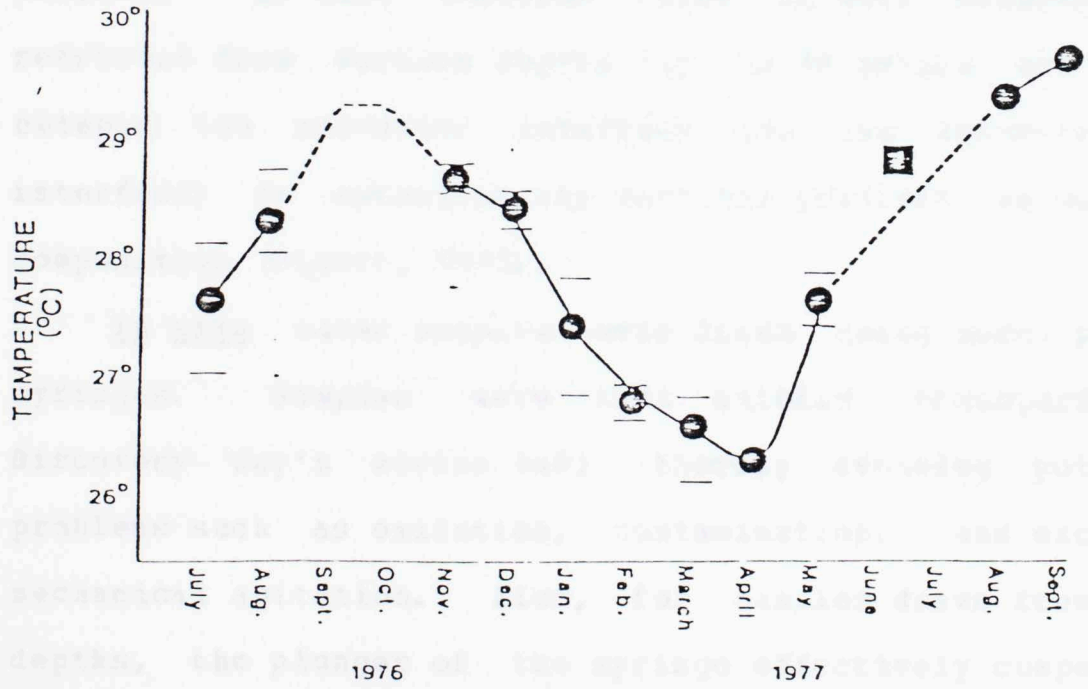


Figure 3: Monthly variation in water temperature at Discovery Bay (from Ohlhorst, 1980).

CHAPTER III

METHODS AND PROCEDURES

Procedure

In order to document lateral variations in the water chemistry of Discovery Bay, water samples were gathered from six locations across the bay during two separate sampling periods. At each location three or more samples were retrieved from various depths (up to 18 meters and spaced between the air-water interface and the water-sediment interface) to establish any vertical gradient in chemical composition (Pigott, 1977).

In situ water samples were drawn using 50cc plastic syringes. Samples were then quickly transported to Discovery Bay's marine lab, thereby avoiding potential problems such as oxidation, contamination, and excessive mechanical agitation. Also, for samples drawn from great depths, the plunger of the syringe effectively compensated for ambient pressure changes when surfacing. All possible precautions were taken not to disturb the waters during

retrieval.

Immediately upon returning to the marine lab (as short as ten minutes but no longer than forty minutes after the first samples were collected), samples of approximately 15 ml were forced from the syringes into a beaker, stirred with a magnetic stirrer, and analyzed for pH, O2, and temperature. The calibration of these instruments is discussed in Appendix A and was performed prior to each sample retrieval time.

The two separate episodes of sample retrieval were performed from 11:30 am, June 17, 1983 to 9:40 pm the following day and from 3:30 pm, June 29, 1983 to 3:00 pm the following day. Samples from the three locations in the western region of the bay were collected June 17 (Fig. 4) while eastern region samples were collected June 29.

After measurements were completed, 35 mls of the remaining sample waters were bottled and capped with parafilm to prevent unnecessary contamination. Samples were then frozen until after returning to Oklahoma where analyses for chloride, calcium, magnesium, and alkalinity were performed.

Methods

In order for chemical analyses of samples from

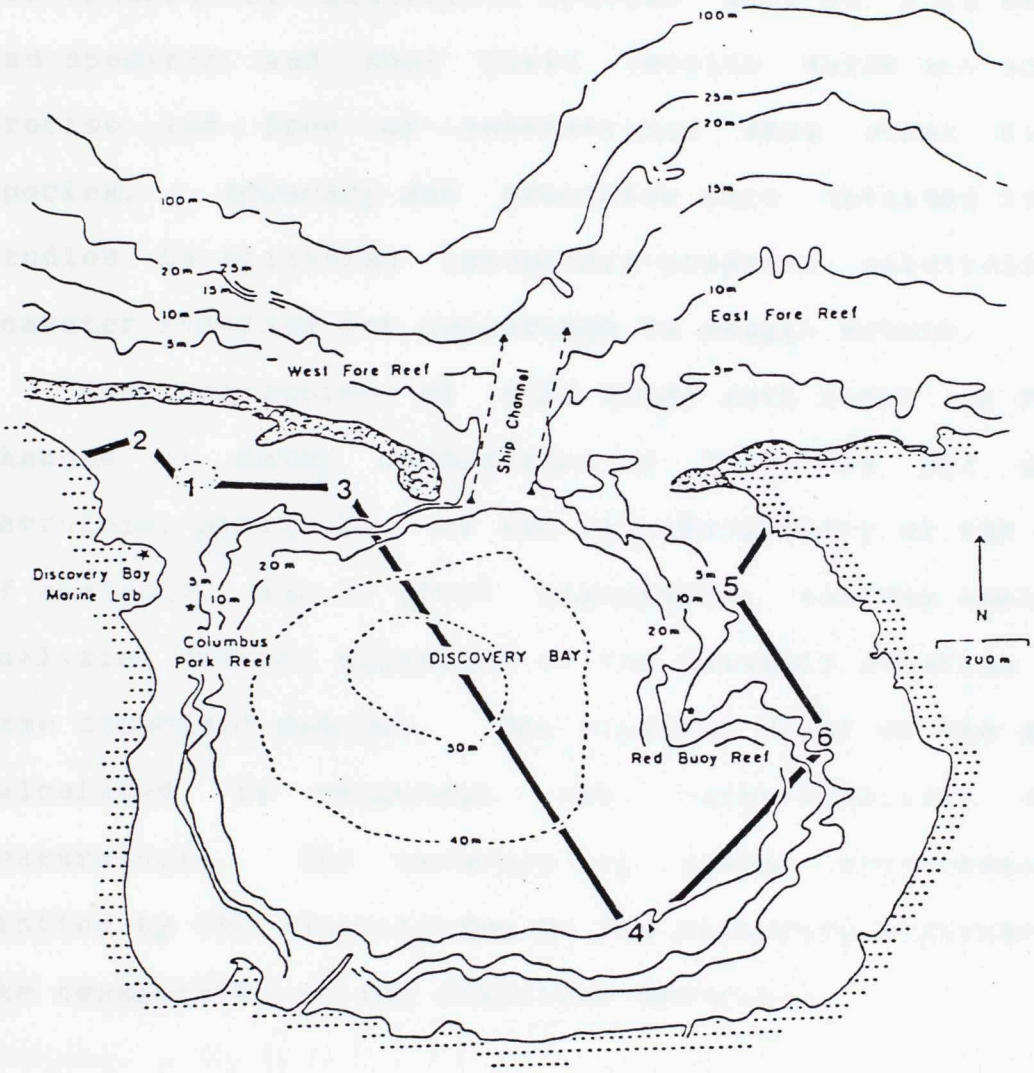


Figure 4: The six sampling locations for bay water chemistries. Heavy line represents cross-section line for profiles (see Figs. 14 - 29).

Discovery Bay to be representative of *in situ* waters, measurements of individual species must be both sensitive and specific and must yield results which are accurate, precise and free of interference from other dissolved species. Accuracy and precision were obtained in these studies by utilizing laboratory-prepared solutions and a seawater standard for comparison to sample waters.

Many conclusions of this study were based on relative changes in water chemistries of Discovery Bay samples. Therefore, precision, or the reproducibility of the results of analysis, was of great importance, and was enhanced by analyzing several aliquotes of the standard solution for the same dissolved species. The standard error of the mean was calculated to represent the reproducibility of the measurement. The accuracy of sample measurements was limited by the capabilities of the measuring instruments and the sensitivity of ion selective membranes.

Analyses Performed in Jamaica

Set-Up

Speed and accuracy were required for measurements performed in Jamaica's Discovery Bay Marine Laboratory. Combining the Corning pH/Temp Meter 4 and the Fisher Accumet

Electrode Switch provided the versatility to make the necessary measurements on a single sample within 15 minutes; thus, measurements of the 10-11 samples from each retrieval were completed before the next retrieval. The results are recorded in Appendix B.

pH

A Ross R combination pH sensitive electrode was calibrated with Fisher buffers of pH 10.4 and pH 6.86 before analyses began. The temperatures of the samples and buffer solutions were within 2 degrees Celsius of each other. All samples equilibrated with the electrodes within ten seconds. The absolute accuracy was determined to be 0.01 pH units.

Oxygen

Calibration of the Orion R oxygen electrode was made assuming a barometric pressure of 1 atmosphere. Corrections for salinity variations were determined according to Orion (model 97-08). As changes in temperature affect both the permeability of the electrode membrane to oxygen and the solubility of oxygen in water, a scheme of thermocompensation is incorporated into the oxygen electrode. The absolute accuracy obtained for oxygen measurements was 3% of the reading.

Temperature

The temperature probe did not require calibration. However, as a result of the high lab temperatures, some samples may have been affected while waiting to be measured. Over the first thirty minute period of measuring, the samples measured between 1200 and 1500 hours may have warmed up by as much as 2 degrees Celsius. These sample temperatures were assumed to have increased linearly with time and were corrected by monitoring the first sample again, noting the change which had occurred over time. The precision of temperature is 0.1 degree Celsius.

Analyses Performed at The University of Oklahoma

Set-Up

Conservative properties of seawater which were of interest in this study were analyzed at the University of Oklahoma. The dissolved species investigated were calcium, magnesium, chloride, and the carbonate species, carbonate ion and bicarbonate ion. Two different set-ups were used to facilitate the necessary measurements. In contrast to the Jamaican analyses, speed was not as important during either of the two set-ups, more emphasis was directed toward absolute accuracy. The results are recorded in Appendix B.

The first phase of measurements was similar to the

analyses performed in Jamaica (i.e., measurements of dissolved ionic constituents by potentiometric analysis). The Fisher R Accumet Model 750 Selective Ion Analyzer was used in conjunction with a multiple Electrode Switch mentioned reading to the nearest millivolt. Thawed samples of approximately 15 ml were stirred with a magnetic stirrer and analyzed while the remaining sample was again frozen and stored until the second phase of measurements.

The second phase of measurements performed at The University of Oklahoma was arranged for the determination of total alkalinity. For this a Ross R combination pH electrode together with the Fisher R Titrimeter II Titration System, a Hewlett Packard R HP-97S calculator, the Fisher R Balance/Calculator Interface Kit, and the Houston Instrument R Series B-5000 Omniscribe Recorder were used for automated titrations.

Calcium, Magnesium, and Chloride

The standard used for comparison in potentiometric titrations was an "average" seawater collected from the open Jamaican sea area. For this water, several aliquotes were titrated for determination of chloride, calcium, and magnesium ionic concentrations. Concentrations were converted to activity using activity coefficients for "average" seawater. The procedure followed the standard

methods of potentiometric titration proscribed by Strickland and Parsons (1968). The results were as follows:

(Cl) = 563.5 mM/l +/- 3 n = 4

(Ca) = 9.805 mM/l +/- 0.5 n = 5

(Mg) = 55.08 mM/l +/- 1.6 n = 5

Laboratory-prepared solutions of CaCl2 and KCl were used for the calibration of the calcium/magnesium and chloride electrodes, respectively. Three solutions were used for each of the three electrodes for an accurate determination of the Nernstian response (see Appendix A). Using the above results of "average" seawater as standards, samples were measured. Electrodes were recalibrated with the standard every 15 samples. Such precautions minimized errors due to the inherent drift in the electrodes.

Variations in ambient laboratory temperatures also caused disturbances in potentiometric measurements. The dependency of electrode response on temperature variations was determined and the results are shown in Figure 5. Potentiometric measurements were Nernstian corrected so that all measurements were consistent with lab temperatures of 25 degrees Celsius. The absolute error for the Cl, Ca, and Mg potentiometric measurements were 0.58%, 4.4%, and 2.9% of these measured activities, respectively.

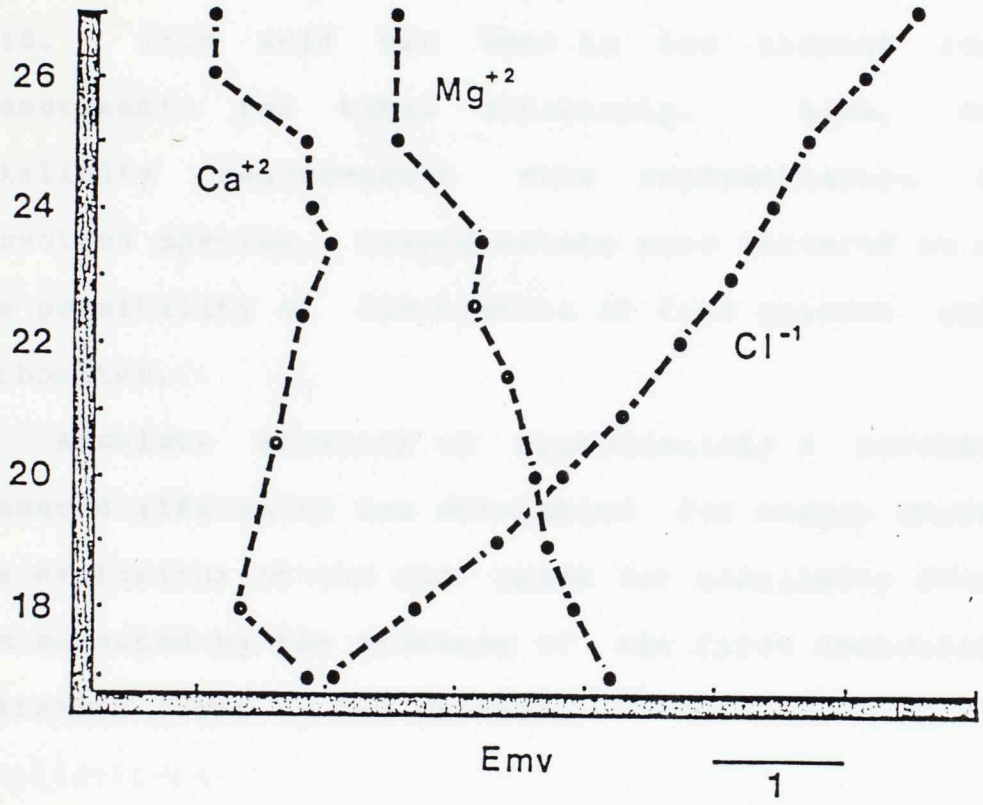


Figure 5: Calcium, magnesium, and chloride electrode responses to sample temperature variations. Used for correcting errors in potentiometric analyses due to lab temperature variations.

Alkalinity

In preparation of alkalinity measurements, a measured solution of sodium hydroxide (NaOH) was titrated with hydrochloric acid (HCl) to determine the normality of the acid. This acid was used as the titrant for sample measurements for total alkalinity. Also, to ensure alkalinity measurements were representative of only dissolved species, sample waters were filtered to eliminate the possibility of dissolution of fine grained solid phase carbonates.

Absolute accuracy of approximately 3 percent of the measured alkalinity was determined for sample measurements. The evaluation of the end point for alkalinity measurements was enhanced by the plotting of the first derivative of the titration curve by the plotter.

CHAPTER IV

CARBONATE CHEMISTRY

Introduction

If the system of CO_2-H_2O-metal carbonate were simplified so as to contain a single mineral, and if the solubility of that mineral varied with only pressure and temperature, then the chemical problems encountered in dealing with the carbonate environment would be few. Instead, the natural environment presents numerous complications. In order to better understand the processes that culminate in the synthesis of a carbonate environment, the dynamics of the simple system, CO_2-pure H_2O-calcite must be understood.

The interaction between water, CO_2, and calcite can be appropriately described by

$$H_2O + CO_2 + CaCO_3 \rightleftharpoons Ca^{+2} + 2HCO_3^{-}. \qquad \text{eq. 1}$$

When the equilibrium of this equation moves to the right, as in a forward reaction, the dissolution of both CO_2 and $CaCO_3$

occurs. The reverse reaction requires precipitation of CaCO3 and CO2 removal. The effects of naturally occurring phenomena on such a simplified system can then be illustrated. The phenomenon of dilution is an addition of H2O which drives the equilibrium to the right; evaporation is a subtraction of water which drives the equilibrium to the left. Thus, we associate dilution and evaporation to dissolution and precipitation, respectively. Another naturally occurring phenomenon important to this environment is biogenic productivity. Photosynthesis of aquatic plants removes CO2 from the system and shifts equilibrium to the left. Carbon dioxide removal during photosynthesis should be accompanied by the precipitation of carbonate minerals. On the other hand, respiration should accompany dissolution.

Numerous authors have evaluated the complexities of the natural environment relative to the simple system described above. Bathurst (1975), Berner (1971), Berner and Morse (1974), Berner and Wilde (1972) each contributed a thorough review of carbonate chemistries in natural and ideal settings, and although not everything is understood regarding carbonate chemistries, empirical relationships between these two settings have been determined by Edmond and Gieskes (1970). These empirical relationships represent the state of equilibrium of equation 1 as it varies with the temperature, pressure, and chlorinity of the natural environment.

Dissolved carbon dioxide dissociates by the series of reactions:

$$CO2 + H2O \rightleftharpoons H^+ + HCO3^- \rightleftharpoons 2H^+ + CO3^{-2} \quad \text{eq. 2}$$

to produce hydrogen, bicarbonate, and carbonate ions. Because the ionization reactions equilibrate very rapidly (Kern, 1960), changes in the activity of dissolved carbon dioxide are reflected almost immediately by changes in pH, even in well-buffered solutions such as seawater.

Parameters Governing Aquatic Chemistry

Chlorinity

Chlorinity measurements on the sample waters of Discovery Bay were used primarily for the determination of the solution ionic strengths, and subsequently the activity coefficients of the carbonate species as they varied. The activity of chloride was the actual measured parameter and chlorinity was determined by converting these activities to concentration (indicated by "()"), molality, and then to chlorinity. Activity coefficients of chloride ion were determined from the experiments of Neese (personal communication, 1983) for different ionic strengths, and seawater densities were calculated assuming consistent

temperatures of 30 degrees Celsius (from Riley and Skirrow, p. 103). The empirical relationship between $\{Cl^-\}$ and Cl‰ ascribed from these precedents is:

$$Cl‰ = (62.3)\ \{Cl^-\}^{1.11}. \qquad \text{eq. 3}$$

Edmond and Gieskes (1970) related ionic strength to chlorinity:

$$I = 0.00147 + 0.03592 \times Cl‰ + 0.000068 \times Cl‰^2. \qquad \text{eq. 4}$$

Both Ionic strength (I) and chlorinity are used for determination of apparent dissociation constants of carbonate and borate species

Chlorinity also provides information concerning the total concentration of boron (boron is assumed constant for a constant chlorinity; Culkin, 1965). This relationship is suggested to be:

$$Bsum = 2.1 \times 10^{-4} \times Cl‰. \qquad \text{eq. 5}$$

Boron concentration will be required for the calculation of borate alkalinity.

Aside from the geochemical necessities of chlorinity measurements, chlorinity measurements also provide insight into the hydrodynamic events (e.g., fresh-water mixing) occurring within Discovery Bay.

Temperature and pressure are physical parameters which also govern the thermodynamic properties of seawater. Both

are used in the calculations of dissociation constants, although for such shallow waters, temperature is the more important variable.

Alkalinity and Carbonate Speciation

Carbonate alkalinity is defined as:

$$Alkc = 2(CO_3^{=}) + (HCO_3^{-}) \qquad \text{eq. 6}$$

and is calculated from measurements of total alkalinity, pH, temperature, and chlorinity using apparent dissociation constants empirically derived by the work of Edmond and Gieskes (1970):

$$Alkc = Alkt - Bsum/((H/K'B) + 1) \qquad \text{eq. 7}$$

where Alkt = total alkalinity;
= carbonate + borate alkalinities;
Bsum = total boron concentration;
H = hydrogen activity;
and K'B = apparent borate acidity constant.

Carbonate speciation is determined using the apparent acidity constants of the respective carbonate species, the pH, and the carbonate alkalinity:

$$(CO3^{=}) = Alkc/((H^{+}/K'2) + 2); \quad \text{eq. 8}$$

$$(HCO3^{-}) = Alkc - 2\,(CO3^{=}); \quad \text{eq. 9}$$

$$(H2CO3^{*}) = H^{+}(HCO3^{-})/K'1; \quad \text{eq. 10}$$

$$= (H2CO3) + (CO2d). \quad \text{eq. 11}$$

By definition, the total CO2 (CO2) can be determined by adding the concentrations of the above carbonate species.

Another measurement common in literature regarding aqueous CO2 is the partial pressure of CO2 (pCO2). pCO2 is related to H2CO3* by Henry's Law:

$$K'H = \{H2CO3^{*}\}/pCO2. \quad \text{eq. 12}$$

The solubility constant of CO2 is also reviewed by Edmond and Gieskes (1970).

Activity Coefficients of Carbonate Species

As stated previously, potentiometric analysis with ion-selective electrodes eliminates the need for calculation of activity coefficients which relate concentrations to activities. Thus, the direct measurements of calcium and magnesium ion activities were performed. However, the activities of carbonate species cannot be directly measured at present and must be derived from alkalinity measurements which are expressed as concentrations. It is therefore necessary to derive the activity coefficients of the

carbonate species as they may vary from each sample.

Edmond and Gieskes (1970) empirically evaluated the dependence of apparent carbonate dissociation constants on temperature, chlorinity, and pressure. The first and second acidity constants are defined by:

$$K1 = \{H^+\}\{HCO3^-\}/\{H2CO3^*\}, \qquad \text{eq. 13}$$

$$K'1 = \{H^+\}(HCO3^-)/(H2CO3^*), \qquad \text{eq. 14}$$

$$K2 = \{H^+\}\{CO3^=\}/\{HCO3^-\}, \qquad \text{eq. 15}$$

$$\text{and } K'2 = \{H^+\}(CO3^=)/(HCO3^-). \qquad \text{eq. 16}$$

Activity is defined as the product of concentration and the activity coefficient so that $\{i\} = \gamma(i)$. Therefore, from:

$$\frac{K1}{K'1} = \frac{\{H^+\}\{HCO3^-\}(H2CO3^*)}{\{H^+\}(HCO3^-)\{H2CO3^*\}} = \frac{\gamma HCO3^-}{\gamma H2CO3^*} \qquad \text{eq. 17}$$

$$\frac{K2}{K'2} = \frac{\{H^+\}\{CO3^=\}(HCO3^-)}{\{H^+\}(CO3^=)\{HCO3^-\}} = \frac{\gamma CO3^=}{\gamma HCO3^-} \qquad \text{eq. 18}$$

$$\frac{K1\ K2}{K'1\ K'2} = \frac{\gamma HCO3^-\ \gamma CO3^=}{\gamma H2CO3^*\ \gamma HCO3^-} = \frac{\gamma CO3^=}{\gamma H2CO3^*} \qquad \text{eq. 19}$$

the activity coefficient of carbonate ion is derived:

$$\gamma CO3 = (K1/K'1)(K2/K'2)(H2CO3^*). \qquad \text{eq. 20}$$

In this way, the data of Edmond and Gieskes can be used to express relative changes in activity coefficients of the carbonate ionic species with respect to temperature, chlorinity, and pressure. From one activity coefficient the others may be determined.

Randall and Failey (1927) and later Markam and Kobe (1941) derived empirical equations which represent the solubility of carbon dioxide in various salt solutions over wide ranges of concentration and temperature. The activity coefficient is defined as:

$$\gamma = \frac{b - a - abm}{1 + bm} \qquad \text{eq. 21}$$

where a and b are empirical constants dependent upon the particular solute present, and m is the molality of that solute. Using their data activity coefficients for dissolved carbon dioxide.

For these salt solutions, ionic strength equals the molality of the solute. The ionic strengths of seawater samples can be approximated from chlorinity. Substituting these ionic strengths for molality, the activity coefficients of dissolved CO2 may be determined for each

Values of a and b in Equation 21 for CO2

Soln.	Temp,°C	a	b	CO2
NaCl	0.2	-0.0181	0.285	1.29
"	25	-0.0134	0.229	1.23
"	40	-0.0113	0.217	1.22
KCl	0.2	0.0207	0.216	1.18
"	25	0.0201	0.168	1.14
"	40	0.0380	0.190	1.14

Table 1: Values of a and b in equation 21 for solutions of sodium and potassium chloride at varying temperatures (from Markam and Kobe, 1941).

sample. For example, for normal seawater (I = 0.724) in a solution of KCl at 25 °C, the calculated activity coefficient of CO2 is 1.10. Calculations in this thesis for the activity coefficient of carbonate use CO2 derived from KCl because it is the basis for the mean salt method. Deviations from 25 C +/- 7 °C change these activity coefficients less than 1%.

For a chlorinity of 19.37‰ , this method calculates a $\gamma CO3$ of 0.02. Direct calculation using the mean-salt equation (Garrels and Christ, 1965), the Davies equation (Stumm and Morgan, 1981), and the extended Debye-Huckel equation (Stumm and Morgan, 1981), yield, instead, values of 0.20, 0.31, and 0.19, respectively. Note that the activity coefficients calculated from these equations appear to differ by approximately one order of magnitude from those calculated using the acidity constants determined by Edmond and Gieskes (1970). However, the latter value and method is the approach adopted here as it is internally consistent with the disassociation constants, and furthermore, agrees favorably with the 0.021 value determined experimentally by Berner (1971).

Saturation Indices of Carbonate Minerals

Previous studies (Plummer and Mackenzie, 1974; Thortenson and Plummer, 1977) have investigated the

solubility of magnesium calcites. Assuming congruent dissolution, stoichiometric reactions involving magnesium calcite minerals can be written:

$$Ca_{1-x}\,Mg_x\,CO3\,(s) \;\rightleftharpoons\; (1-x)\,Ca^{+2} + (x)\,Mg^{+2} + CO3^{=} \qquad \text{eq. 22}$$

where x denotes the mole percent magnesium within the solid phase carbonate mineral. The solubility product of the above reaction is defined by

$$K'sp \;=\; \frac{\{Ca^{+2}\}^{|1-x|}\,\{Mg^{+2}\}^{x}\;\;\{CO3^{=}\}}{\{Ca_{1-x}Mg_x\,CO3\}} \qquad \text{eq. 23}$$

Assuming the activity of any solid phase carbonate mineral is unity, the solubility product is the product of the ionic activities which are at stoichiometric equilibrium with that carbonate mineral within the solution. Equilibrium constants were established from kinetic dissolution studies by Plummer and Mackenzie (1974) to represent the solubilities for a spectrum of magnesium calcites.

The saturation state, Ω, defines the product of ionic activities (I.A.P.) of a solution relative to the product of ionic activities at equilibrium (K'sp). Therefore,

$$\Omega \;=\; (I.A.P.)/K'sp. \qquad \text{eq. 24}$$

A saturation state greater than one (supersaturation) implies that the reverse reaction of equation 21 (precipitation) is preferred, while a saturation state less

than one (undersaturation) implies that the forward reaction (dissolution) is preferred.

Saturation states for calcite, aragonite, and magnesium calcites ranging from 2 mole percent to 26.7 mole percent magnesium were calculated for each water sample retrieved from Discovery Bay and are recorded in Appendix C.

Field Observations

The eastern region of the bay displayed more stable chemistries with chlorinity varying 7 parts per thousand between 16‰ and 23‰. Total alkalinities varied 1 meq/l from 1.8 to 2.8. The pH varied 0.15 pH units from 8.15 to 8.30. For comparison, the western region varied in chlorinity 21 ppt (3‰ to 24‰), in alkalinity 2.5 meq/l (0.5 meq/l to 3.0 meq/l), and in pH 0.35 pH units (7.95 to 8.20 pH units). Calcium and magnesium both varied conservatively with respect to chlorinity.

Diurnal variations were observed in the measurements of temperature and oxygen (Figs. 6 and 7). Waters in Discovery Bay attain maximum concentrations of oxygen between 3:00 pm and 6:00 pm and minimum concentrations between 3:00 am and 5:00 am. At these peaks oxygen measurements are generally 0.25 parts per million (ppm) greater in the eastern region

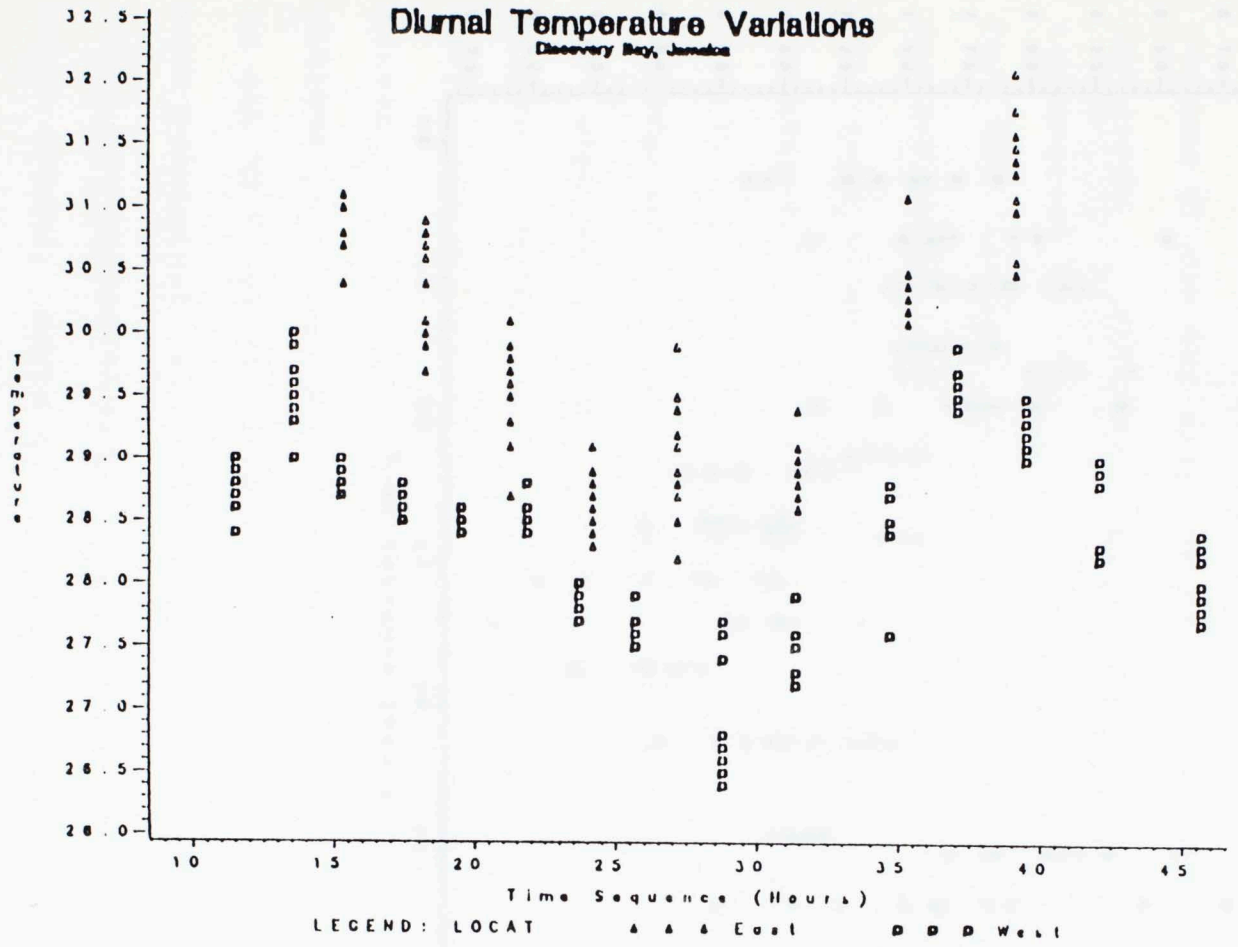


Figure 6: Diurnal variations of temperature. Note the generally cooler temperatures of the west due to the greater influence of groundwater invasion.

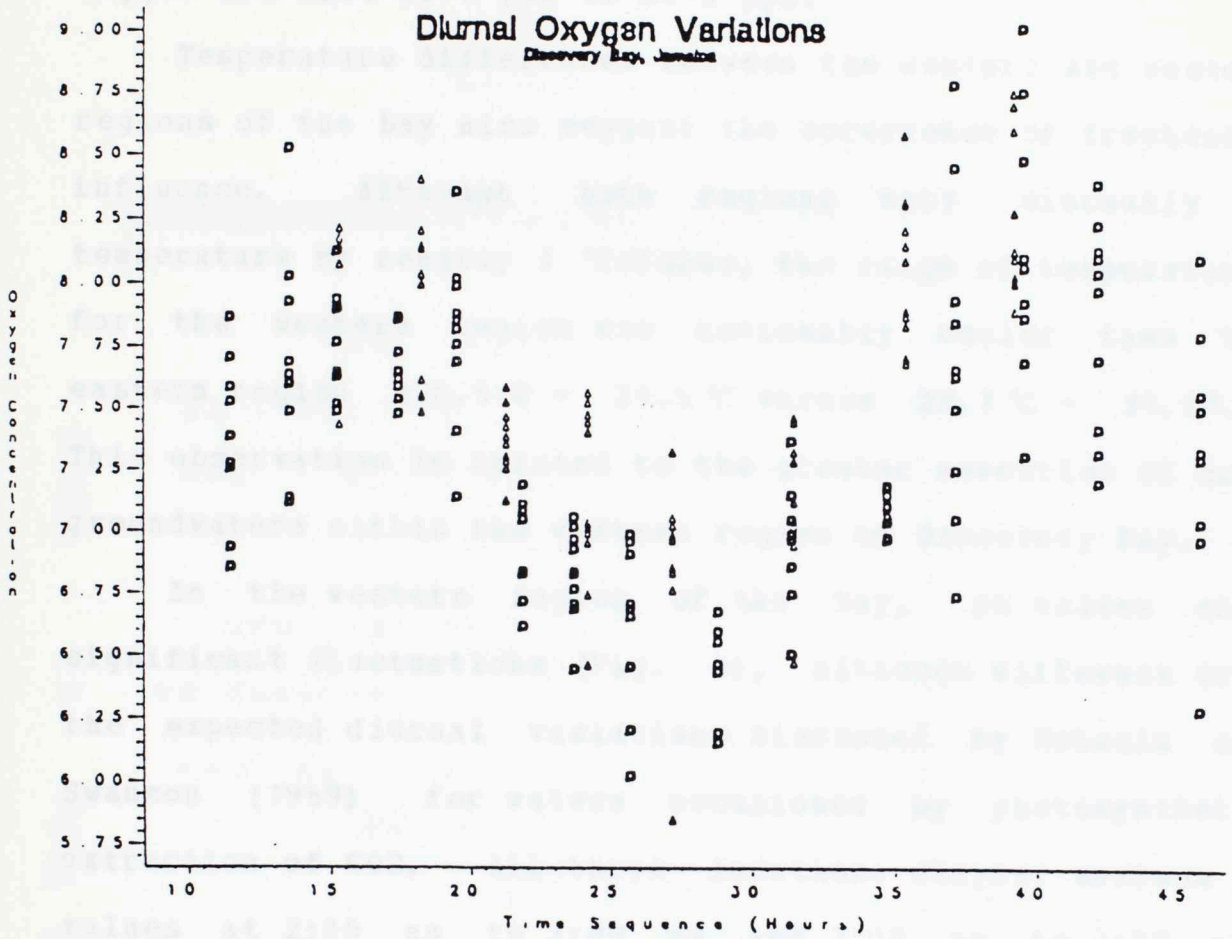


Figure 7: Diurnal variations of oxygen. Note the distinct oscillation resulting from metabolic processes occurring within the bay.

than the western region. Average diurnal variations of oxygen are from 6.75 ppm to 8.15 ppm.

Temperature differences between the eastern and western regions of the bay also suggest the occurrence of freshwater influence. Although both regions vary diurnally in temperature by roughly 3 °Celsius, the range of temperatures for the western region was noticeably cooler than the eastern region (26.5 °C - 29.5 °C versus 28.7 °C - 31.3 °C). This observation is related to the greater advection of cool groundwaters within the western region of Discovery Bay.

In the western region of the bay, pH values show significant fluctuations (Fig. 8), although different from the expected diurnal variations discussed by Schmalz and Swanson (1969) for waters occasioned by photosynthetic extraction of CO2. All three locations display maximum pH values at 2:00 am to 3:00 am and 2:00 pm to 3:00 pm. Minimum pH values were displayed between 10:00 am and 11:00 am and 10:00 pm and 11:00 pm. These observations tend to be more consistent with the findings of Davies (1974), who noted the interesting variation of pH at One Tree Island and Heron Island, where an increase in pH occurred in the night as well as the day. However, comparison of pH and tidal data suggests that pH values of the western region of Discovery Bay are related to tidal incursion (Fig. 8). Owing to a lack of sample density, it is not possible to

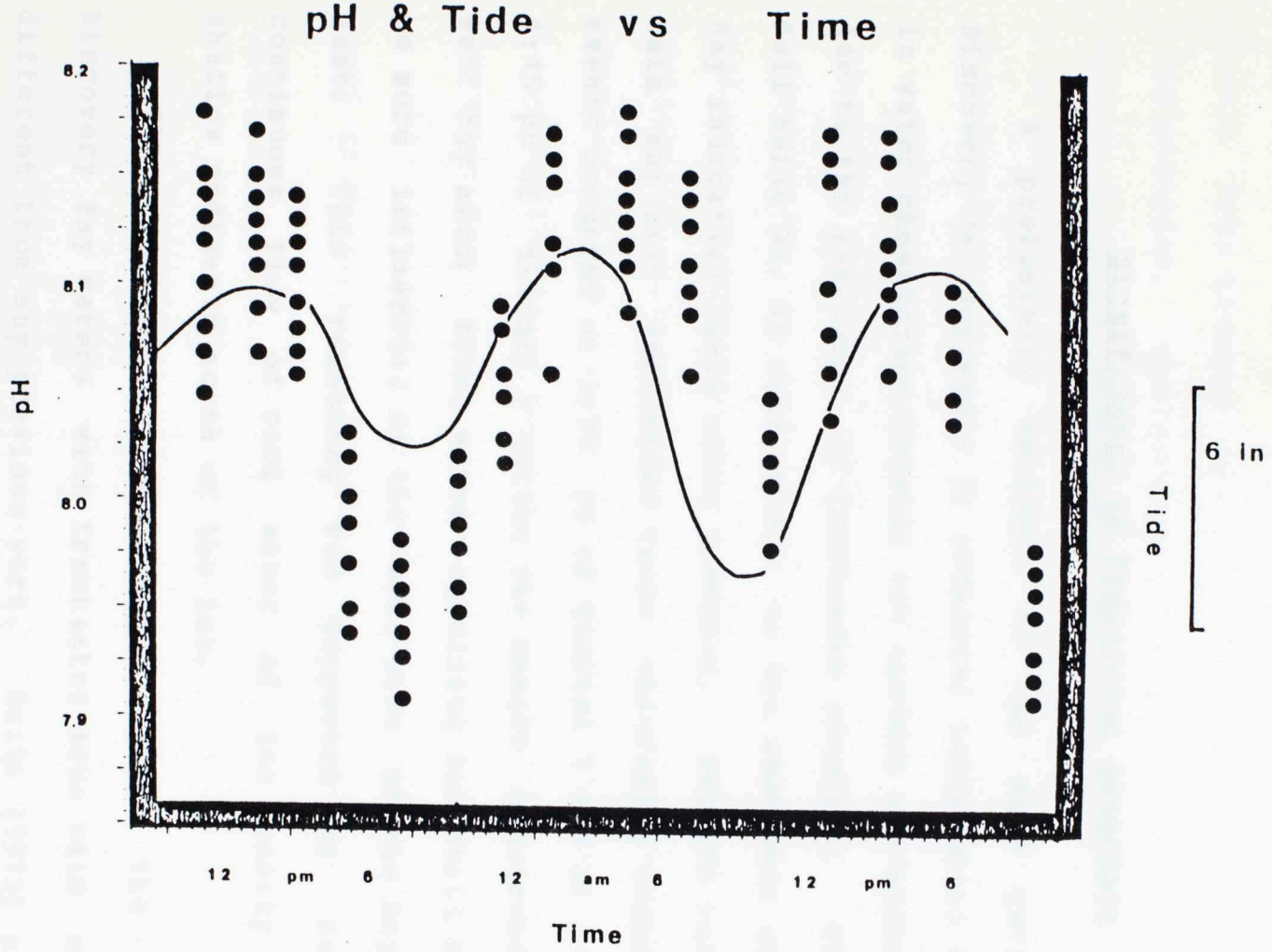


Figure 8: Tidal data and pH variations plotted through time. Groundwater advection rates peak with low tide allowing large quantities of CO2-charged waters to influence bay water chemistries.

constrain fluctuations in pH values on the eastern side of the bay at this time.

Significance of Freshwater Advection

A preliminary analysis of the data gathered from Discovery Bay (Appendix B) indicated substantial differences in water chemistries between the eastern and western regions due to the influence of freshwater invasion. Chlorinities fell below 8‰ in some waters on the west side of Discovery Bay indicating fresh water invasion. Despite the fact that rain may have influenced these chlorinity readings (rain events occurred at 3:30 pm of diurnal 1 and at 1:30 pm and 4:15 pm of diurnal 2 during the sample retrievals from the west bay area) fresh water upwelling was still believed to be more influential on the west side of the bay than the east. This reasoning was supported by an observed continuous flow of cool water of low density from the shallow sediments north of the lab.

The complexities encountered due to the mixing of Discovery Bay waters with freshwater make this study quite different from any previous work. Smith (1973) and Schmalz and Swanson (1969) do not discuss variations in chlorinity, owing to the stability of this variable at their locations. Davies (1974) and Broecker and Takahashi (1966) present

salinities that vary only as a result of evaporation. In order to reveal the small changes in water chemistries which result from biomass activity and carbonate solution and precipitation, corrections must be made for the larger changes in water chemistries (i.e. alkalinity) resulting from the mixing of bay waters with other waters (primarily groundwaters).

Waters that flow into Discovery Bay via a large unconfined aquifer originated from rains occurring in the watershed to the south. These waters pick up additional soil CO2 as they percolate downward and begin to approach equilibrium with the surrounding carbonate rocks (i.e., increase in Alkc) as they flow toward Discovery Bay. Figure 9 schematically represents the hydrologic setting of the Discovery Bay area.

O'Neil (1974) analyzed groundwaters from the north coast of Jamaica for various ionic concentrations in an

	Ca	Mg	Cl	HCO3	pH	T
SW-avg	9.750	55.1	533.1	2.295	8.17	27.2
HG-avg	1.108	0.77	1.177	4.426	7.60	25.9
FM>48	4.053	15.6	149.8	3.406	7.57	29.8
FM<48	2.039	5.48	50.44	2.393	7.75	28.5

*Concentrations are in moles per kilogram.
**Temperatures are in °C. (From O'Neil, 1974)

Table 2: Average observed values for measurements of Hope Gate (HG-avg) , Falmouth (FM>48 and FM<48), and seawater (SW-avg). Average values for Falmouth waters measured less than 48 hours after heavy rainfall are listed separately (FM<48).

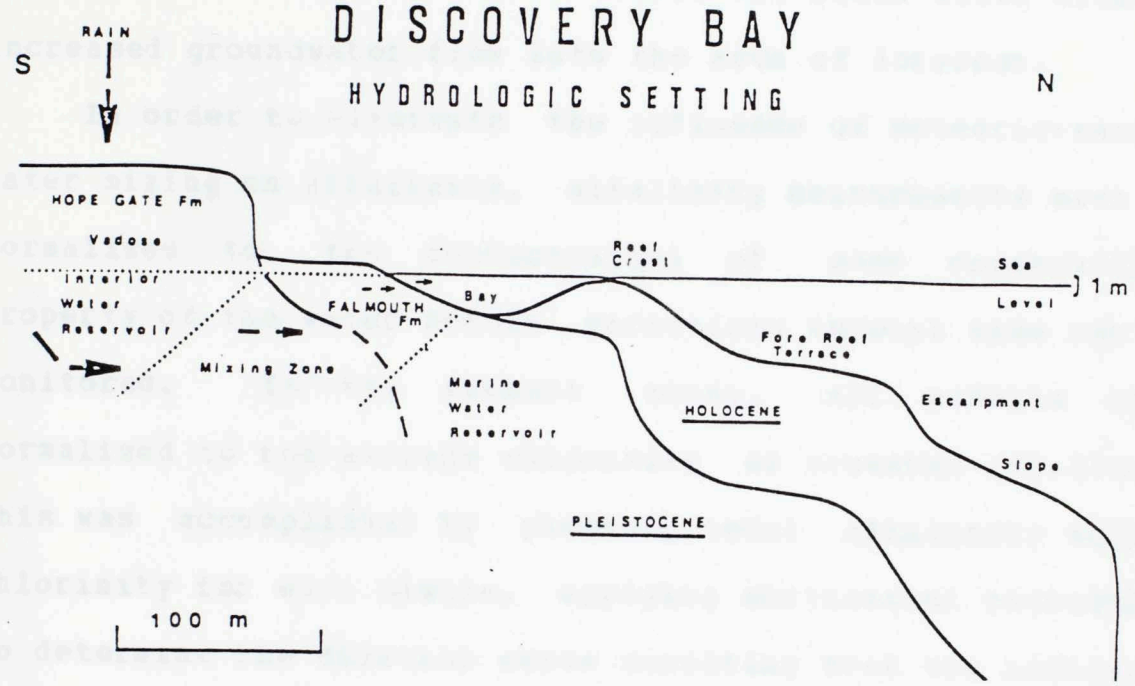


Figure 9: Schematic cross-section depicting the hydrologic setting of Discovery Bay (from O'Neil, 1974).

investigation of the geochemical processes occurring during subsurface mixing of meteoric and marine waters (see Table 2). Fluctuations in water chemistries of O'Neil's study appear to be linked to the intermittent rains which created increased groundwater flow into the area of interest.

In order to eliminate the influence of meteoric-marine water mixing on alkalinity, alkalinity measurements must be normalized to the concentration of some conservative property of the water before variations through time can be monitored. In the present study, all results were normalized to the average chlorinity of seawater (19.37‰). This was accomplished by plotting total alkalinity versus chlorinity for each sample, applying statistical regression to determine the dilution curve resulting from the influence of meteoric waters on bay waters, and correcting algebraically for the observed decrease in alkalinity. This dilution curve (Fig. 10) has a slope which represents a dilution of 35% groundwater. The two data points falling below 4‰ chlorinity and 1 meq/l alkalinity were surface samples affected directly by rainwater. An important assumption for using this method of alkalinity correction is that the invading freshwaters maintain a constant chemistry during the sampling period relative to the associated dilution curve.

As a result of freshwater invasion, pH values were also

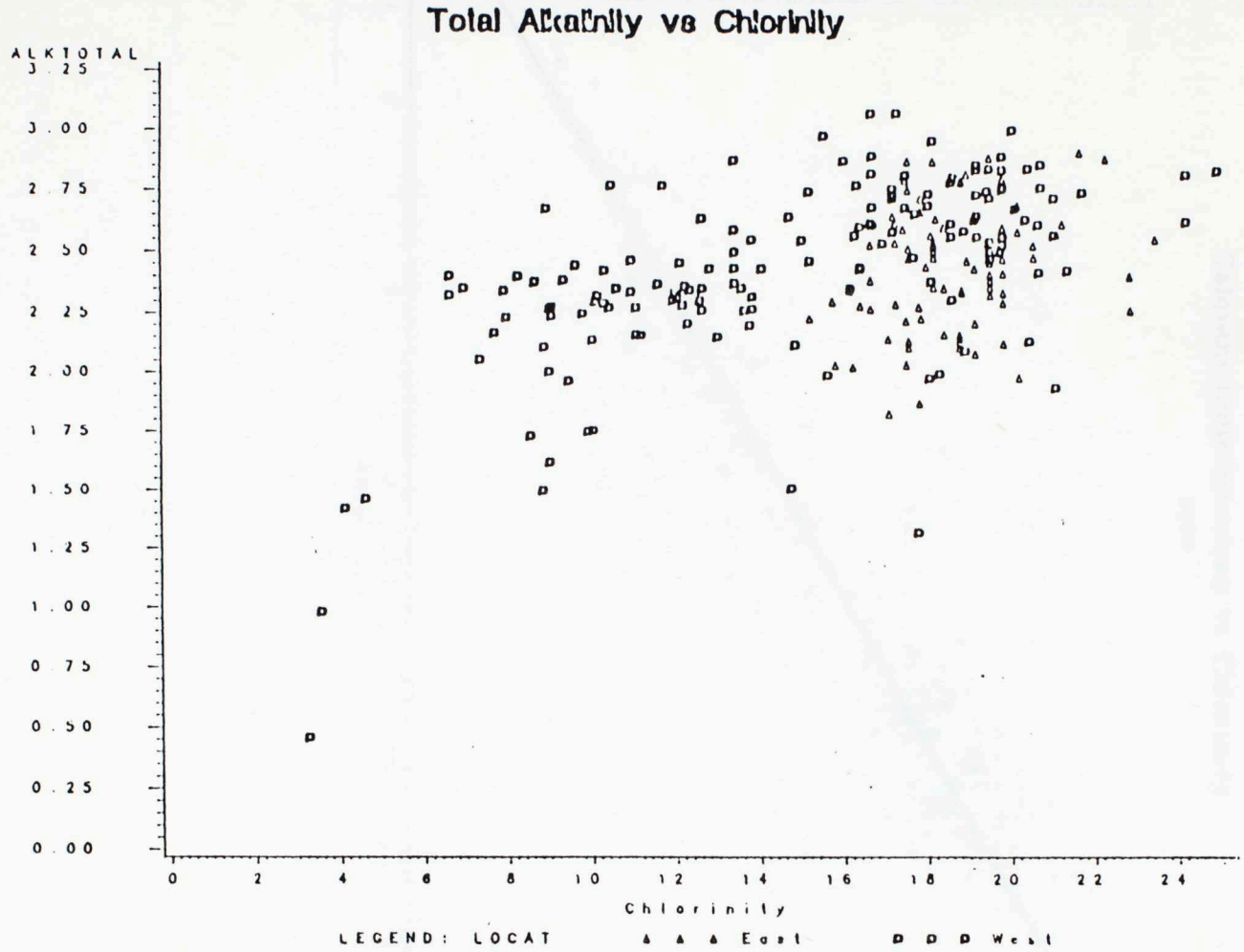


Figure 10: Total alkalinity as a function of chlorinity. Groundwaters appear undersaturated with respect to carbonate reservoir.

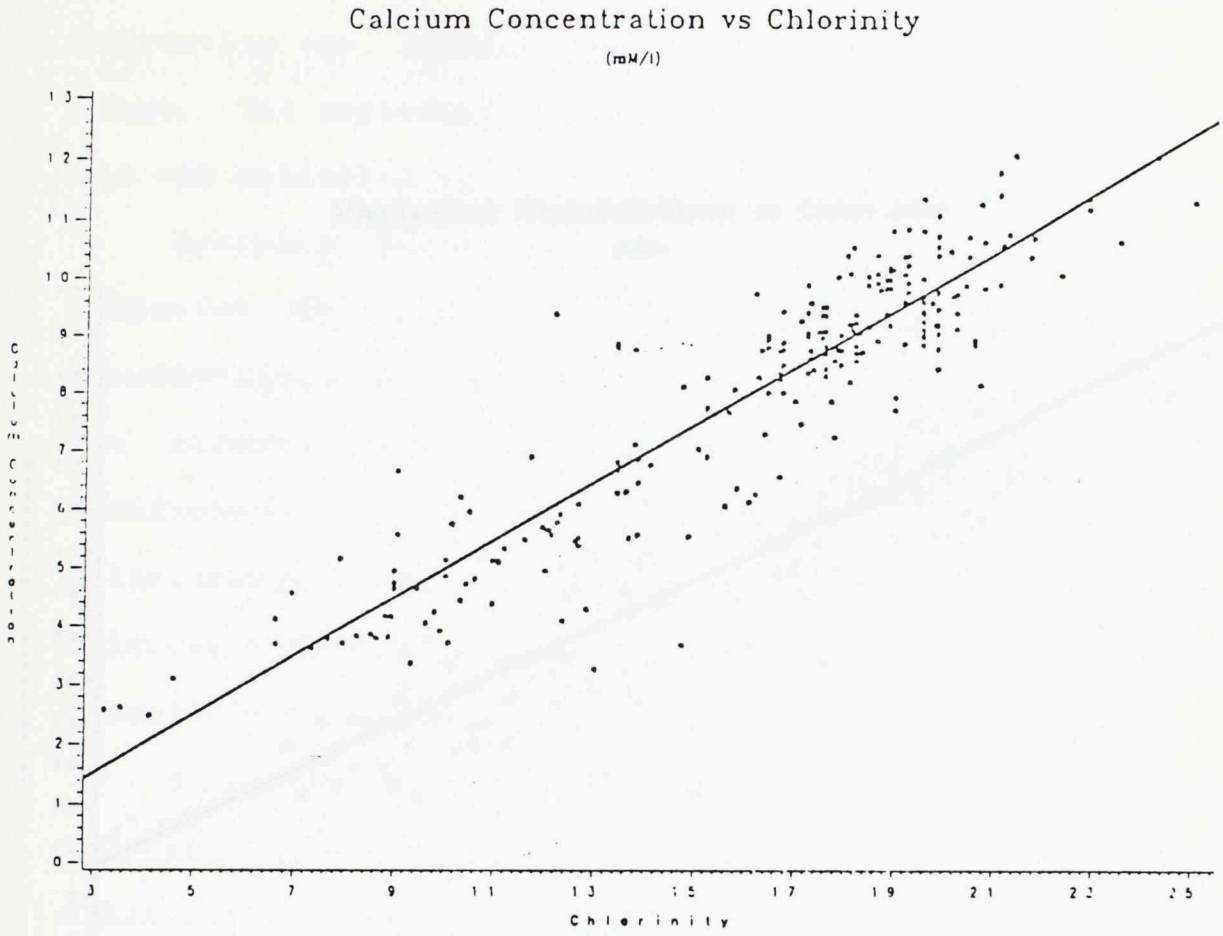


Figure 11: Calcium concentration as a function of chlorinity. A simple dilution.

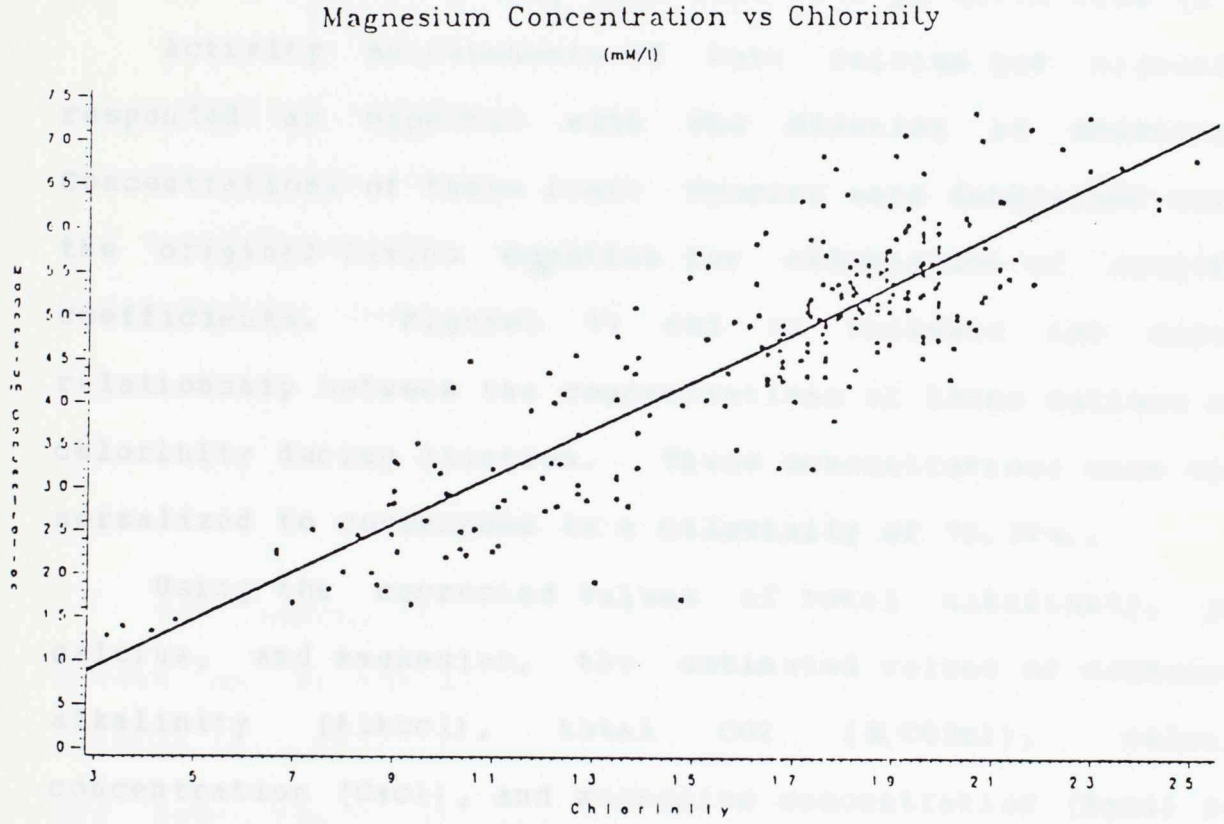


Figure 12: Magnesium concentration as a function of chlorinity. A simple dilution.

slightly lowered, and a slight trend was observed relating pH to chlorinity. This trend was compensated for by correcting the linear regression of $\{H^+\}$ vs Cl‰ to zero slope. The corrected value of $\{H^+\}$ will be abbreviated $\{H^+_{cl}\}$ and was estimated to vary less than 0.15 pH units from $\{H^+\}$.

Activity measurements of both calcium and magnesium responded as expected with the dilution of seawaters. Concentrations of these ionic species were determined using the original Davies equation for calculation of activity coefficients. Figures 11 and 12 indicate the direct relationship between the concentrations of these cations and chlorinity during dilution. These concentrations were also normalized to correspond to a chlorinity of 19.37‰.

Using the corrected values of total alkalinity, pH, calcium, and magnesium, the estimated values of carbonate alkalinity (Alkccl), total CO2 (ΣCO2cl), calcium concentration (Cacl), and magnesium concentration (Mgcl) may be calculated for an environment without an influence of freshwater invasion.

The effects of freshwater invasion on the above parameters is calculated by subtracting these corrected measurements from the original uncorrected measurements. For example, the change in total CO2 attributable to freshwater invasion (ΣCO2fw) during the period t1 to t2 may be calculated:

$$d(\Sigma CO2)/dt = \Sigma CO2/t1 - \Sigma CO2/t2$$

$$d(\Sigma CO2cl)/dt = \Sigma CO2cl/t1 - \Sigma CO2cl/t2$$

$$\text{thus, } d(\Sigma CO2fw)/dt = d(\Sigma CO2)/dt - d(\Sigma CO2cl)/dt. \qquad \text{eq. 25}$$

= change in $\Sigma CO2$ due to freshwater invasion.

where $\Sigma CO2/t1$ and $\Sigma CO2/t2$ are the measured CO_2 values from the same sample location and depth but at different times, and where $\Sigma CO2cl/t1$ and $\Sigma CO2cl/t2$ are the same CO_2 values corrected for freshwater invasion.

Dissolution-Precipitation

The amount of $CaCO_3$ precipitated from Discovery Bay waters can be estimated by comparing the concentration of calcium or alkalinity at one time with the concentration of the same ionic species at another time. Having been normalized with respect to chlorinity, changes in either concentration will represent either precipitation or dissolution. Carbonate alkalinity should be depressed by 2 milliequivalents for each mMole of $CaCO_3$ precipitated according to the reaction in Table 3. Calcium concentration should be depressed by 1 mMole for each mMole of $CaCO_3$ precipitated. Dissolution, on the other hand, should increase the concentrations of these species in sample

	(1)		(2)
	$H_2O + CO_2 + CaCO_3$	$\rightleftharpoons$	$Ca^{+2} + 2HCO_3^-$
(1)	$\Delta Alkc = 0$ equiv $\Delta Ca = 0$ Mole $\Delta \Sigma CO_2 = 1$ Mole	(2)	$\Delta Alkc = 2$ equiv $\Delta Ca = 1$ Mole $\Delta \Sigma CO_2 = 2$ Mole
Dissol (1 - 2)	$\Delta Alkc = +2$ equiv $\Delta Ca = +1$ Mole $\Delta \Sigma CO_2 = +1$ Mole	Precip (2 - 1)	$\Delta Alkc = -2$ equiv $\Delta Ca = -1$ Mole $\Delta \Sigma CO_2 = -1$ Mole

Table 3: Stoichiometry of the dissolution and precipitation reactions.

waters.

Carbonate alkalinity variations are conveniently both a larger and a more accurately resolvable indicator of CaCO3 precipitation than are changes in calcium content. Consequently, carbonate alkalinity is the <u>modus operandi</u> used to quantify this chemical reaction. The effect of precipitation on total CO2 concentration (ΣCO_{2c}) is to decrease this value 1 Mole for each Mole CaCO3 precipitated. Therefore, changes in total CO2 attributable to precipitation-dissolution during a period of time (dt) with the effects of chlorinity variations removed can be calculated:

$$d(\Sigma CO_{2c})/dt = 1/2\ d(Alkccl)/dt \qquad \text{eq. 26}$$

where d(Alkc/cl)/dt is the change in carbonate alkalinity corrected for chlorinity variations over a period of time

(dt).

Production and Respiration

Marsh and Smith (1975) discuss the methods of measuring the productivity of coral reefs using oxygen as the primary indicator. This method was similarly used by Sargent and Austin (1949) and Odum and Odum (1955) and is advantageous due to the relative ease of O2 determinations and the possibility of continuous monitoring (Kinsey and Domm, 1974). Marsh and Smith (1975) also point out that a disadvantage of using O2 as an indicator of productivity is the speed with which this gas exchanges across the air-sea interface when partial pressure differences exist between these two media.

The use of O2 as an indicator of CO2 variations related to photosynthesis and respiration is based on the stoichiometry of the oxidation and reduction reaction in Table 4. The following equation represents the changes in total CO2 that are attributable to productivity variations (ΣCO2p) during a period of time (dt):

$$d(\Sigma CO2p)/dt = -d(pO2/32\ (K'H)\ (1 + K'1/H + K'1 \times K'2/H\ ))/dt \qquad \text{eq. 27}$$

where pO2/32 (32 being the molecular weight of O2) converts parts per million to mMoles/liter (equivalent to pCO2) and

$$CH_2O + O_2 \underset{2}{\overset{1}{\leftrightharpoons}} H_2O + CO_2$$

1) Photosynthesis (Production)

2) Respiration or Aerobic Decay

	ΔAlkc	ΔΣCO2	ΔCO2	ΔO2
1)	0	-1	-1	+1
2)	0	+1	+1	-1

Table 4: Stoichiometry of the photosynthesis and respiration reactions.

K'H is Henry's Law constant which converts pCO2 to H2CO3*. The remaining part of the equation converts H2CO3* to total CO2 and is derived by rearranging equations 14 and 16:

$$HCO_3^-/H_2CO_3^* = K'1/(H^+)$$

$$CO_3^=/H_2CO_3^* = K'1 \times K'2/(H^+).$$

Therefore, the product of H2CO3* and $(1 + K'1/H^+ + K'1 \times K'2/H^+)$ is $H_2CO_3^* + HCO_3^- + CO_3^=$, or ΣCO2.

Gas Exchange

As previously stated, total CO2 changes in the Discovery Bay system can be accounted for by precipitation-dissolution, production, groundwater seepage, decay of organic waste, and gas exchange across the air-sea

interface. Having quantified the changes resulting from the first four of the above processes leaves us with only gas exchange. Thus,

$$d\Sigma CO2ev/dt = d\Sigma CO2/dt - d\Sigma CO2fw/dt - d\Sigma CO2c/dt - d\Sigma CO2p/dt \quad \text{eq. 28}$$

where $d\Sigma CO2ev/dt$ is the total CO2 change resulting from evasion while the others represent changes in measured CO2, and changes in total CO2 resulting from freshwater invasion, dissolution-precipitation, and productivity, respectively. This equation summarizes the effects of gas exchange on total CO2 changes during the period of time (dt).

Saturation Indices of Discovery Bay

Saturation indices of Discovery Bay were calculated for a spectrum of solid phase carbonate minerals and are recorded in Appendix C. The results indicated that all samples were undersaturated with respect to magnesium carbonates greater than 17.9 mole percent magnesium. However, the mole percent magnesium carbonate with which these waters were supersaturated appears to be dependent upon the location of the sample, or more specifically, the amount of dilution experienced by the sample. The combined effects of freshwater invasion of cold, CO2-charged waters and the dilution of bay water alkalinities, calcium

activities, and magnesium activities lower the maximum mole percent of magnesium carbonate that is at stoichiometric equilibrium with the sample water chemistries.

Locations 1 and 2 were nearest the freshwater springs and, therefore, experienced the greatest effects of freshwater invasion and dilution (Fig. 13). Saturation states of these samples indicate that aragonite and magnesium calcites greater than 8 mole percent magnesium were below saturation at various times during the 24 hour study.

Measured saturation states from location 3 appeared to fluctuate less than those measured from the first two locations. Water chemistries remained supersaturated with respect to aragonite throughout the study period while the maximum magnesium content of magnesium calcite remaining supersaturated was less than 10.4 mole percent magnesium.

The stability of the water chemistries from the east side of the bay, locations 4, 5, and 6, was represented by the lack of fluctuations in saturation states. Virtually all samples measured from these locations were supersaturated with respect to 12.7 mole percent magnesium calcite. Water chemistries were supersaturated with respect to aragonite throughout the study period.

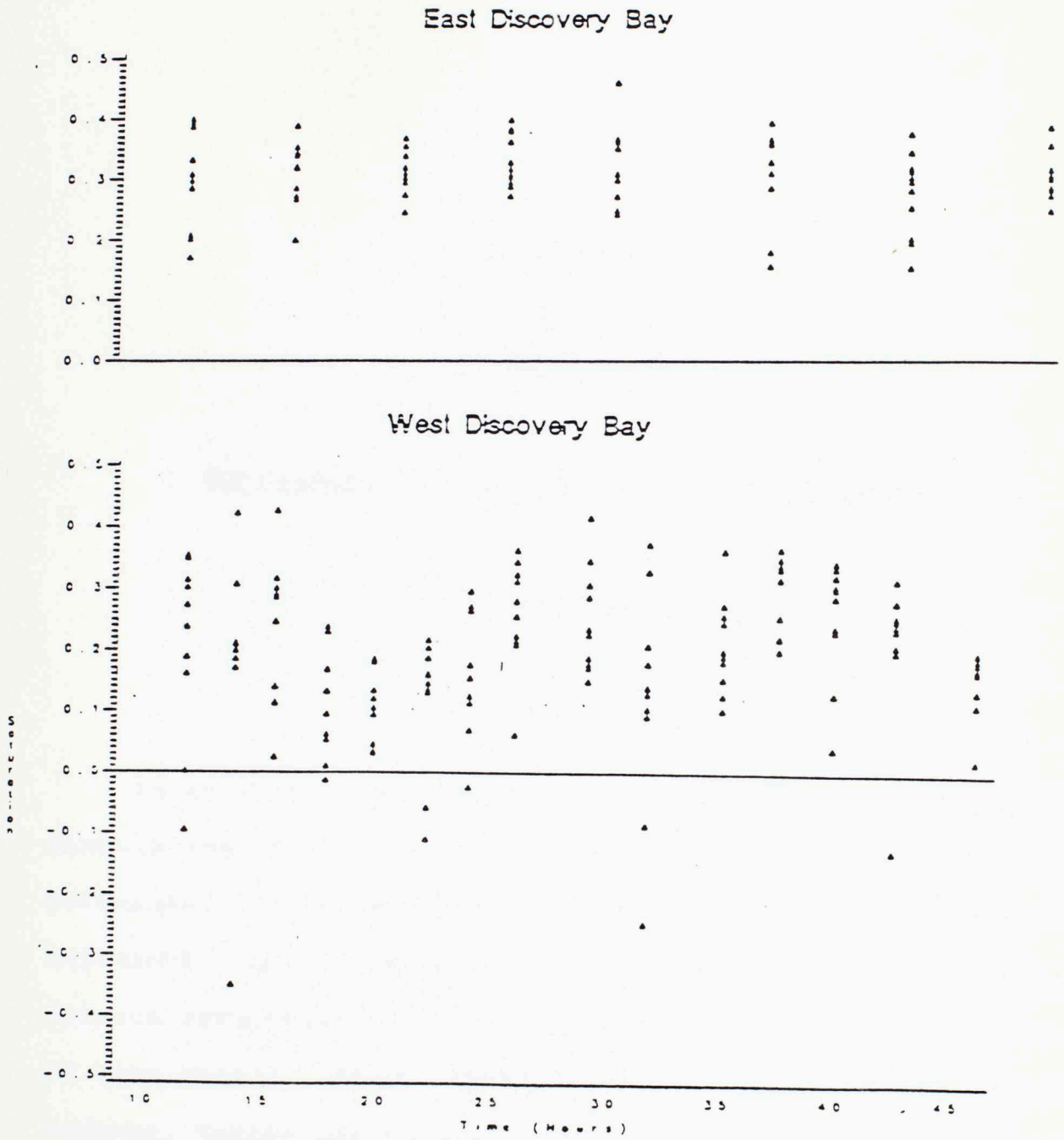


Figure 13: Variation of mean saturation states through time. Log saturation is plotted against time so that 0 is a saturation state of 1. Eastern region (Loc 4-6) shows more stable chemistries, yet both appear to fluctuate with the tide.

CHAPTER V

DISCUSSION

Precipitation-Dissolution and Productivity Within Discovery Bay

Introduction

In an effort to quantify the rate of precipitation or dissolution occurring within Discovery Bay, changes in carbonate alkalinity were contoured for each time profile to represent the precipitation and dissolution occurring between measurements. Eight contours were generated for the 24 hour period (Figs. 14-21) using Surface II (by Robert Sampson, Kansas Geological Survey) software. Integration of these contours allowed the calculation, in mMoles $CaCO_3$/liter, for both precipitation and dissolution. Net precipitation-dissolution was determined by the addition of these competing processes.

Oxygen variations (Figs. 22-29) and chlorinity

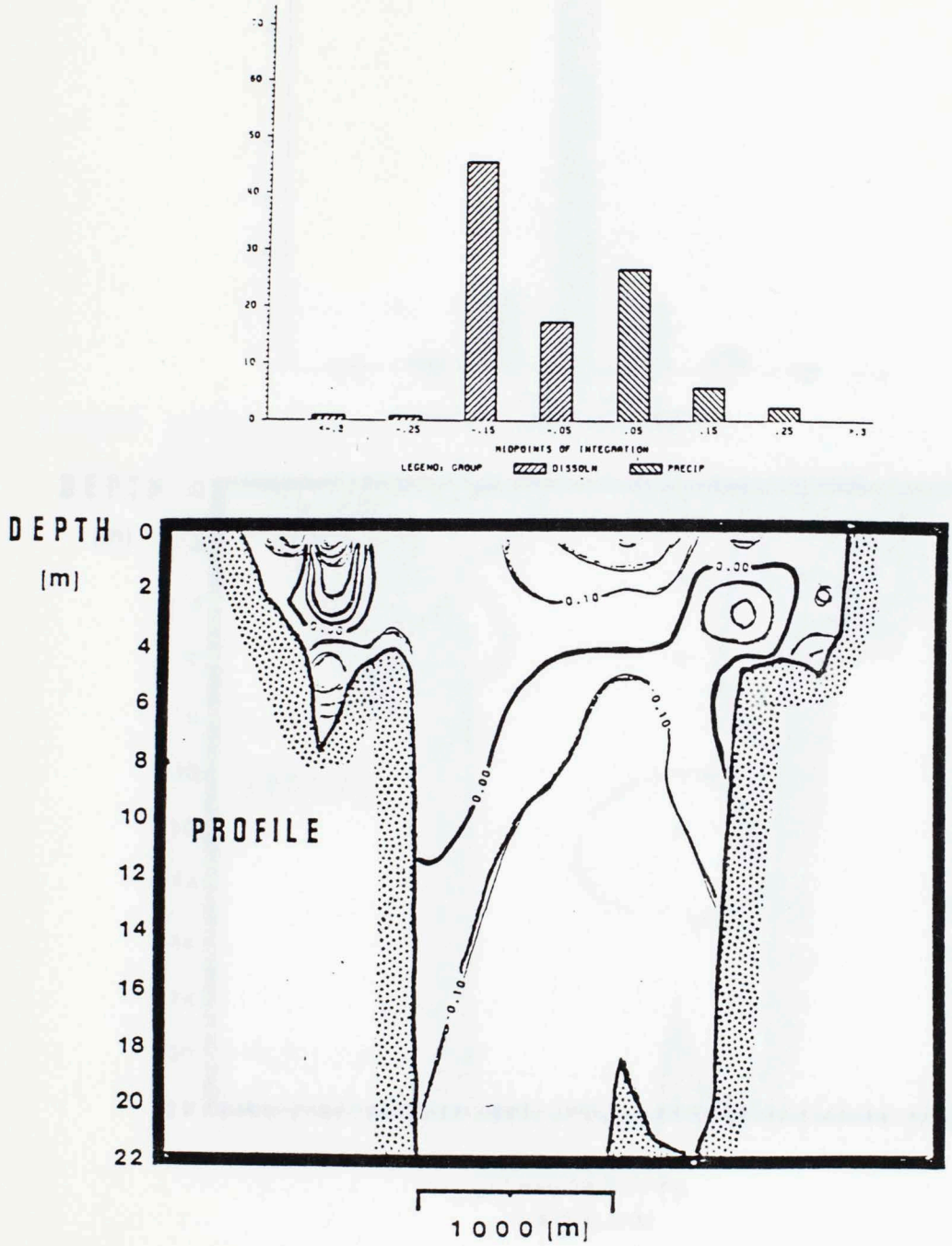


Figure 14: Precipitation-Dissolution contour. Time: 1 - 4 pm. Net dissolution of 0.055 mM/l CaCO3, predominantly from the deeper regions of the bay.

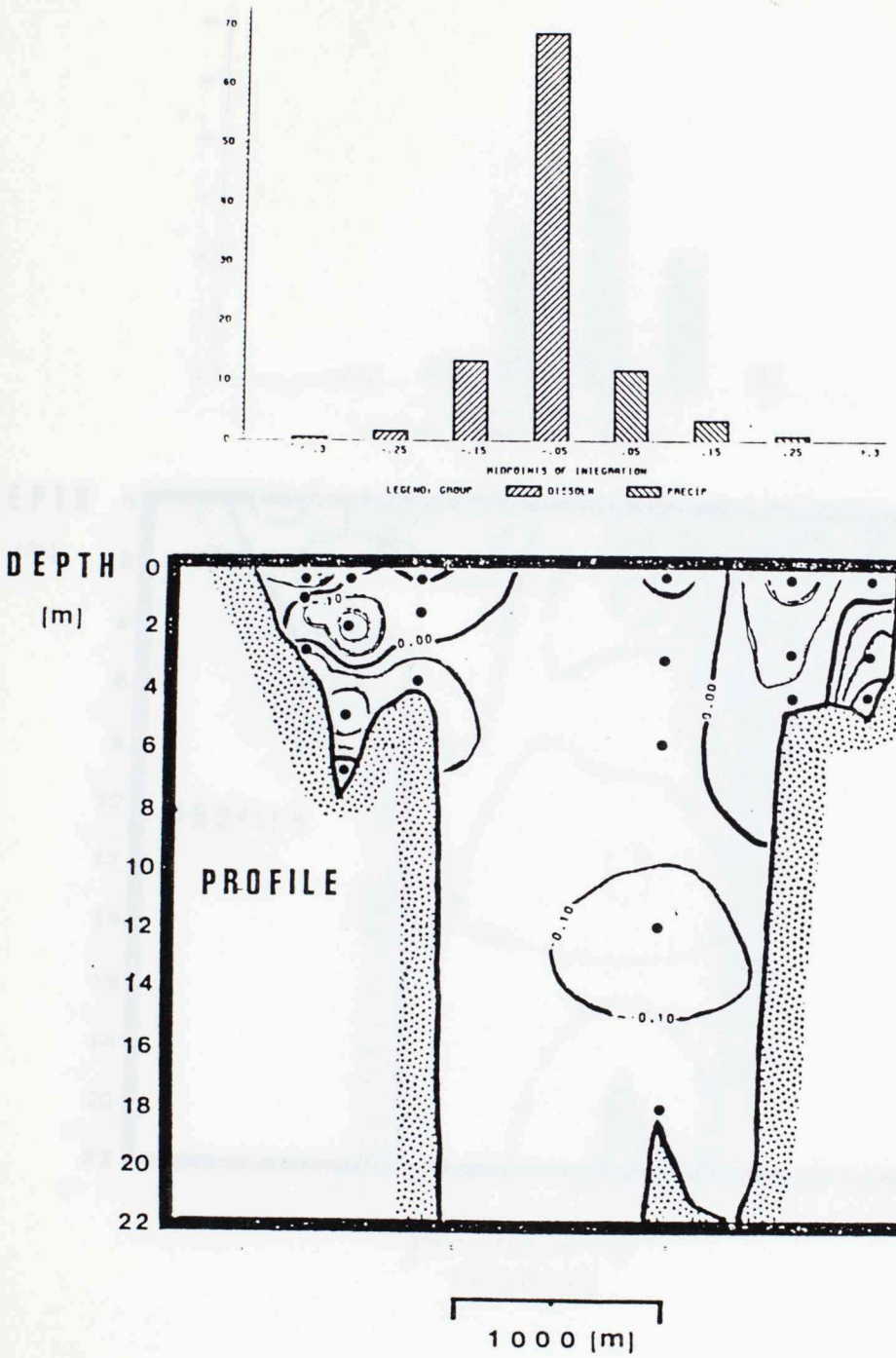
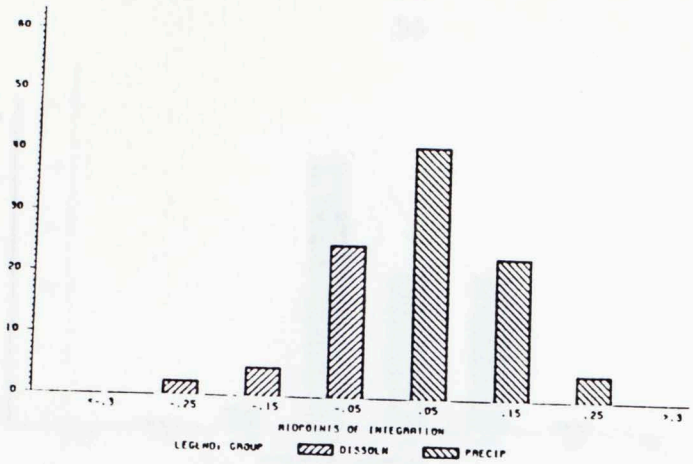


Figure 15: Precipitation-Dissolution contour. Time: 4 - 7 pm. Net dissolution of 0.047 mM/l CaCO3. Distribution of samples is shown by dots.



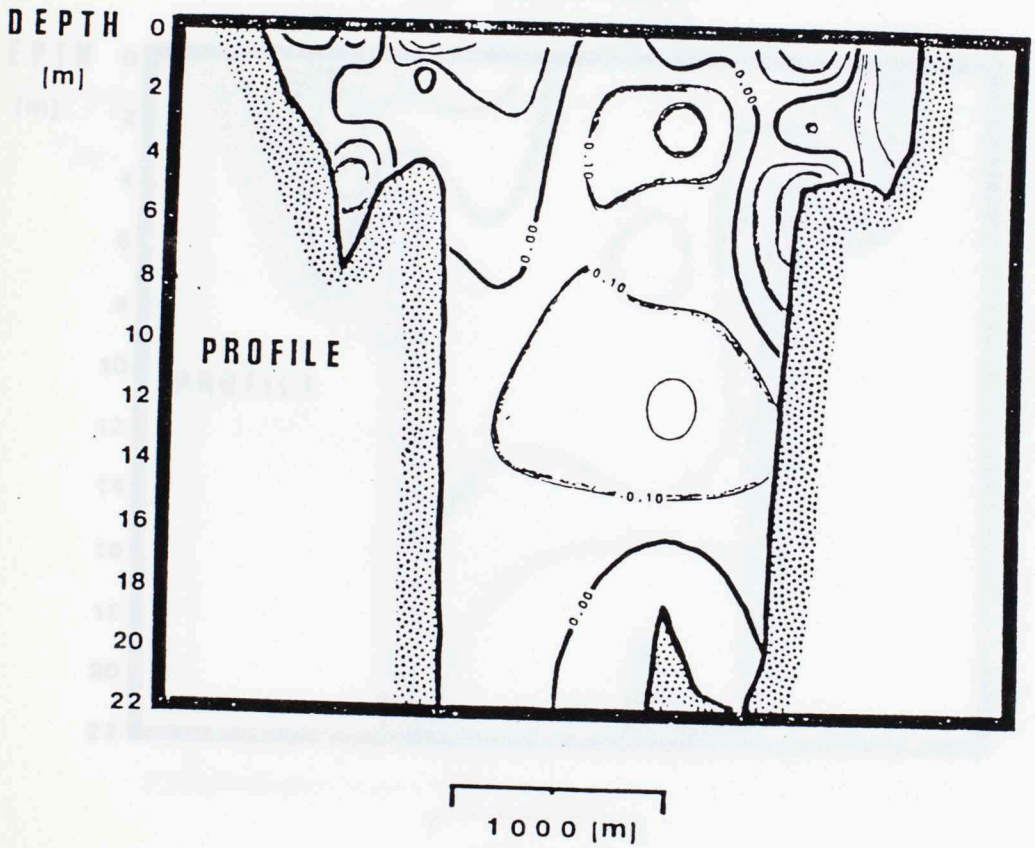


Figure 16: Precipitation-Dissolution contour. Time: 7 - 10 pm. Net precipitation of 0.041 mM/l CaCO3.

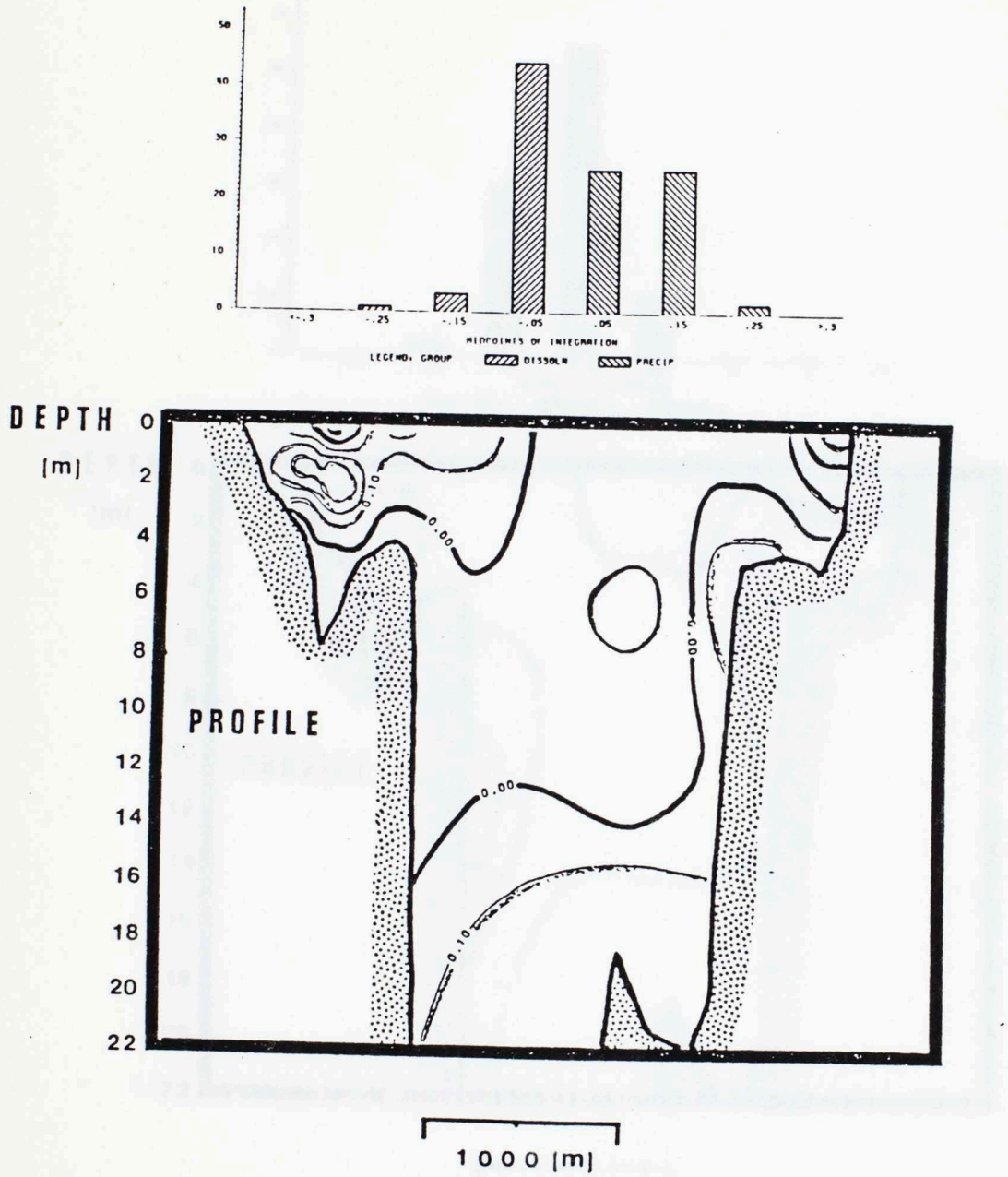


Figure 17: Precipitation-Dissolution contour. Time: 10 - 1 am. Net precipitation of 0.026 mM/l CaCO3.

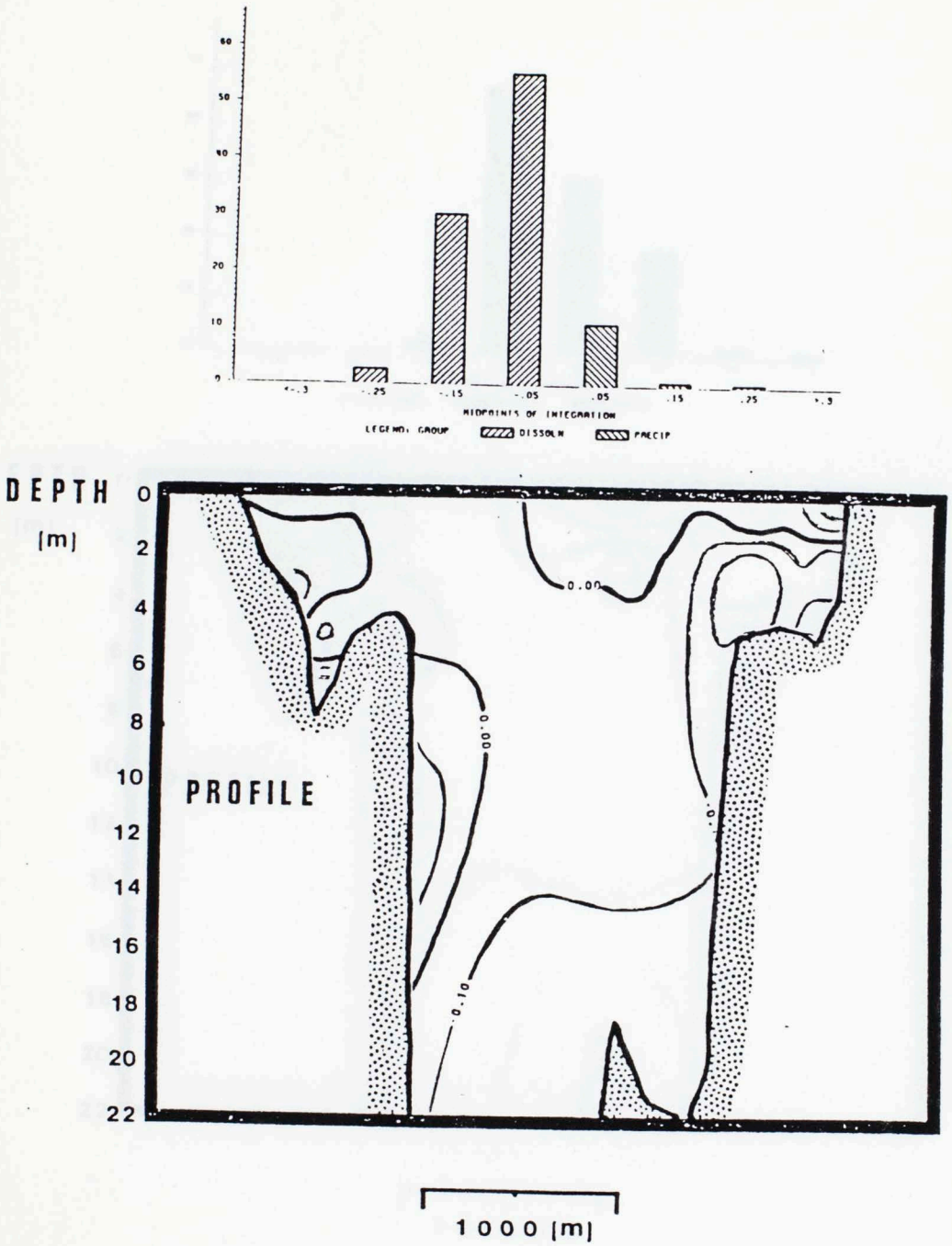


Figure 18: Precipitation-Dissolution contour. Time: 1 - 5 am. Net dissolution of 0.071 mM/l CaCO3.

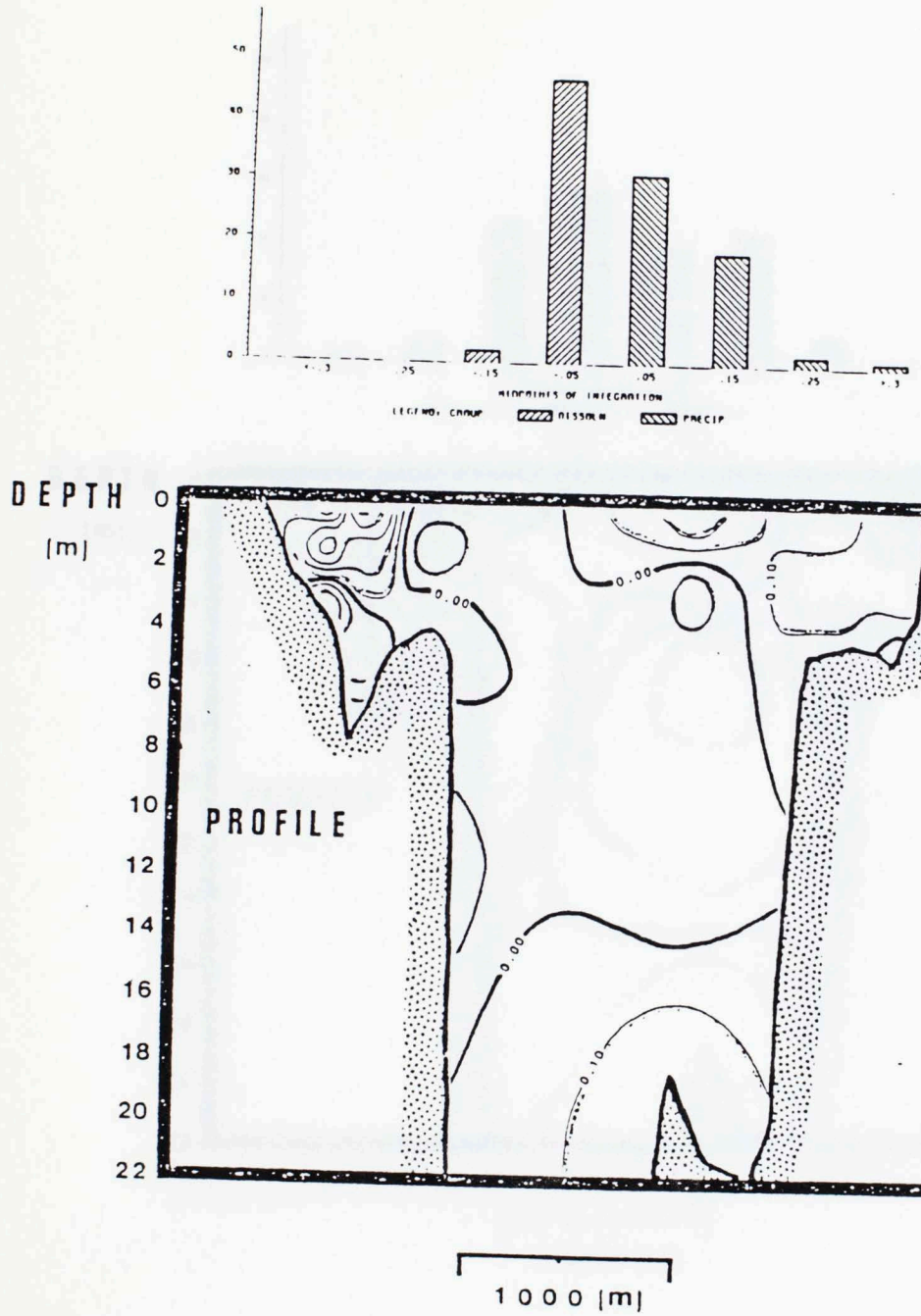


Figure 19: Precipitation-Dissolution contour. Time: 5 - 8 am. Net precipitation of 0.024 mM/l CaCO3.

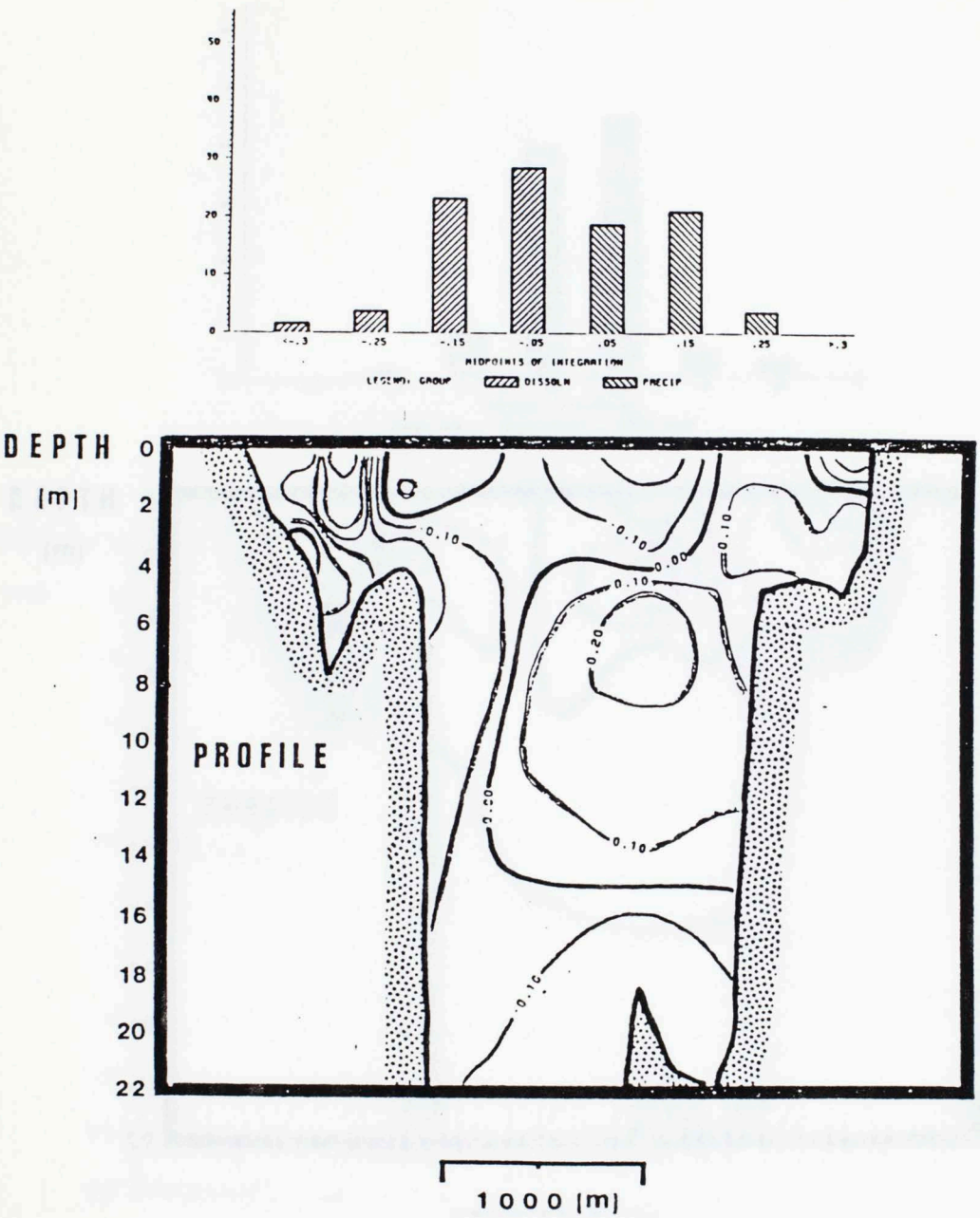


Figure 20: Precipitation-Dissolution contour. Time: 8 - 12 pm. Net dissolution of 0.015 mM/l CaCO3.

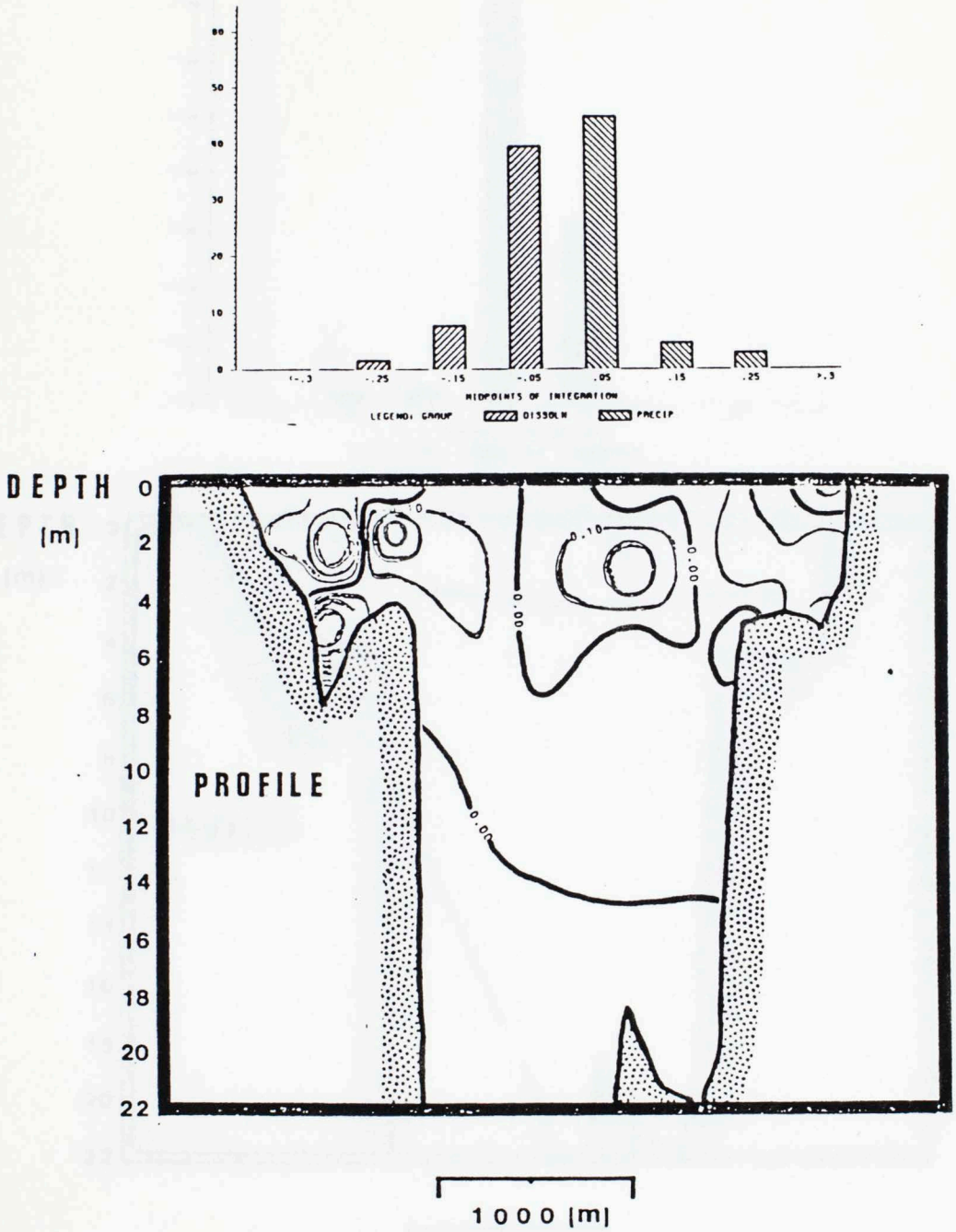


Figure 21: Precipitation-Dissolution contour. Time: 12 - 4 pm. Net precipitation of 0.001 mM/l CaCO3.

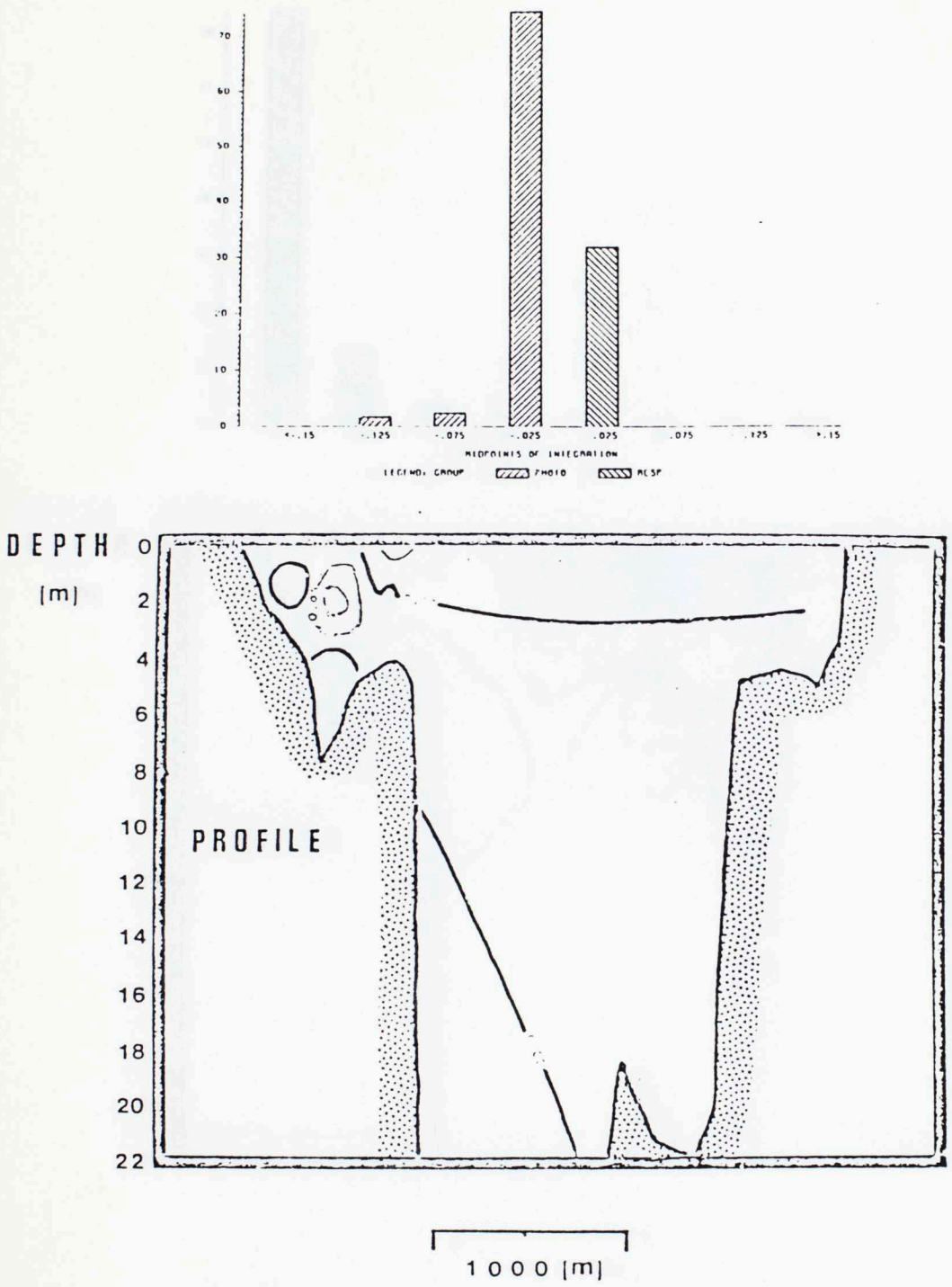


Figure 22: Photosynthesis-Respiration contour. Time: 1 - 4 pm. Net photosynthesis of 0.015 mM/l. Respiration observed within deep regions.

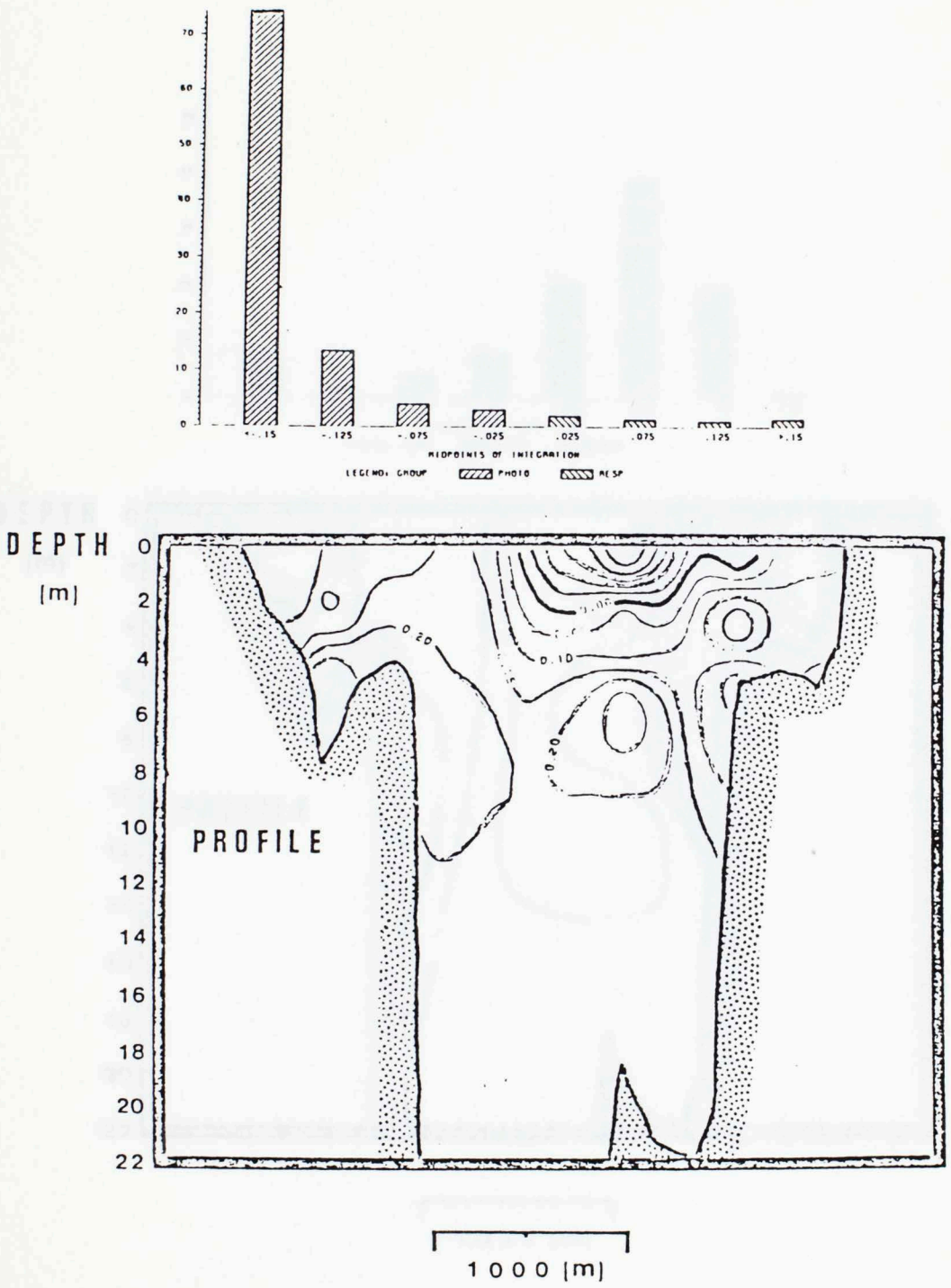


Figure 23: Photosynthesis-Respiration contour. Time: 4 - 7 pm. Net photosynthesis of 0.102 mM/l. Photosynthetic effects are strongest during this period.

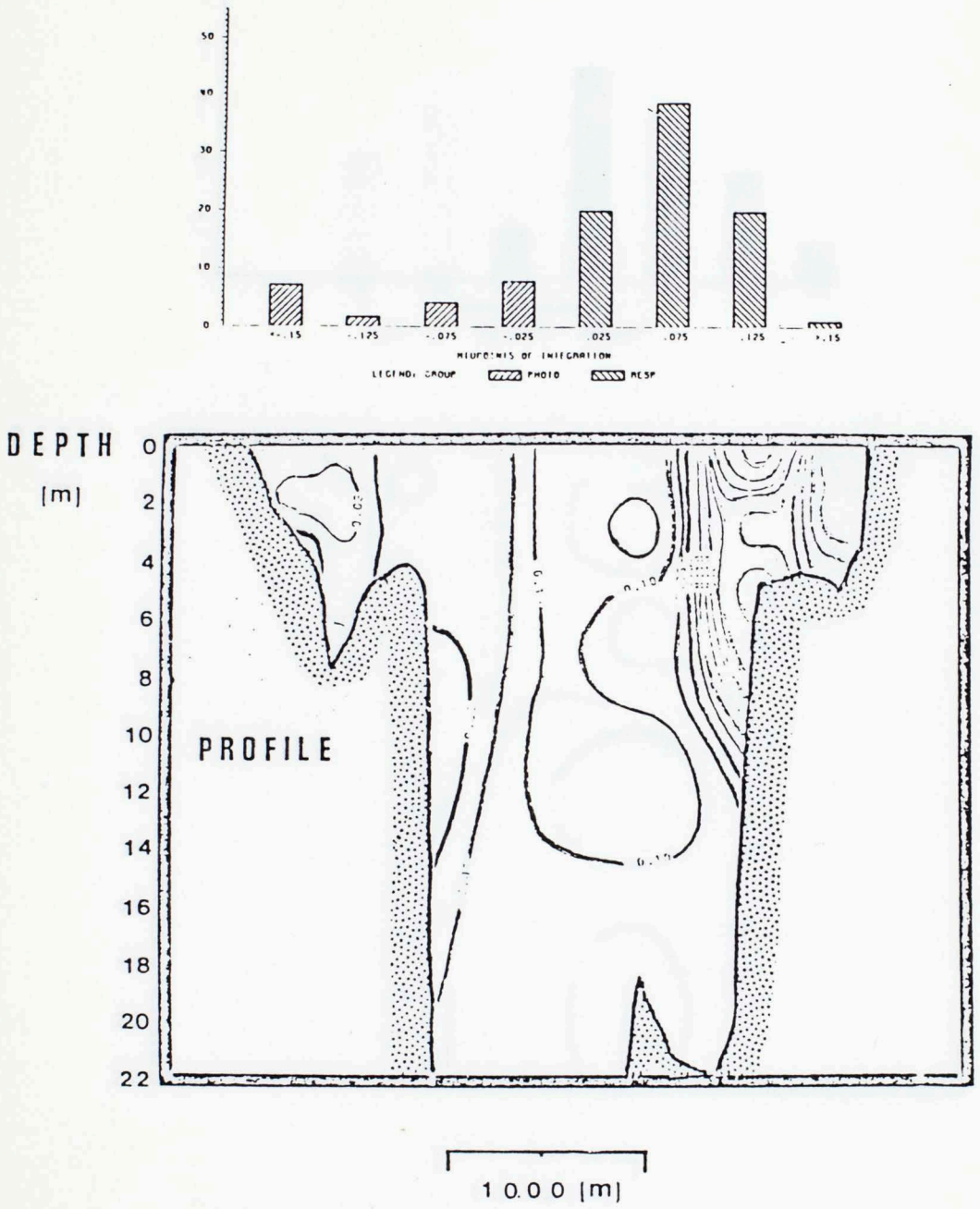
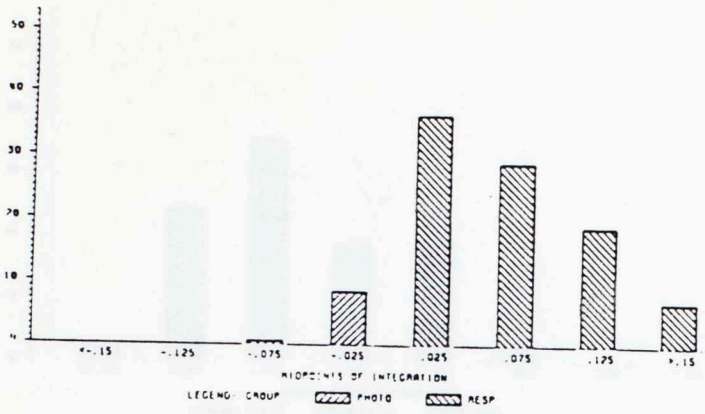


Figure 24: Photosynthesis-Respiration contour. Time: 7 - 10 pm. Net respiration of 0.061 mM/l. Respiration is strongest within the central region of the bay.



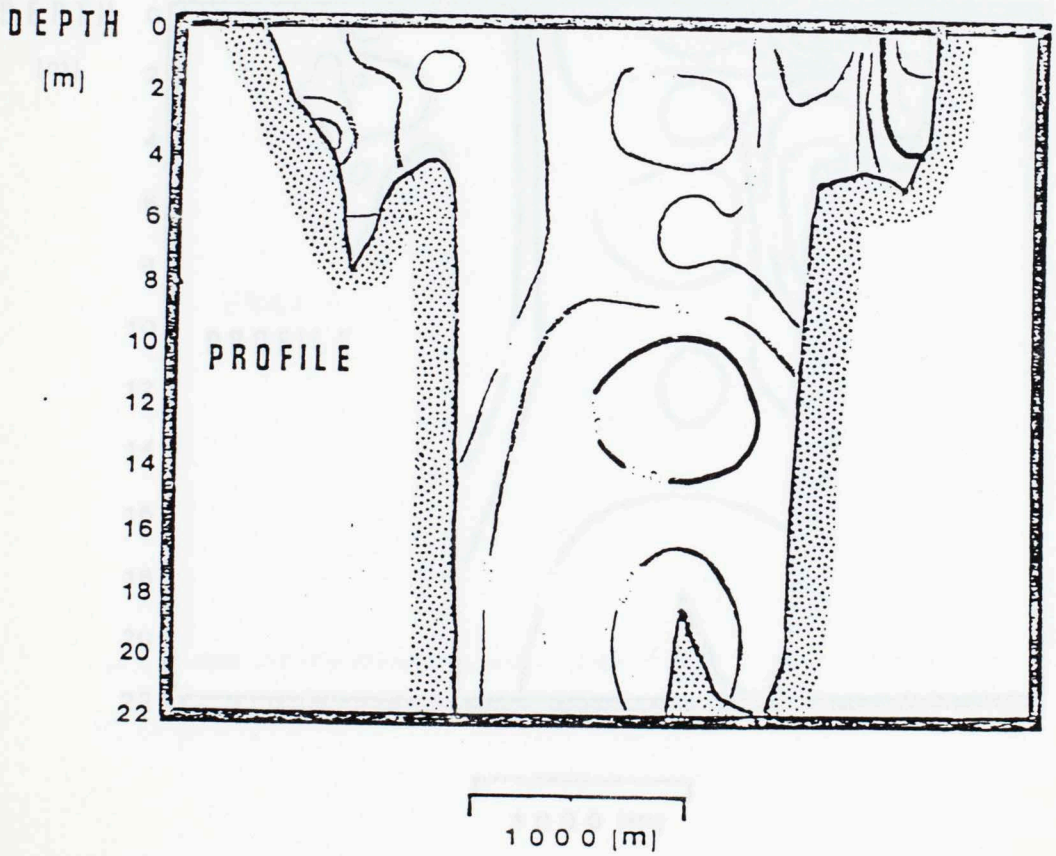


Figure 25: Photosynthesis-Respiration contour. Time: 10 - 1 am. Net respiration of 0.065 mM/l. Respiration dominates throughout the entire bay region.

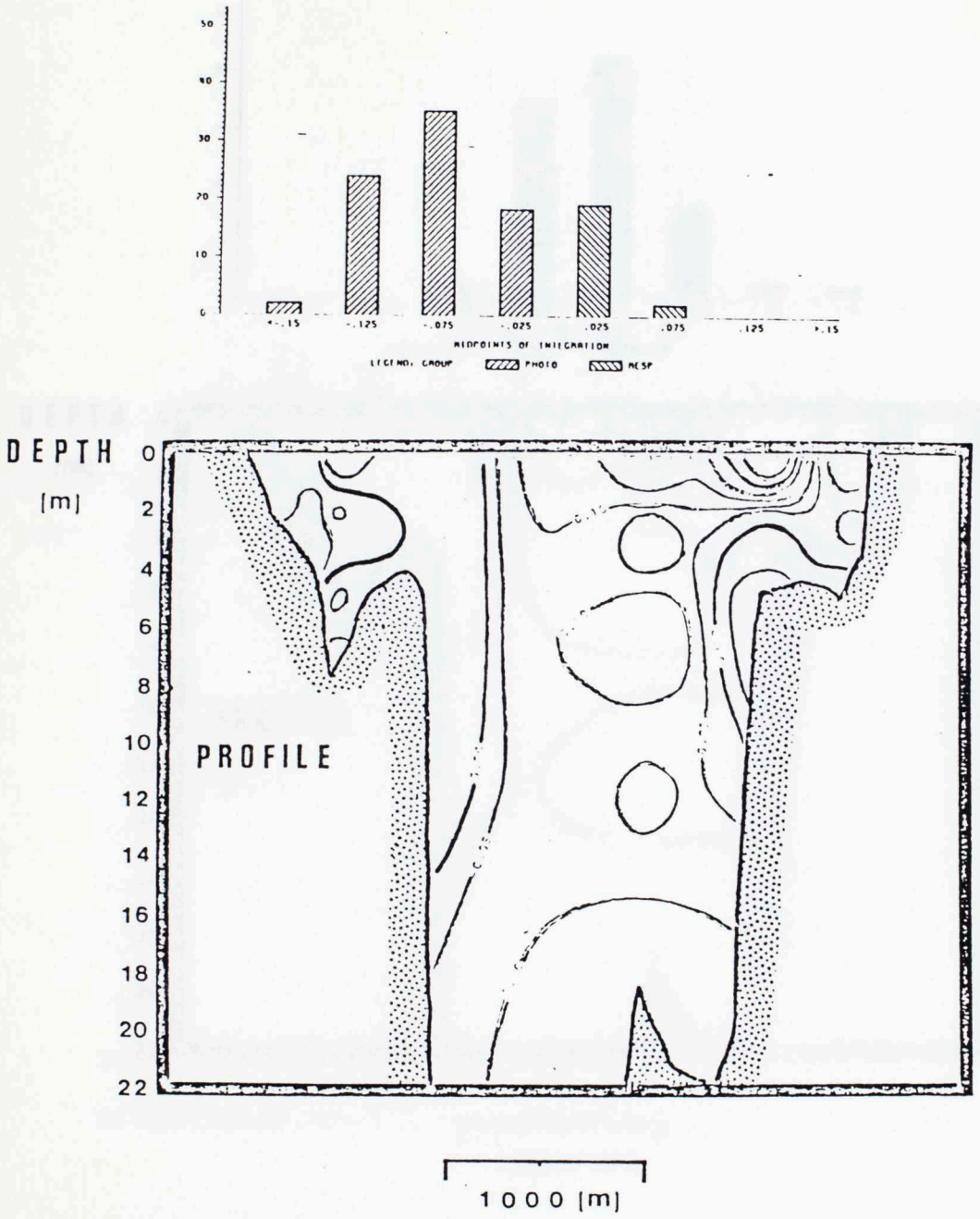


Figure 26: Photosynthesis-Respiration contour. Time: 1 - 5 am. Net photosynthesis of 0.058 mM/l. This may be more representative of a lag in respiration.

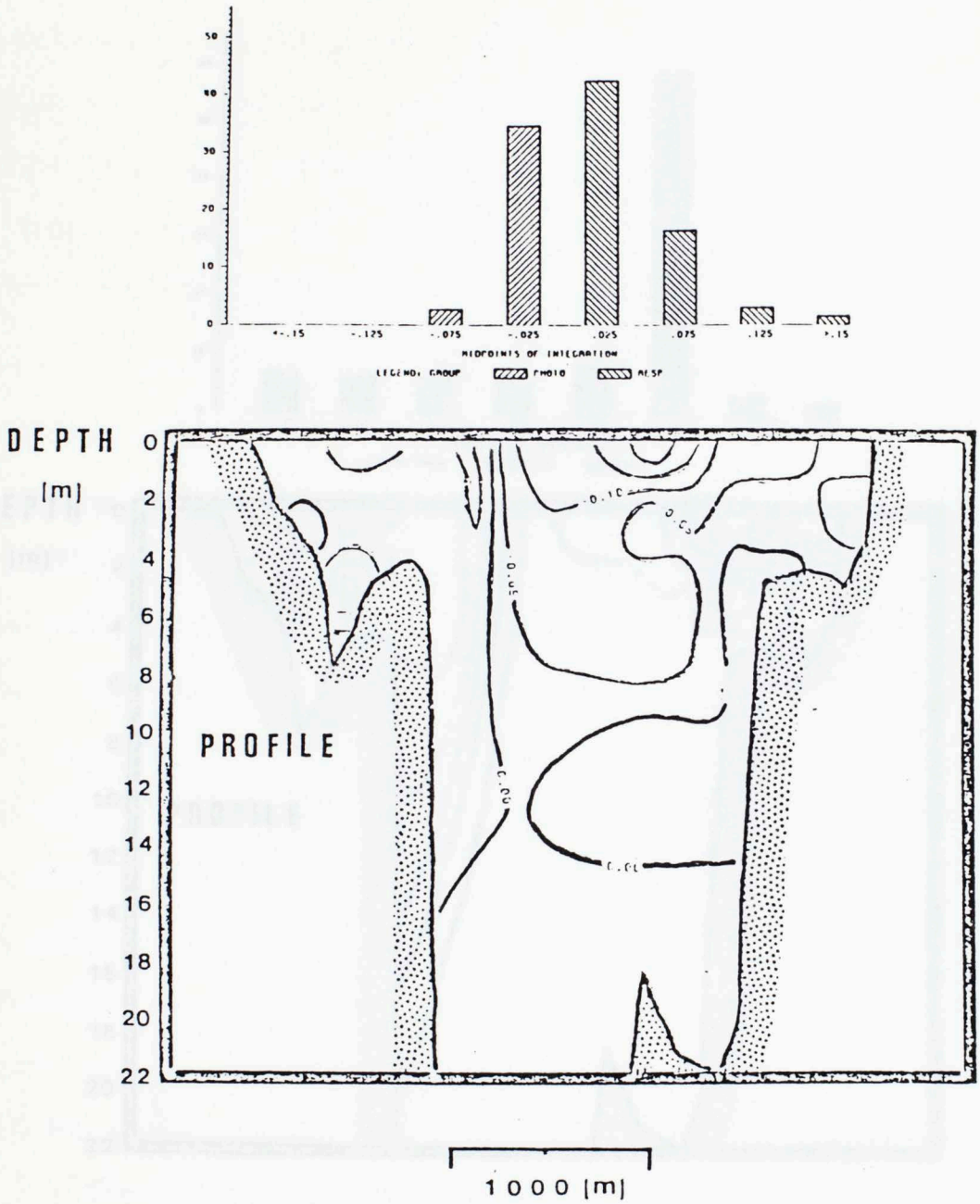


Figure 27: Photosynthesis-Respiration contour. Time: 5 - 8 am. Net respiration of 0.039 mM/l.

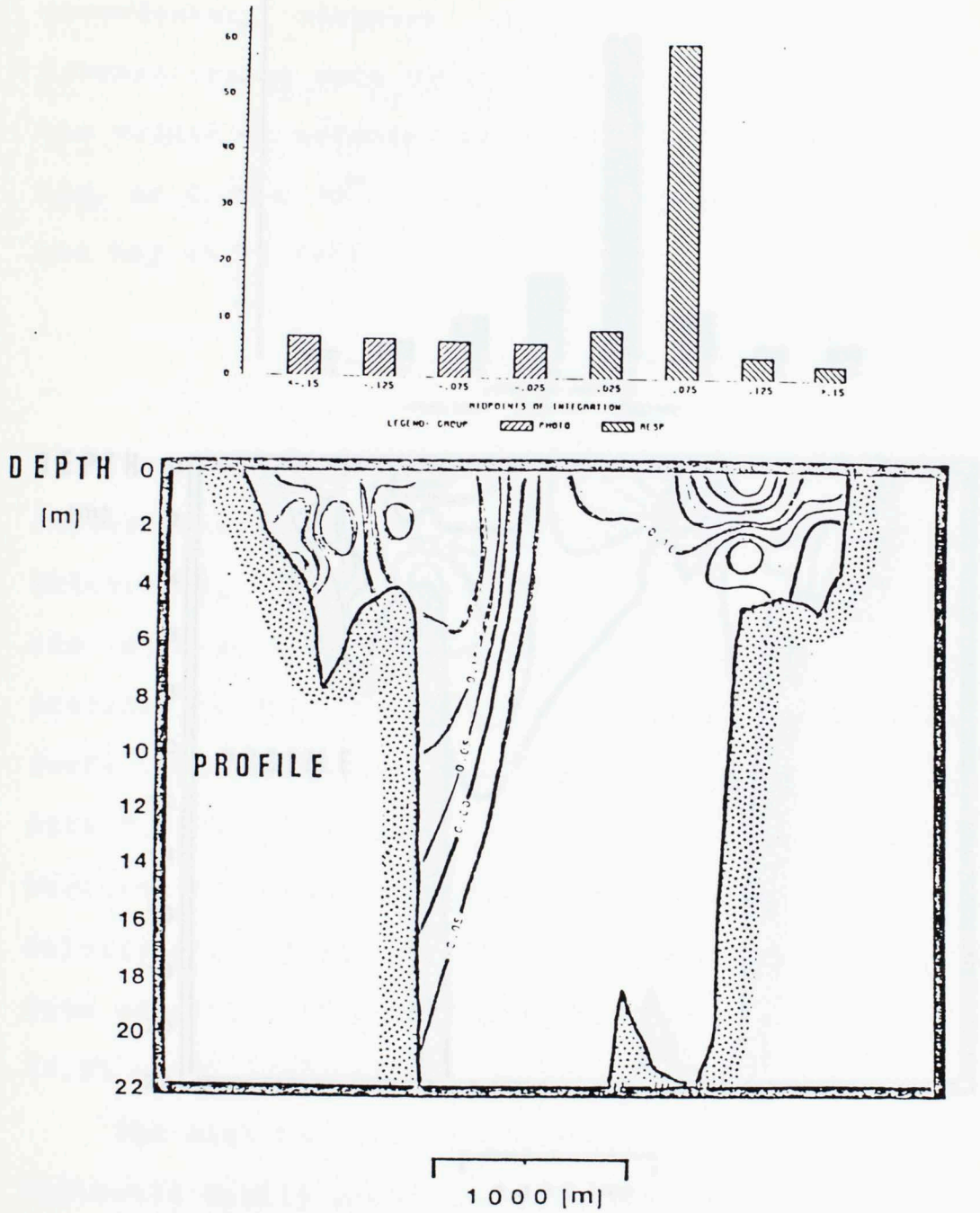


Figure 28: Photosynthesis-Respiration contour. Time: 8 - 12 pm. Net respiration of 0.049 mM/l. Effects of photosynthesis observed as sun rises in the east.

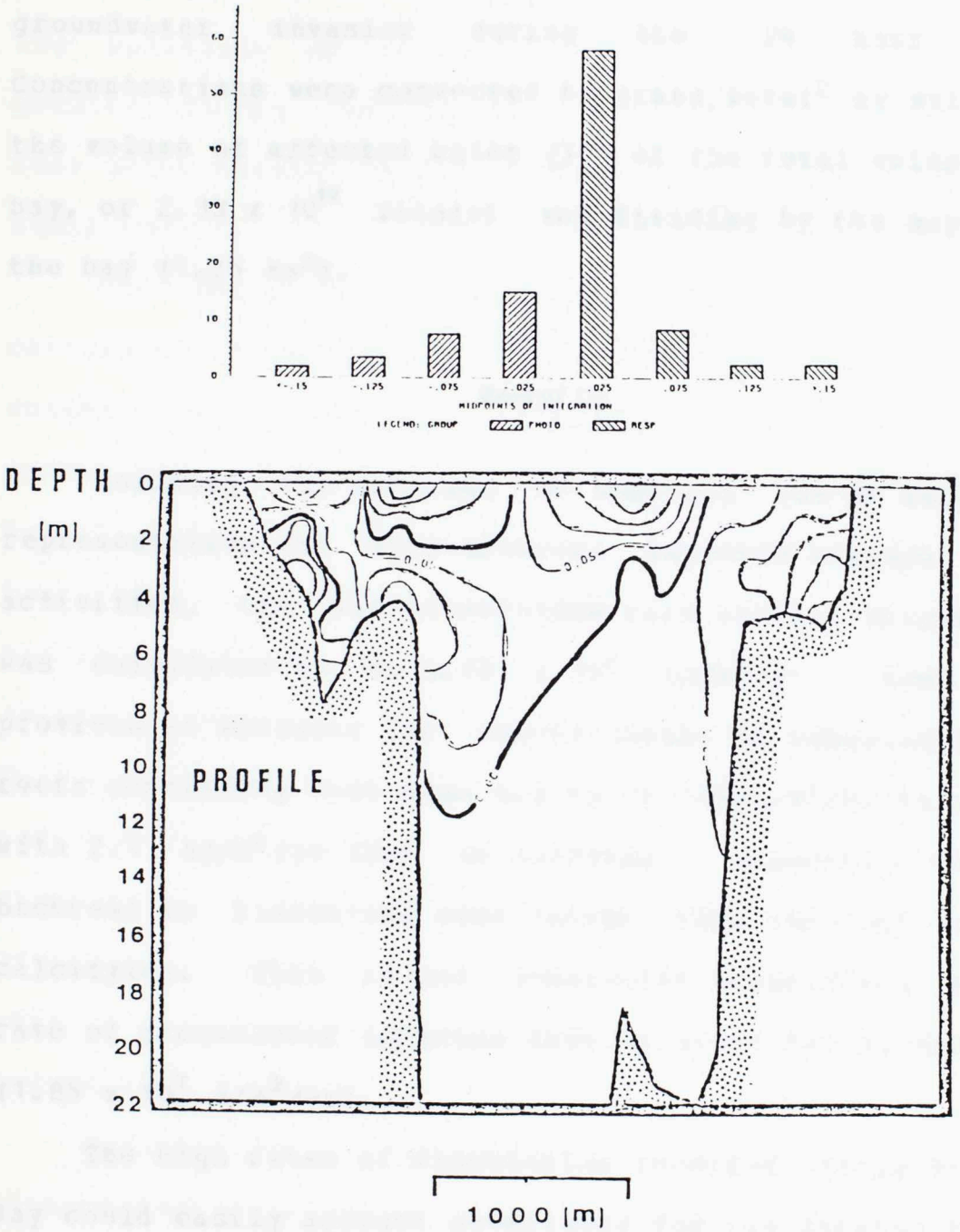


Figure 29: Photosynthesis-Respiration contour. Time: 12 - 4 pm. Net respiration of 0.031 mM/l. Effects of photosynthesis dominant in west.

variations were also contoured to represent productivity and groundwater invasion during the 24 hour period. Concentrations were converted to grams/meter^2 by multiplying the volume of affected water (30% of the total volume of the bay, or 2.33 x 10^{12} liters) and dividing by the map area of the bay (1.25 km^2).

Results

Assuming the duration of sampling (24-36 hours) is representative for this tropical lagoon's average diurnal activities, the net dissolution rate within Discovery Bay was calculated to be 6.48 x 10^3 kg/m^2/yr. Land (1979) provides an estimate for calcification on Jamaican fringing reefs concluding that some 5.2 kg of CaCO3/m^2/yr is produced with 2.9 kg/m^2/yr lost to solution, suggesting that the backreef is dissolving even faster than the reef crest is calcifying. This is not unexpected considering the high rate of groundwater invasion that occurred during this study (1.85 x 10^7 l/m^2/yr).

The high rates of dissolution recorded within Discovery Bay could easily account materially for the karstic features observed in this lagoon environment. In fact, extrapolating the present rate of dissolution back 10,000 years (to early Holocene) can account for the chemical erosion of four times the carbonate mass absent from the bay area (8.75 x 10^{13}

versus 2.05×10^{13}). Although it is generally accepted that the weakening of structures below these karst features occurred during Pleistocene when sealevel was hundreds of feet below present sealevel, these rates suggest dissolution still occurs.

The net productivity rate within Discovery Bay was calculated to be -4.5×10^{7} g carbon/day (based on the same volume of affected waters). This rate compares to 2×10^{8} g carbon/day production in Rongelap Lagoon (Sargent and Austin, 1949), a shallower, flatter lagoon, and suggests that within Discovery Bay and the underlying sediment package oxidation of carbon - and reduction of sulfate (Pigott, 1977) - occurs faster than reduction of carbon. This conclusion is supported by the observations of Westrum and Meyers (1978) which indicate a consumption of total organic carbon (TOC) landward from the fringing-barrier reef crest (Fig. 30). Furthermore, measurements of oxygen from this study along vertical profiles suggest that the bay serves as a sink for oxygen (Fig. 31).

Importantly, if total CO2 variations could be explained without regard to gas exchange across the air-sea interface, as Smith (1973) assumes, then the combined effects of dissolution, productivity, and groundwater invasion on total CO2 variations within Discovery Bay should be equivalent to the measured values of total CO2 variations. However, another means of CO2 escape must be present in order to

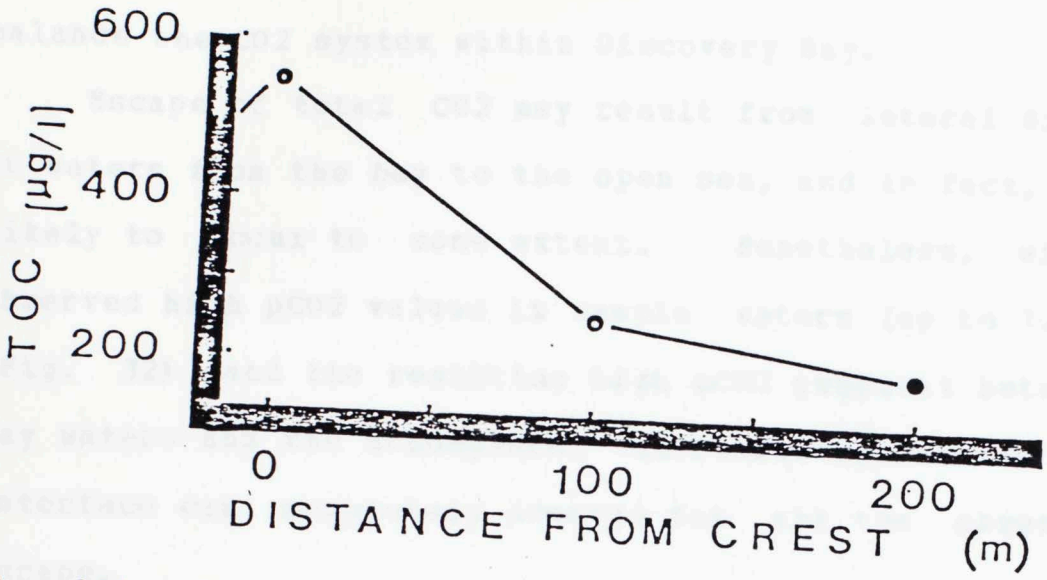


Figure 30: Lateral profile of total organic carbon measured from Discovery Bay waters. The backreef is depleted in TOC relative to the reef crest (from Westrum and Meyers, 1978).

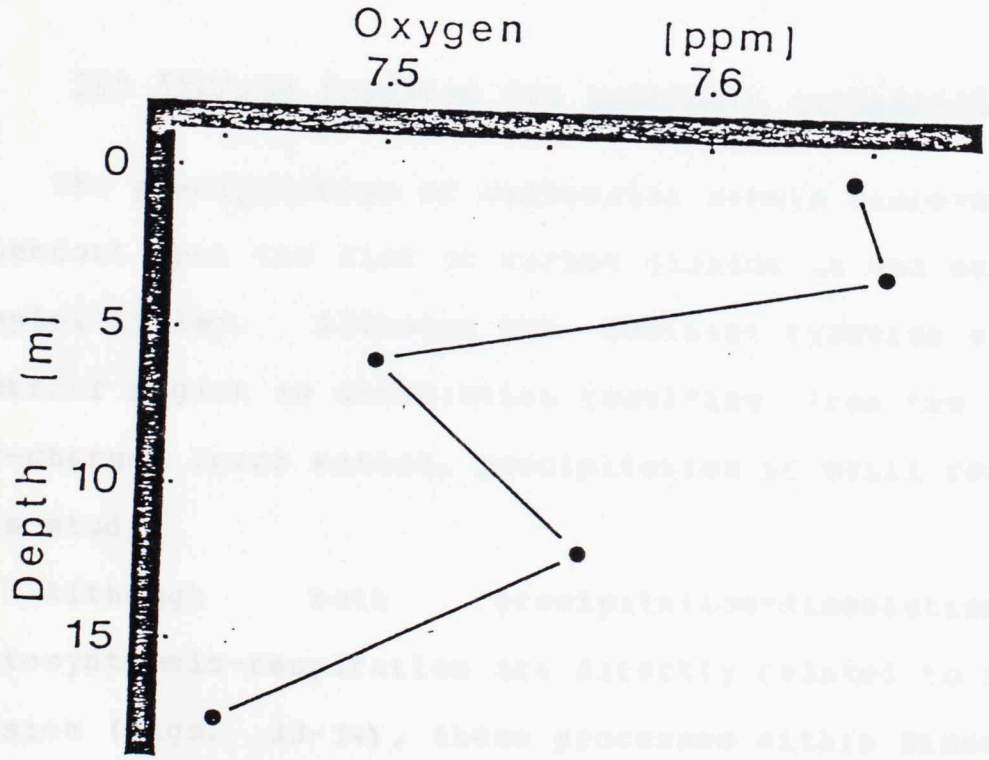


Figure 31: Vertical profile of oxygen concentrations within Discovery Bay. Samples are from Loc. 4. The bay serves as a sink for O2.

balance the CO2 system within Discovery Bay.

Escape of total CO2 may result from lateral diffusion of waters from the bay to the open sea, and in fact, this is likely to occur to some extent. Nonetheless, with the observed high pCO2 values in sample waters (up to 1200 ppm) (Fig. 32) and the resulting high pCO2 gradient between the bay waters and the atmosphere, diffusion across the air-sea interface can completely account for all the observed CO2 escape.

CO2 Evasion

The Forcing Function for Carbonate Precipitation

The precipitation of carbonates within Discovery Bay is dependent upon the flux of carbon dioxide in and out of this complex system. Although the dominant reaction within the backreef region is dissolution resulting from the influx of CO2-charged fresh waters, precipitation is still recorded in this study.

Although both precipitation-dissolution and photosynthesis-respiration are directly related to invasion-evasion (Figs. 33-34), these processes within Discovery Bay are not directly related to each other (Fig. 35). If, on the other hand, they were related we would expect to see precipitation to display the same diurnal variations found

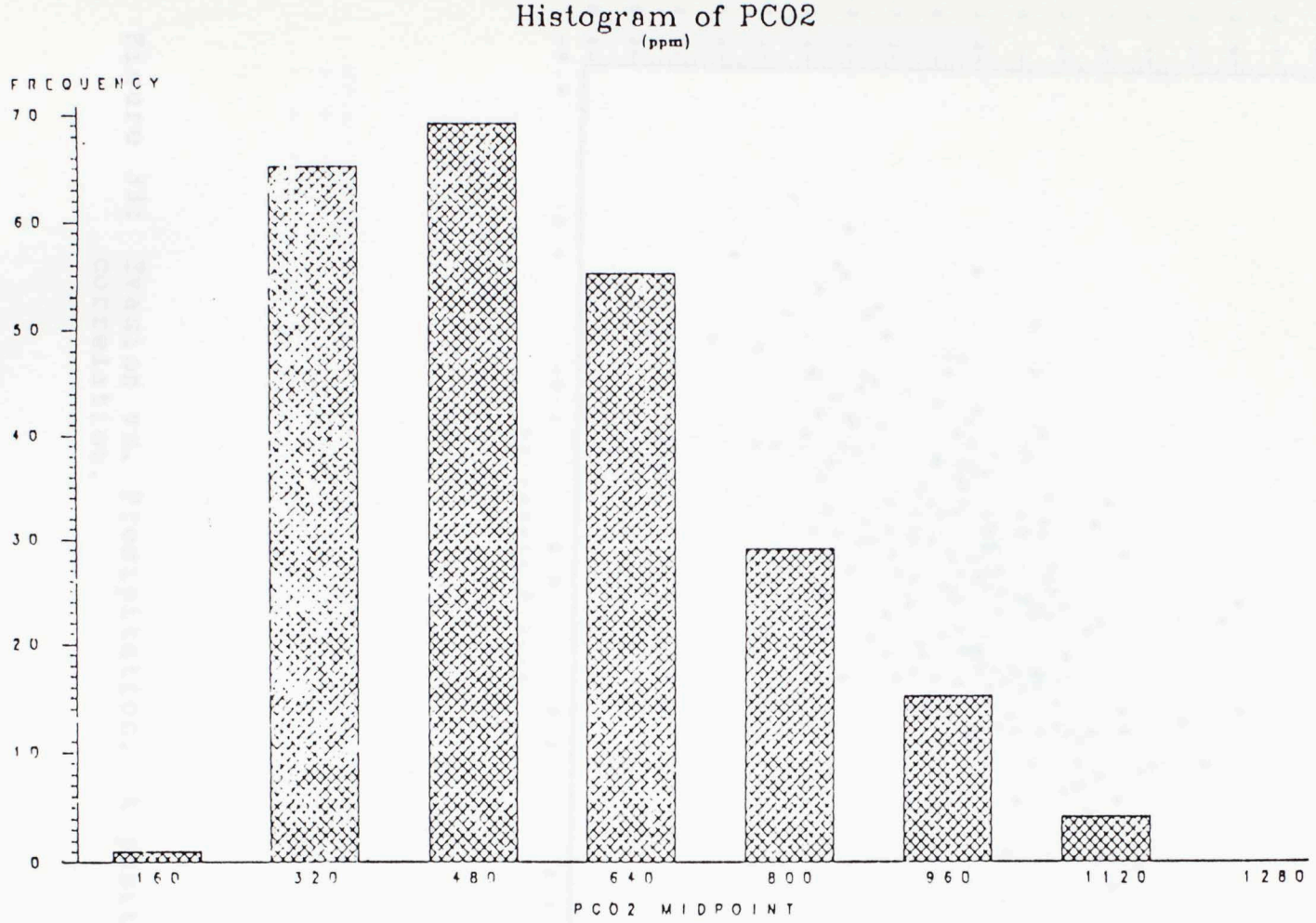


Figure 32: Histogram representing distribution of pCO2 in bay waters.

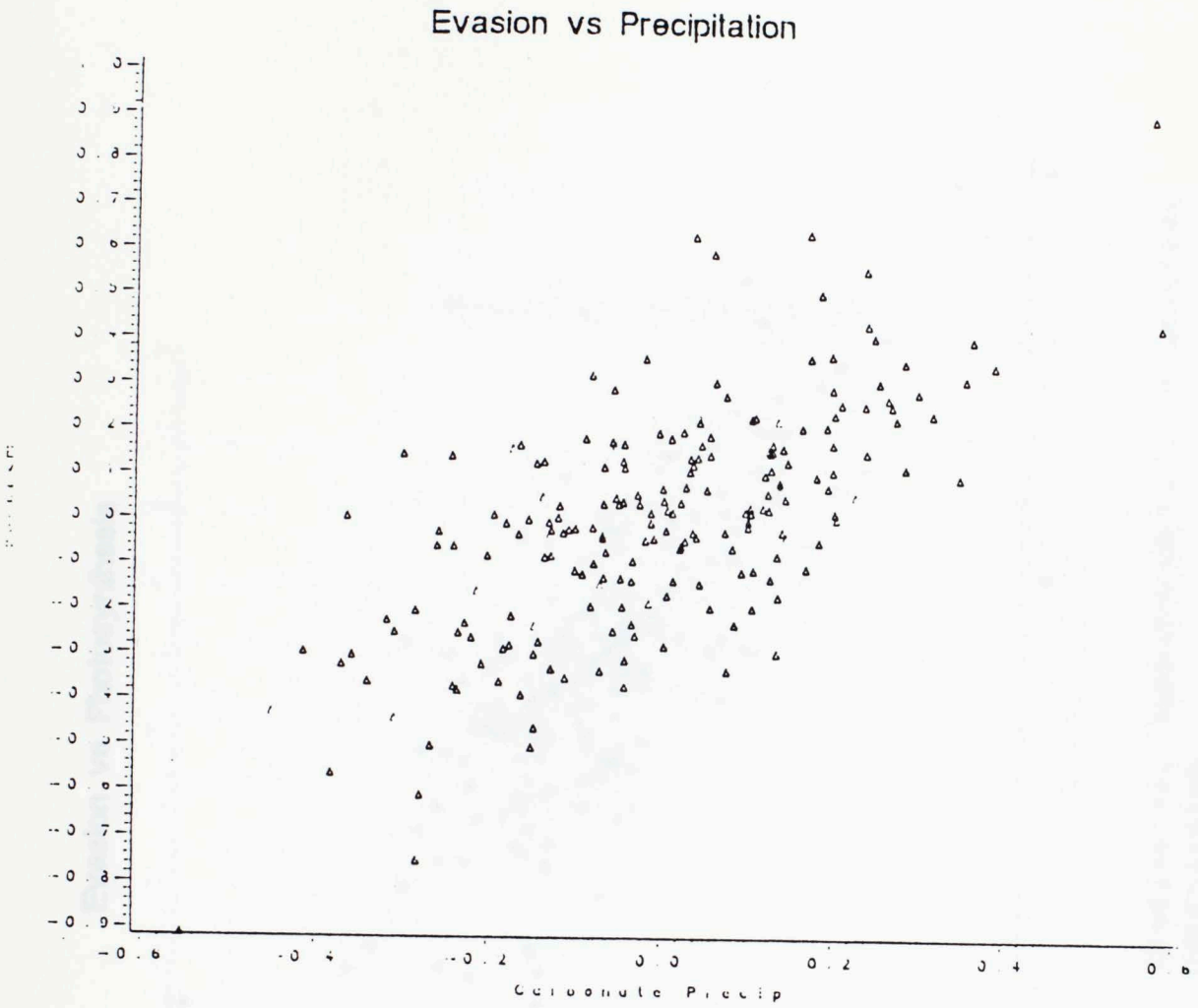


Figure 33: Evasion vs. Precipitation. A positive correlation.

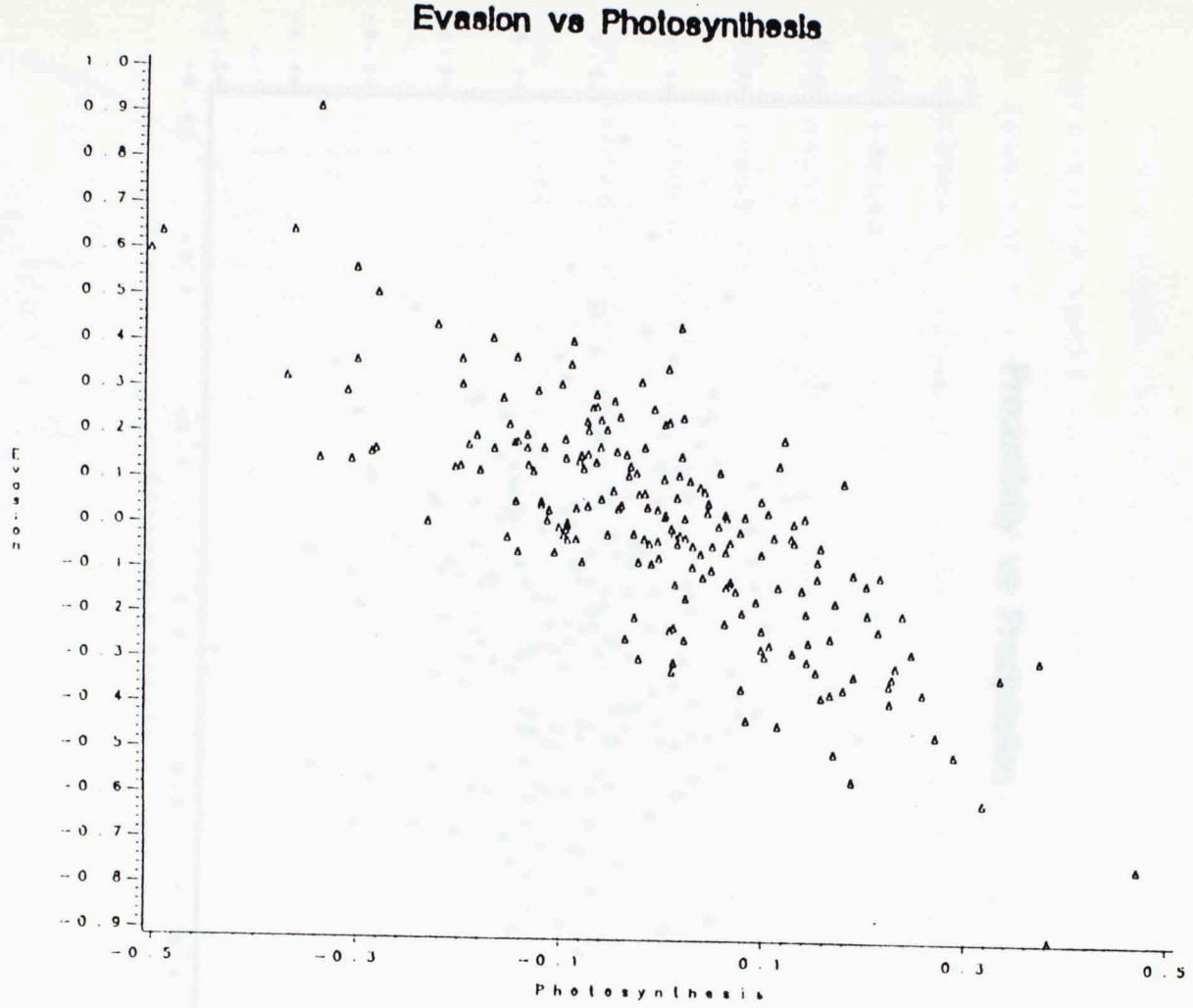


Figure 34: Evasion vs. Photosynthesis. A negative correlation.

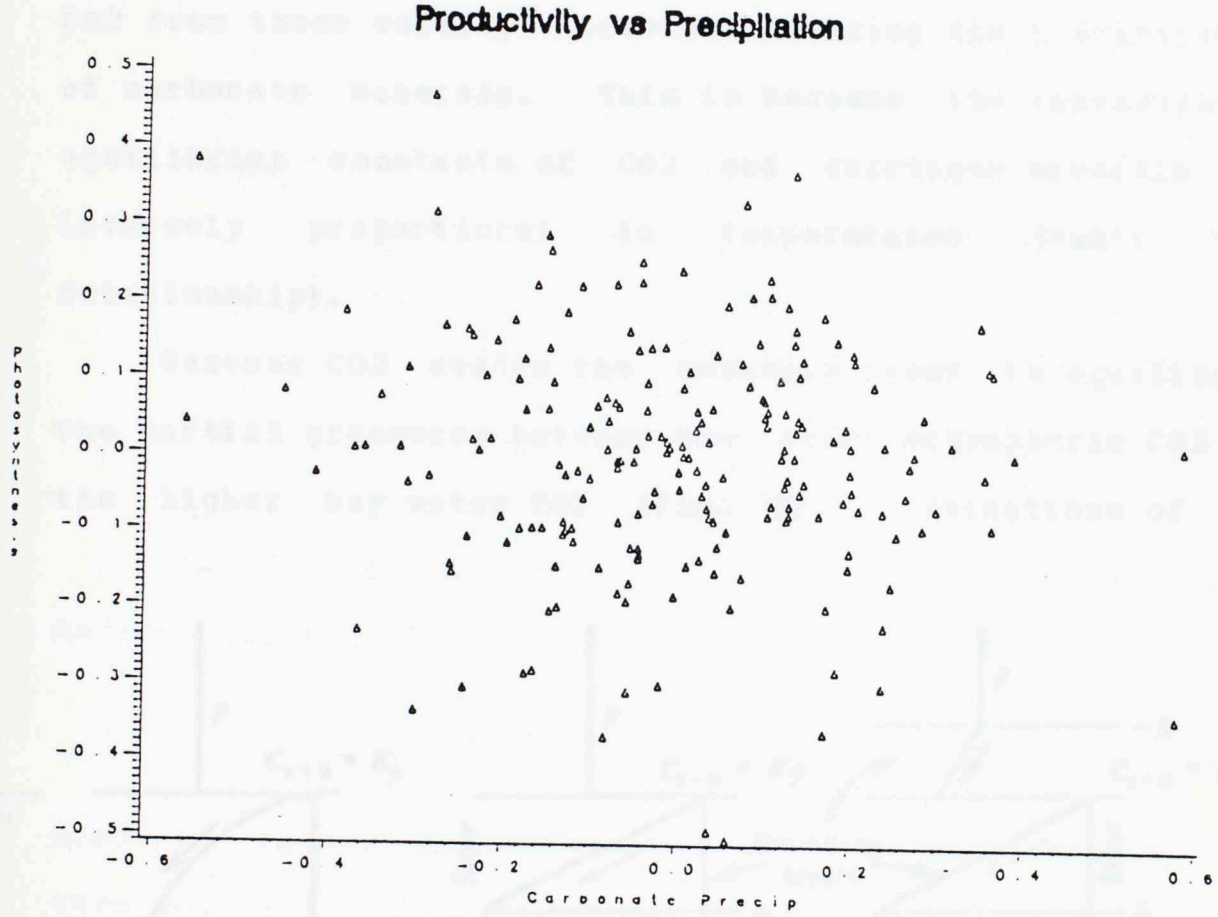


Figure 35: Photosynthesis vs. Precipitation. Unrelated variables.

by Schmalz and Swanson (1969) and others. Instead, precipitation is an inorganic event controlled by the evasion of CO2 to the atmosphere (Fig. 33).

Temperature changes from groundwater to surface water temperatures would also enhance the expulsion of dissolved CO2 from these waters, therefore favoring the precipitation of carbonate minerals. This is because the thermodynamic equilibrium constants of CO2 and carbonate minerals are inversely proportional to temperatures (van't Hoff relationship).

Gaseous CO2 evades the boundary layer to equilibrate the partial pressures between the lower atmospheric CO2 and the higher bay water CO2 (Fig. 36). Estimations of the

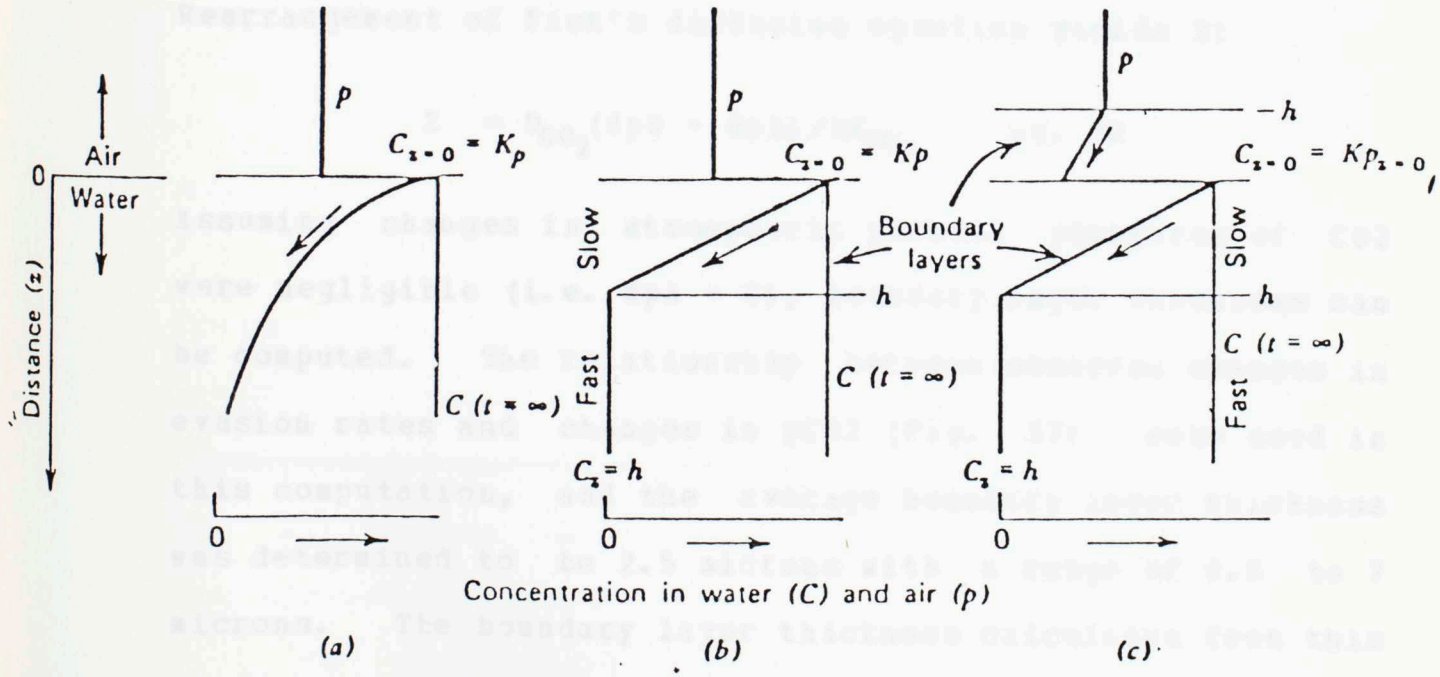


Figure 36: Three schematic models of transport across an air-water interface (from Lerman, 1979).

thickness of this boundary layer can be made by derivating Fick's diffusion equation:

$$dF_{CO_2} = D_{CO_2}(dpW - dpA)/Z \qquad \text{eq. 29}$$

where dF_{CO_2} = evasion of CO2 which occurs from $time_1$ to $time_2$ across the air-sea interface (in $mM/l/cm^2/sec/dt$),

D_{CO_2} = the diffusion constant of CO2 at 25 °C (1.9×10^{-5} cm^2/sec from Lerman, 1979),

dpW = the changes in partial pressure of CO2 in bay water (mM/l/dt),

dpA = the changes in atmospheric partial pressure of CO2 (mM/l/dt),

and Z = the thickness of the boundary layer (cm).

Rearrangement of Fick's diffusion equation yields Z:

$$Z = D_{CO_2}(dpW - dpA)/dF_{CO_2} \qquad \text{eq. 30}$$

Assuming changes in atmospheric partial pressures of CO2 were negligible (i.e. dpA = 0), boundary layer thickness can be computed. The relationship between observed changes in evasion rates and changes in pCO2 (Fig. 37) were used in this computation, and the average boundary layer thickness was determined to be 2.5 microns with a range of 0.8 to 7 microns. The boundary layer thickness calculated from this study compares within an order of magnitude to 17 μm (Broecker, 1974) and 50 um (Berner, 1971) determined from

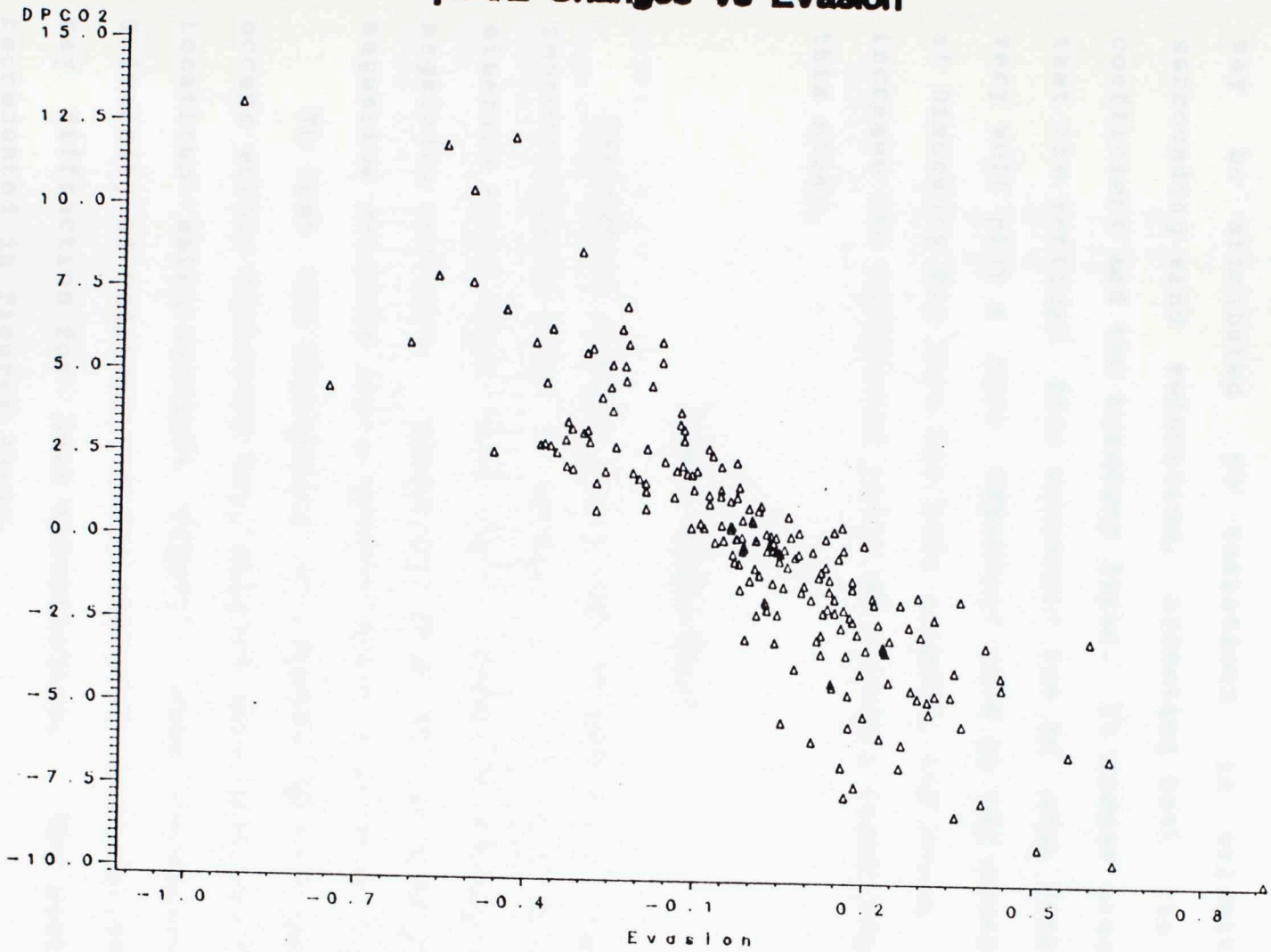


Figure 37: Partial pressures of CO2 vs. Evasion (flux-out of CO2 from Discovery Bay). pCO2 units are mM/l.

studies on seawater samples. The differences in boundary layer thicknesses between previous studies and this study may be attributed to variations in salinities and surrounding wind velocities, affecting both the diffusion coefficient and the boundary layer. It should also be noted that the vertical flux component due to eddy diffusion may very well play a more important role in the evasion of CO2 at Discovery Bay than has been assumed, and would, in turn, increase the calculated value of boundary layer thickness in this study.

X-Ray Diffraction

Saturation indices imply that preferential solution and reprecipitation might be occurring. Solution of carbonate minerals would favor those solid phase carbonates with high magnesium contents. Reprecipitation of the more stable low magnesium calcites and aragonite would also be expected.

To test the hypothesis on whether modern neomorphism occurs within Discovery Bay, samples were gathered from five locations using sediment traps. Upon returning to The University of Oklahoma, these sediments were analyzed by x-ray diffraction for bulk mineralogies. The results are represented in Figures 38-42.

The magnesium content of magnesium calcites systematically decreases with distance from the reef crest

Composition of Biogenic Mg-Calcites

Range	Mode	Specimen
0-7	1	Ostrea sp.
0-10	2	"Barnacle"
2-13	6	Diadema spine
6-18	11	Diadema test
10-19	16	"Sand Dollar"
9-32	17	Goniolithon sp.
6-34	19	Amphiroa r.
11-32	20	"

Table 5: Biogenic magnesium calcites indicating the variety and ranges of magnesium carbonate composed species. All data are in mole percent magnesium. (From Plummer and Mackenzie, 1974).

within the backreef lagoon (Fig. 43). The sources for high magnesium calcite observed in these sediments are probably biogenic in origin (see Table 5). Two hypotheses to explain the observed decrease in magnesium content with distance from the reef crest are:

1) the occurrence of organisms composed of high magnesium calcite near the reef crest, thereby, creating a bias in sediment composition;

and 2) sediments further from the reef crest represent older sediments, composed originally of high magnesium calcites, which have had more time to undergo neomorphism.

Although it is tempting to hypothesize that these

samples analyzed by x-ray diffraction suggest the neomorphism of high magnesium calcites to lower magnesium calcites and aragonite, more rigorous studies from a more dense sampling network which would include including petrography and spectroscopy would be required to verify the occurrence of neomorphism.

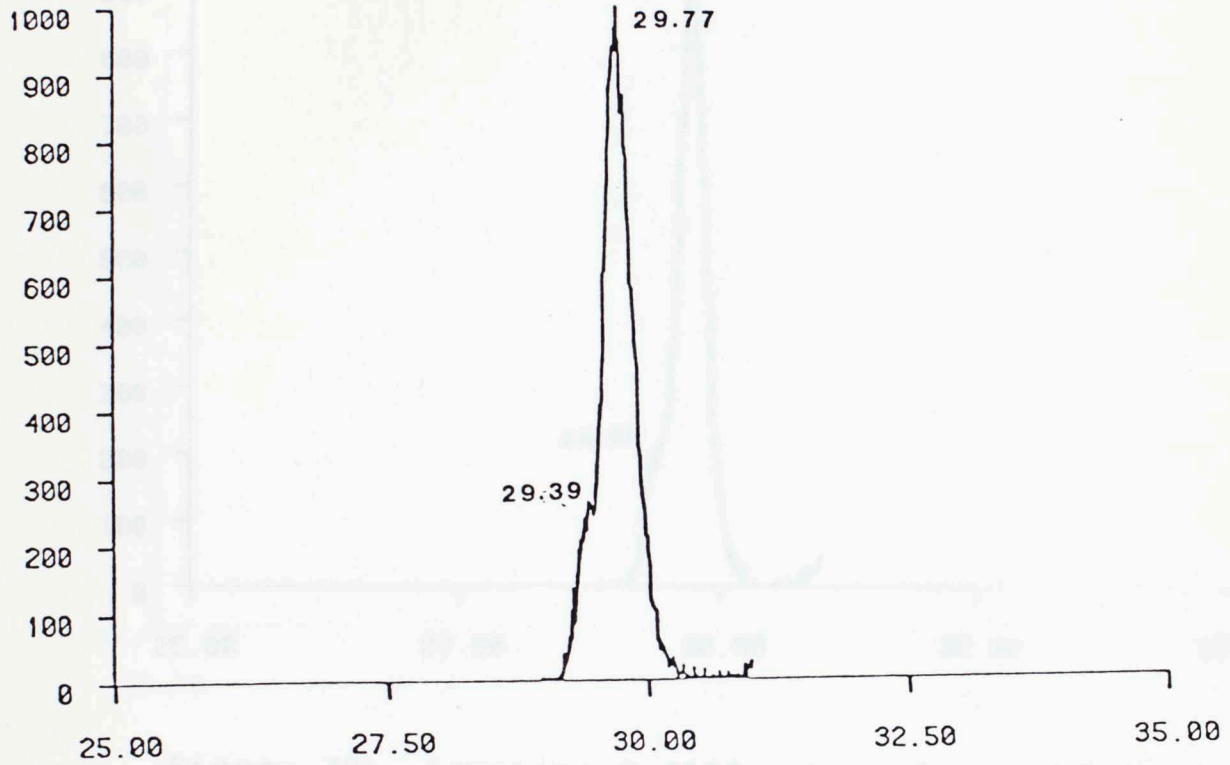


Figure 38: Location A (180 meters from reef crest).

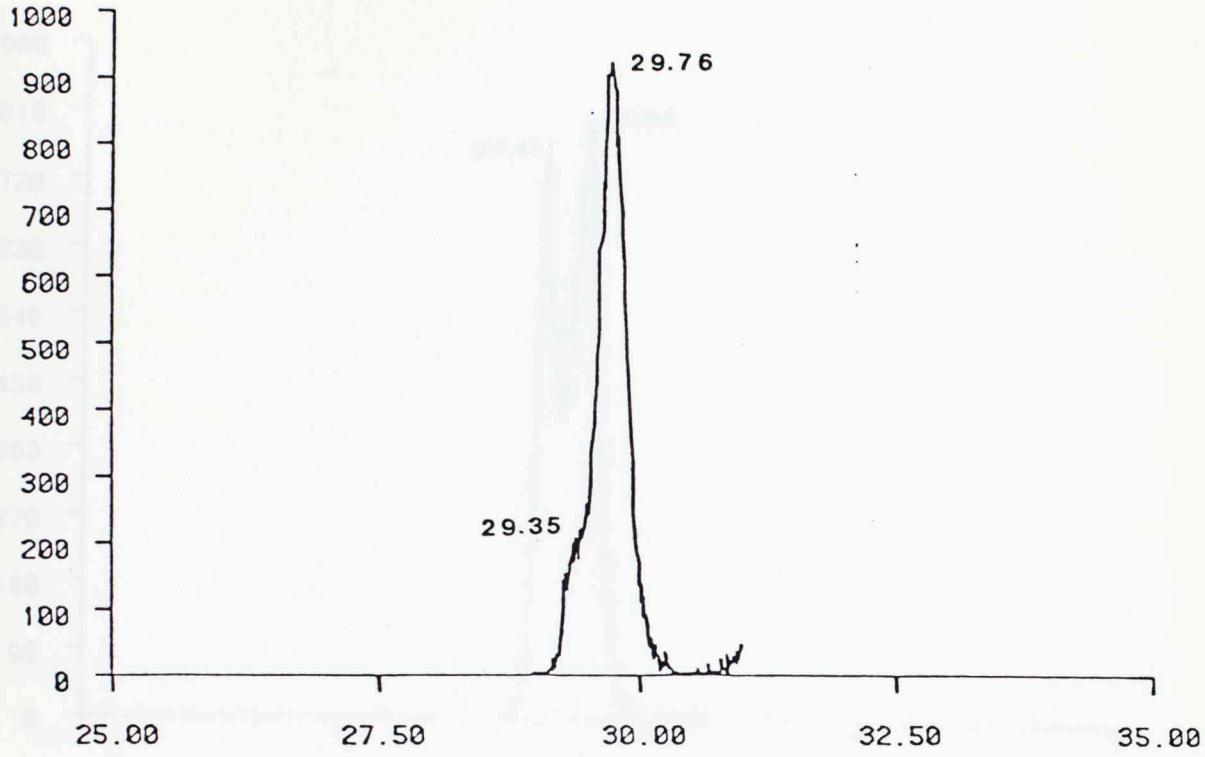


Figure 39: Location B (100 meters from reef crest).

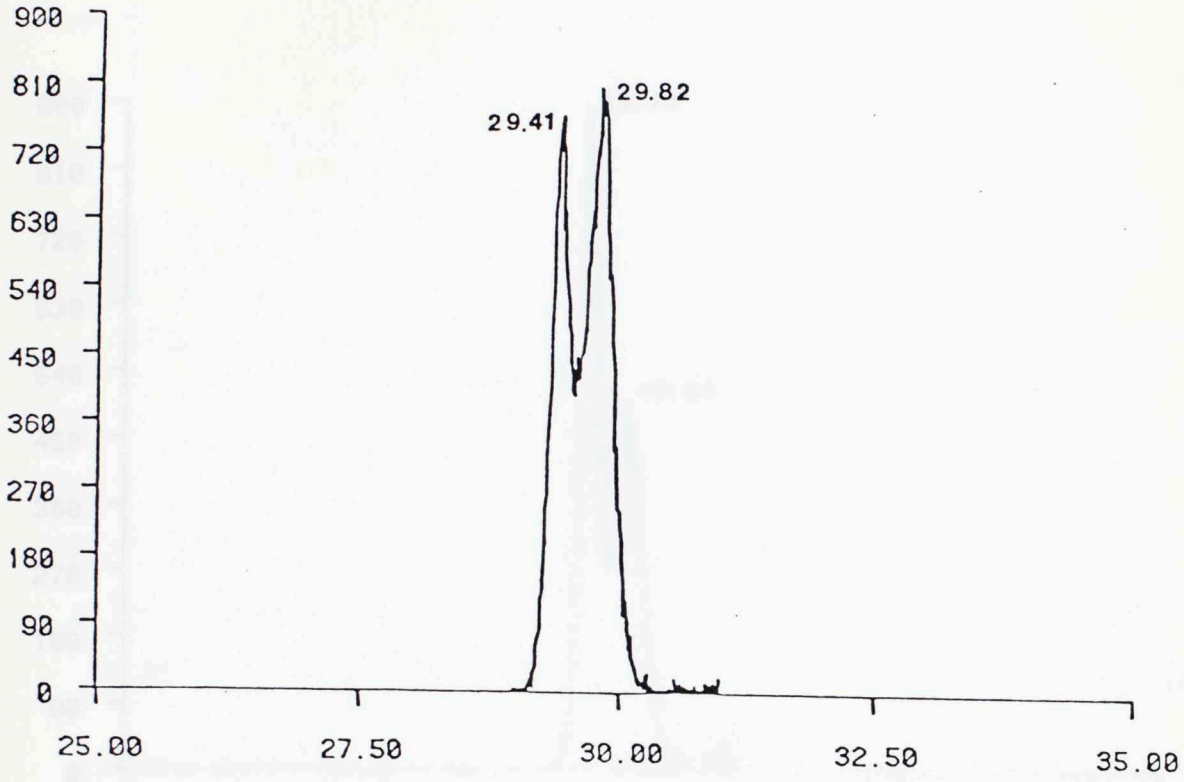


Figure 40: Location C (850 meters from reef crest).

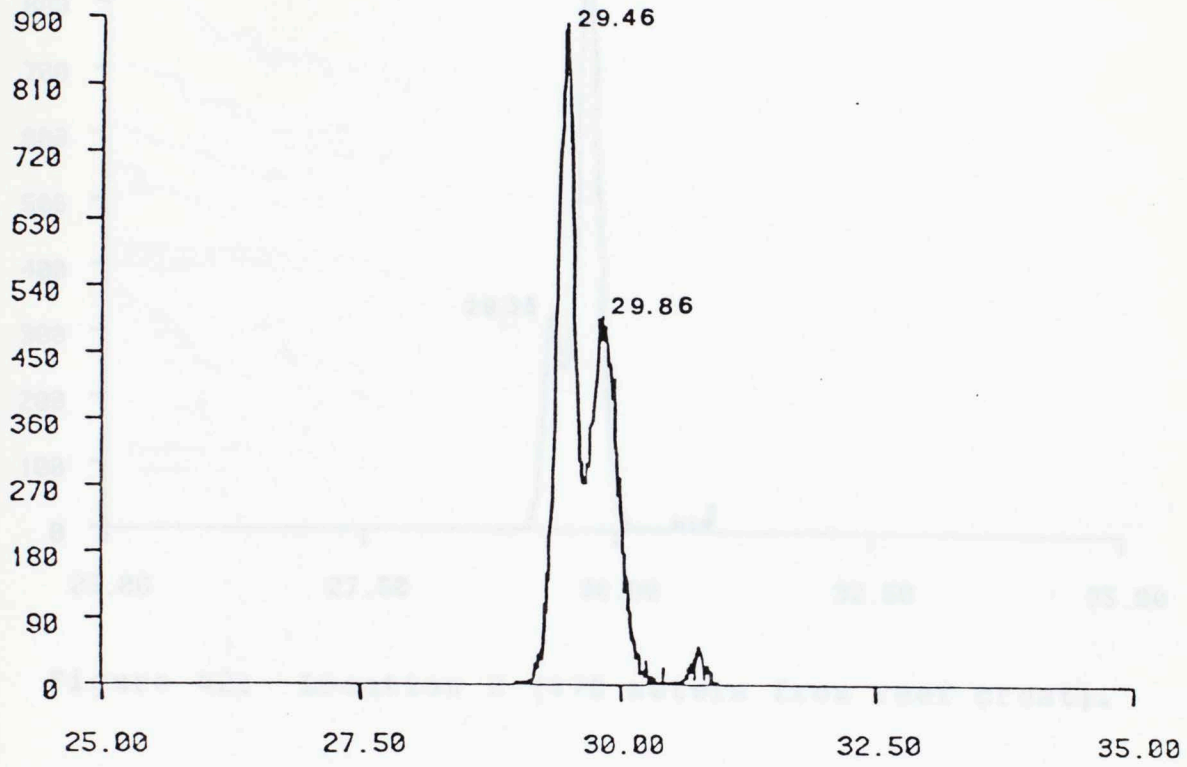


Figure 41: Location D (1150 meters from reef crest).

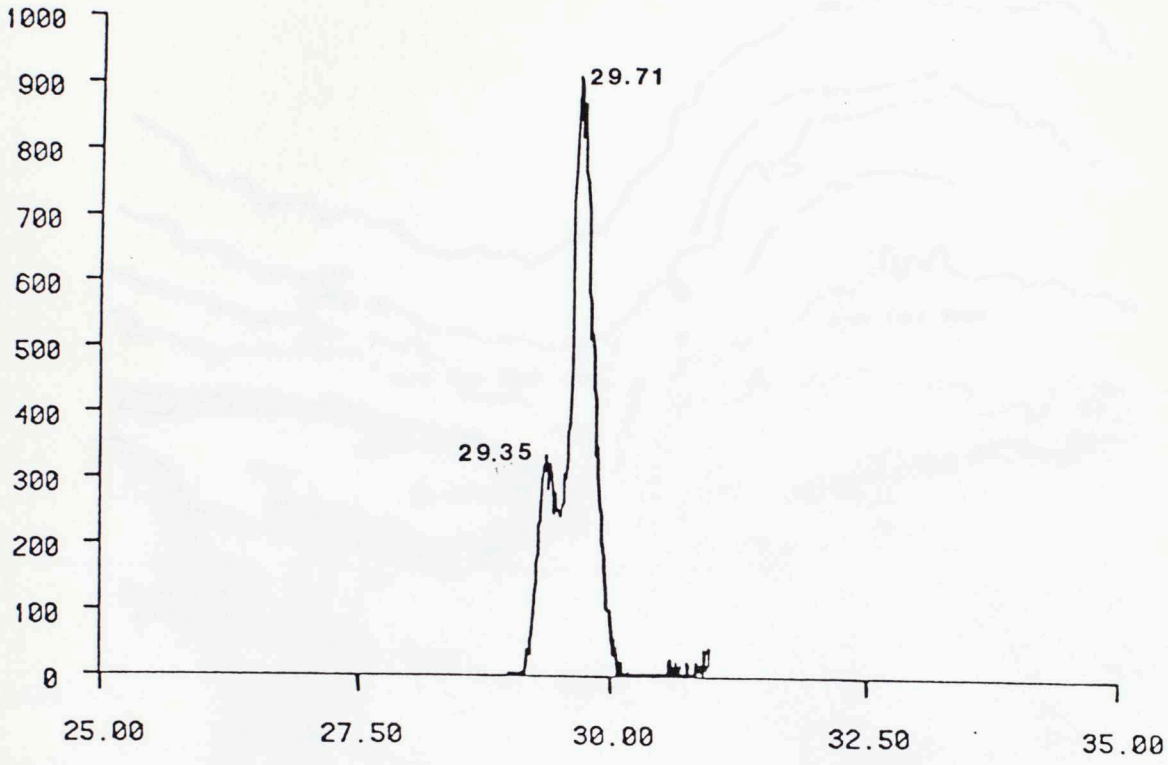


Figure 42: Location E (470 meters from reef crest).

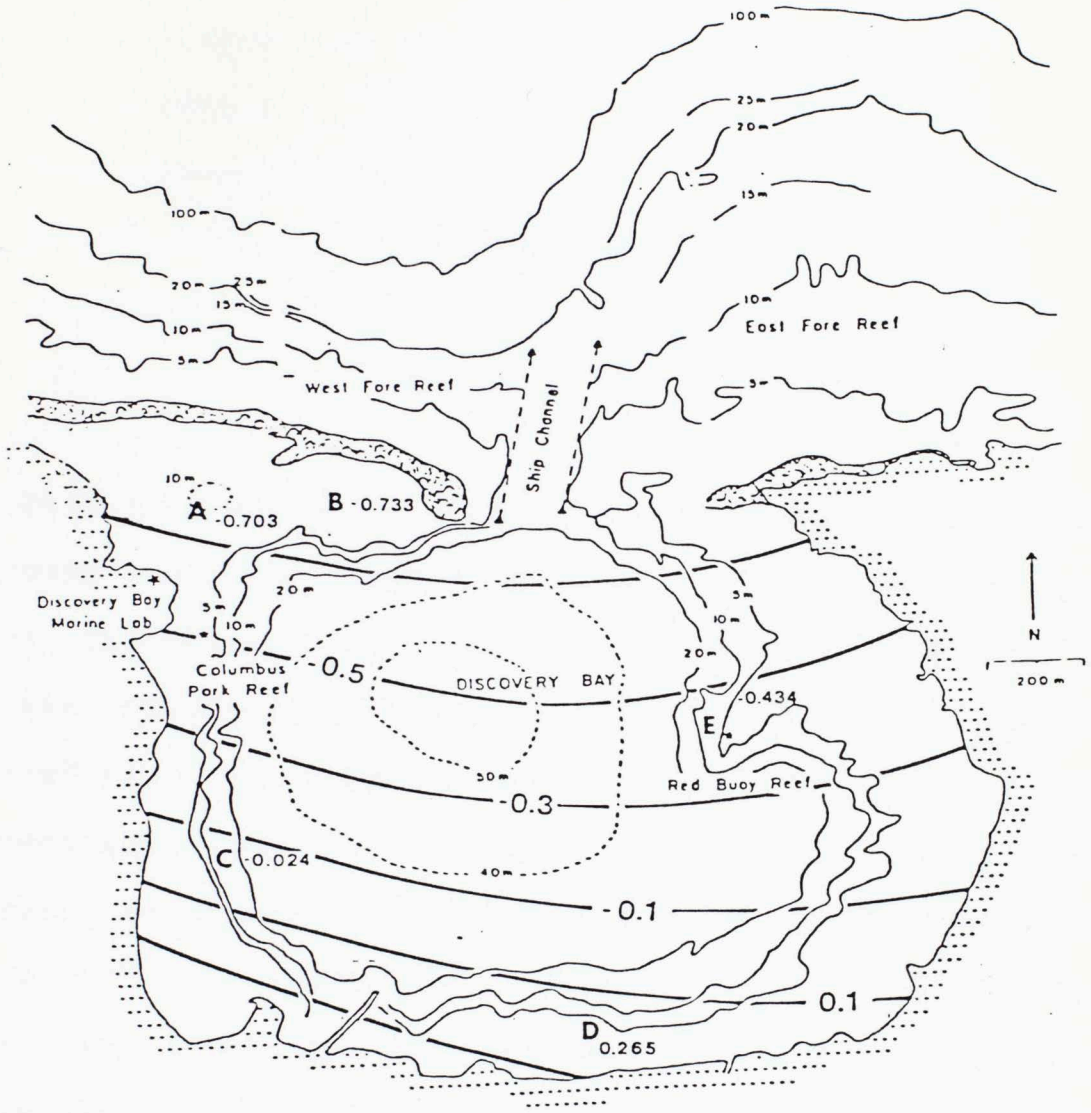


Figure 43: Schematic representation of the increasing ratio between low magnesium carbonate and high magnesium carbonate with distance from the reef crest. Values shown are log (low MgCO3/high MgCO3).

CHAPTER VI

CONCLUSIONS

From this study the following conclusions can be drawn regarding the carbon system of Discovery Bay, Jamaica.

1. The present-day rate of dissolution of Discovery Bay and the surrounding watershed is 6.48 x 10^3 kg of $CaCO_3/m^2/yr$, an enormous net export of $CaCO_3$ which, interestingly enough, is more than 4 times the amount necessary to dissolve the entire volume of Discovery Bay (7.7×10^{12} l) over 10,000 years if it were filled with solid $CaCO_3$ (2.7 kg/l). Although these structures were likely to have formed during Pleistocene, dissolution of these structures is still observed.

2. Net Respiration within the backreef region of Discovery Bay suggests that oxidative reactions of carbon dominate photosynthetic productivity. Photosynthesis-respiration is directly related to CO_2 evasion and invasion, but shows no relationship to precipitation and dissolution.

3. pCO_2 values within bay waters reach as high as 300% of atmospheric pCO_2 values due to the influence of

CO_2-charged groundwaters. The result is a large flux of CO_2 from the Discovery Bay system by means of evasion across the air-sea interface. This flux-out of CO_2 from bay waters enhances carbonate precipitation and shows a positive correlation with the precipitation occurring within the bay.

4. Using variations in the CO_2 gas exchange rates with associated variations in pCO_2 gradients between bay waters and the atmosphere, a diffusional average boundary layer thickness was calculated to be 2.5 microns.

5. Saturation states of Discovery Bay waters indicate a potential for preferential dissolution and precipitation of carbonate minerals with a varying range of magnesium content. If such geochemical biases are active, then neomorphism may account for part of the mineralogic distribution of sediments found within the bay.

As more is learned about lateral and vertical diffusion of the dissolved ionic species as well as sediment-seawater interaction within Discovery Bay, some of the assumptions made in this thesis will be replaced with applicable data to better define the carbon system of this modern tropical lagoon. Although the conclusions reached in this study may therefore be tentative, these results will contribute to future research at Discovery Bay.

Further research within Discovery Bay should be directed toward

1) a better understanding of the advective fluxes of groundwaters and their influence over longer time spans (in order to eliminate seasonal variations),

2) isotopic analyses for quantification of residence times (the length of time waters reside within the bay),

and 3) a thorough study of Discovery Bay sediments, including the origin of carbonate allochems and the mechanism and degree of their alteration.

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APPENDIX A

Theory of Electrode Potentiometry

One of the most widely used methods for the potentiometric determination of pH or hydrogen ion activity is the use of the glass electrode. The electrode potential was formerly believed to arise because the thin glass membrane was semipermeable, allowing hydrogen ions to diffuse through it, but now it is explained by an ion exchange process occurring at the membrane-solution interface. The glass membrane, when soaked in an aqueous solution, provides hydrated layers on either side of the membrane and allows for the necessary ion exchange process to occur. Among the advantages of the glass electrode are the following: the glass electrode is not affected by the presence of oxidizing or reducing agents, and the glass electrode may be used to measure the pH of small solution volumes.

The Ross pH electrode by Orion Research uses a redox internal system, a sophisticated pH half-cell designed so as to be virtually unaffected by temperature changes. The actual potential observed will be the sum of the separate pH potentials on either side of the glass membrane and reference half cells. Since the potentials inside the pH electrode are fixed by the filling solution and the

reference electrode potential is constant, any change in the potential of the electrode system will be due to changes in the pH of the solution measured. Electrode response is fast and precise, with measurements stable to 0.01 pH units.

The observation and understanding of problems with the ordinary glass membrane electrode has led to the development of cation-sensitive glass membranes. In very basic solutions (above pH 9) the hydrogen ion activity becomes very small, and the ordinary glass electrode begins to respond to other monovalent cations. With the ordinary glass membrane electrode, the ion exchange sites are negatively charged SiO^- sites, which, as a result of their high electrostatic field strength, have a strong affinity for hydrogen ions. An advancement in electrode ion selectivity was brought about by changing the composition of ordinary soda-lime glass by adding aluminum oxide ($AlOSi^-$). Because of their lower electrostatic field strength, these glass electrodes have a greater affinity for cations (e.g. Na^+, K^+, Li^+) than for hydrogen ions.

Another advancement in electrode ion selectivity was the application of liquid ion exchange systems. In addition to fixed-site SiO^- ion exchange membranes, mobil-site ion exchange materials such as liquid ion exchangers are used to monitor ions such as calcium and magnesium.

In the case of the calcium electrode, the interior is filled with a solution of calcium chloride of constant

composition into which a silver/silver chloride internal reference electrode is dipped. A porous membrane separates the external solution from the interior electrode compartment. This porous membrane is saturated with a water-immiscible liquid, di-n-octylphenylphosphonate, containing a calcium-selective ion exchanger, didecyl-phosphoric acid. The liquid flows by gravity from an adjacent reservoir so that the porous membrane is kept saturated with water immiscible organic material. Theoretical reproducibility is +/- 4%.

The solid state membrane electrode was used successfully to determine the activity of chloride in sample solutions. Solid state sensors replace the glass membrane with an ionically conducting membrane. Lattice defects within single crystal membranes (e.g. the fluoride sensitive membrane) and polycrystalline membranes (e.g. the sulfide and chloride sensitive membranes) allow the crystals to behave as semipermeable membranes. The internal reference is again produced by the silver/silver chloride ion half-cell of constant potential.

The sulfide ion electrode has as its active element a polycrystalline Ag2S membrane. The chloride ion sensitivity is developed by pressing the silver sulfide membrane into a silver chloride cast pellet to form a AgCl/Ag2S membrane. The solubility of silver chloride relative to silver sulfide differentiates the selectivity of these electrodes. Limited

by factors such as temperature fluctuations, drift, and noise, chloride electrode measurements are theoretically reproducible to +/- 2%.

A gas-sensing electrode used in this research is the Orion oxygen electrode. This electrode consists of a pair of polarized silver electrodes and an electrolyte separated from the sample by a gas-permeable membrane. Oxygen diffuses across the membrane and is reduced to hydroxyl ions at a silver cathode according to the reaction:

$$O2 + 2(H2O) + 4e^- \leftrightharpoons 4OH^-$$

The electrons necessary for this process are provided by a silver anode. Because the electrolyte contains chloride ions, this reaction occurs at the anode:

$$Ag^\circ + Cl^- \leftrightharpoons AgCl + e^-$$

At any given temperature, the current which flows between the cathode and anode is directly proportional to the level of oxygen outside the membrane.

Analytical Utilization of Electrodes

Analytical methods based on potentiometric measurements may be classified into two broad categories: direct potentiometry based on the Nernst equation and potentiometric titrations.

The primary purpose of potentiometric titrations for this study was to determine the total alkalinities of seawater samples. Also, concentrations of Cl^{-}, Ca^{+2}, and Mg^{+2} in samples of "average" seawater collected from the forereef were determined. These samples were later used as standards in direct potentiometry and, therefore, measurements of samples by potentiometric titration will be discussed first.

In potentiometric titrations, the potential existing between two electrodes - a reference electrode and an indicating electrode - immersed in solution is measured as the titrant is added. The measured potential varies quantitatively with the activity of the measured ion in the solution. For the determination of the total alkalinity within a sample, hydrogen ions are measured by the Ross electrode. Adding a predetermined molarity of hydrochloric acid (titrant) to baywater samples raises the hydrogen activity (lowers pH) through this buffered system. Determination of the final equivalence point allows for the calculation of total alkalinity.

Potentiometric titrations are both tedious and time consuming; therefore, where large numbers of determinations are performed, an apparatus which can automatically perform potentiometric titrations is an asset. The automatic titrator used for potentiometric titrations performed in this study is known as a differential titrator. This instrument adds titrant at a regulated rate and

electronically takes the derivative of the potential versus time curve that is produced. When the recorder is calibrated with the titrator, the time curve can represent the volume of titrant added. As discussed previously, the change in potential is proportional to the change in measured ion activity. The slope (i.e. the first derivative) of a titration curve is a maximum at the equivalence point. The instrument therefore utilizes the first derivative of the titration curve to detect the equivalence point or points.

As a result of the loss of CO2 to the atmosphere during titration, the operational end point of an acidimetric titration for alkalinity generally is not in exact agreement with the calculated equivalence point pH. However, the relative CO2 losses are negligible when minimal agitation with a magnetic stirrer is maintained throughout the course of the titration. Alkalinity was determined fairly precisely without extenuating precautions to less than +/- 3%.

Chloride, calcium, and magnesium ions were analyzed within "normal" seawater samples by using silver nitrate and EDTA as titrants. The corresponding potentiometric changes were monitored by the appropriate ion selective electrode. Quantitative analyses were also enhanced by the automatic titrimeter.

In direct potentiometry, based on the Nernst equation,

a graph of cell potential (Emv) versus ionic activity of a given ion is prepared using a series of standard solutions. This method of comparing the cell potential of a sample of unknown ionic activity with the cell potential of standards of known ionic activity is the calibration curve method. It should be pointed out, however, that the standard solutions were prepared with distilled water and therefore represent infinite dilution. The presence of appreciable quantities of other ions which are not present in the standards will alter the ionic strength of the unknown in comparison with the standards and will, therefore, affect the accuracy of the determination by directly altering the activity of the ion being determined.

As discussed previously, the concentrations of chloride, calcium, and magnesium ions were determined for the "normal" seawater samples. Projecting these concentrations onto the calibrated curve yields an associated ionic potential, assuming no interference from other ions. By monitoring these "average" seawater samples with appropriate ion selective electrodes, the ionic potential of the effective concentration is measured. The ratio of effective concentration to concentration is the activity coefficient for that ion. The following table compares the activity coefficients determined in this research to those determined by others. The similarities reflect the accuracy of these measurements by electrode

potentiometry.

Constituent	Measured γ	Other Seawater Measurements		
Ca^{+2}	0.27 +/- 0.04	0.28	0.20	0.24
Mg^{+2}	0.31 +/- 0.03	0.36	0.26	0.25
Cl^{-}	0.55 +/- 0.04	0.64		

R.M. Garrels and M. Thompson (1962). Amer. J. Sci. V.260,p.57.

M.E. Thompson (1966). Science, V.153,p.866.

R.A. Berner (1965). Geochim. Cosmochim. Acta, V.29,p.947.

R.A. Berner (1971). Chemical Sedimentology, McGraw-Hill, New York,p.48.

Table: Comparison of activity coefficients from this study relative to those measured and calculated by others.

APPENDIX B

Raw Data

RAW DATA

Discovery Bay, Jamaica

June/83

Loc & Diu	Lay	Time	pH	Alk (mM/l)	Temp (C)	pO2 (ppm)	{Ca} (mM/l)	{Mg+Ca} (cM/l)	{Cl} (dM/l)
1	1	11:30	8.07	2.772	28.4	7.86	1.880	1.276	0.221
1	1	13:35	8.15	0.458	29.5	7.60	0.349	0.152	0.069
1	1	15:15	8.07	2.054	29.0	7.63	0.759	0.778	0.145
1	1	17:25	7.94	2.138	28.5	7.64	1.294	0.901	0.192
1	1	19:30	7.91	2.325	28.5	7.40	1.072	0.718	0.132
1	1	21:50	7.86	2.107	28.5	7.08	0.773	0.845	0.172
1	1	23:40	8.03	2.352	28.0	6.83	1.283	0.405	0.138
1	2	1:40	8.06	2.616	27.5	6.02	2.562	1.377	0.370
1	2	4:45	8.11	2.332	26.7	6.55	1.093	0.724	0.226
1	2	7:20	8.06	0.979	27.2	6.98	0.366	0.228	0.075
1	2	10:40	7.93	2.757	28.4	7.10	2.481	1.560	0.356
1	2	13:05	8.04	2.845	29.5	7.65	2.117	1.398	0.351
1	2	15:30	7.96	2.725	29.0	7.30	2.159	1.373	0.376
1	2	18:05	7.98	2.841	28.2	8.13	2.202	1.589	0.356
1	2	21:40	7.92	2.633	27.9	7.55	2.528	1.532	0.427

Loc Lay & Diu	Time ----	pH --	Alk (mM/l)	Temp (C)	pO2 (ppm)	{Ca} (mM/l)	{Mg+Ca} {cM/l}	{Cl} {dM/l}
1 2 1	11:30	8.05	3.009	28.6	7.70	2.387	1.129	0.360
1 2 1	13:35	8.12	2.268	29.6	7.63	1.689	1.062	0.257
1 2 1	15:15	8.06	2.773	28.8	7.48	1.606	1.560	0.200
1 2 1	17:25	7.99	2.231	28.6	7.61	0.767	0.507	0.156
1 2 1	19:30	7.95	2.961	28.5	7.75	2.000	1.180	0.329
1 2 1	21:50	7.95	3.077	28.5	6.61	1.966	0.846	0.315
1 2 1	23:40	8.02	2.206	27.9	6.76	1.449	0.961	0.231
1 2 2	1:40	8.12	2.273	27.7	6.68	1.216	0.787	0.210
1 2 2	4:45	8.09	2.002	26.5	6.59	1.149	0.884	0.174
1 2 2	7:20	8.09	1.461	27.3	6.96	0.630	0.279	0.095
1 2 2	10:40	8.03	2.775	28.4	7.17	1.673	1.715	0.299
1 2 2	13:05	8.10	2.761	29.5	7.62	2.291	1.477	0.313
1 2 2	15:30	8.06	1.754	29.0	7.86	1.171	0.570	0.192
1 2 2	18:05	8.09	2.617	28.3	8.39	2.035	1.373	0.336
1 2 2	21:40	7.98	2.573	27.9	8.10	2.579	1.679	0.376
1 3 1	11:30	8.08	1.420	28.8	7.58	0.246	0.167	0.086
1 3 1	13:35	8.11	2.303	29.0	7.92	1.387	0.905	0.225
1 3 1	15:15	8.14	1.749	28.8	7.93	0.773	0.954	0.190
1 3 1	17:25	7.97	2.166	28.6	7.64	0.820	0.427	0.151
1 3 1	19:30	7.93	2.316	28.5	7.98	1.362	1.374	0.227
1 3 1	21:50	7.99	1.729	28.6	7.10	0.811	0.490	0.166
1 3 1	23:40	8.05	1.990	27.8	6.82	1.844	1.246	0.287

Loc Lay & Diu	Time ----	pH --	Alk (mM/l)	Temp (C)	pO2 (ppm)	{Ca} (mM/l)	{Mg+Ca} {cM/l)	{Cl} {dM/l)
1 3 2	1:40	8.12	2.383	27.5	6.70	2.562	1.522	0.328
1 3 2	4:45	8.15	2.632	26.4	6.67	1.984	1.928	0.345
1 3 2	7:20	8.09	2.378	27.3	6.98	0.775	0.419	0.168
1 3 2	10:40	8.03	2.747	28.4	7.05	2.077	1.182	0.280
1 3 2	13:05	8.16	1.938	29.4	8.45	2.682	1.477	0.376
1 3 2	15:30	8.14	2.529	29.1	8.75	2.479	1.398	0.356
1 3 2	18:05	8.07	2.771	28.2	8.10	2.579	1.504	0.356
1 3 2	21:40	7.98	2.309	28.0	7.79	2.479	1.276	0.336
1 4 1	11:30	8.08	2.659	29.0	7.52	1.984	1.891	0.322
1 4 1	13:35	8.07	2.369	29.3	7.59	1.327	0.870	0.219
1 4 1	15:15	8.08	2.809	28.7	7.51	2.296	1.522	0.337
1 4 1	17:25	7.95	2.249	28.5	7.72	0.920	1.014	0.188
1 4 1	19:30	7.94	2.676	28.4	7.85	0.931	0.697	0.173
1 4 1	21:50	7.96	2.401	28.4	6.71	0.843	0.676	0.132
1 4 1	23:40	8.06	2.877	27.8	6.70	1.307	1.352	0.294
1 4 2	1:40	8.06	2.298	27.7	6.65	0.678	0.828	0.193
1 4 2	4:45	8.12	1.618	26.5	6.43	1.292	1.122	0.174
1 4 2	7:20	8.10	2.261	27.2	6.74	1.216	0.713	0.254
1 4 2	10:40	8.01	2.644	28.4	7.14	2.063	1.178	0.272
1 4 2	13:05	8.08	3.076	29.7	7.24	2.159	1.207	0.305
1 4 2	15:30	8.09	2.681	29.1	8.10	2.159	1.207	0.361
1 4 2	18:05	8.04	2.685	28.2	8.04	2.159	1.348	0.318

Loc Lay & Diu	Time	pH	Alk (mM/l)	Temp (C)	pO2 (ppm)	{Ca} (mM/l)	{Mg+Ca} (cM/l)	{Cl} (dM/l)
1 4 2	21:40	7.96	1.998	27.8	7.03	1.995	1.373	0.331
2 1 1	11:30	8.14	2.440	28.6	6.93	2.226	1.229	0.300
2 1 1	13:35	8.14	2.567	29.9	8.02	2.150	1.350	0.298
2 1 1	15:15	8.12	1.979	28.7	8.12	1.852	1.524	0.327
2 1 1	17:25	8.02	2.685	28.5	7.86	2.119	1.276	0.305
2 1 1	19:30	7.95	2.445	28.4	8.01	0.843	0.733	0.185
2 1 1	21:50	7.99	2.825	28.8	7.04	2.037	1.398	0.305
2 1 1	23:40	8.06	2.841	27.7	6.68	2.293	1.710	0.346
2 1 2	1:40	8.12	2.473	27.6	6.20	2.531	1.504	0.351
2 1 2	4:45	8.12	2.238	26.6	6.19	2.063	1.178	0.175
2 1 2	7:20	8.09	2.353	27.2	6.50	1.507	1.329	0.253
2 1 2	10:40	8.02	2.584	28.5	6.96	2.439	1.466	0.313
2 1 2	13:05	8.20	2.769	29.7	8.78	2.383	1.373	0.371
2 1 2	15:30	8.16	2.565	29.1	7.30	2.336	1.424	0.336
2 1 2	18:05	8.10	1.318	28.3	8.23	1.574	0.969	0.322
2 1 2	21:40	7.92	2.505	27.7	6.28	2.682	1.560	0.351
2 2 1	11:30	8.12	2.150	28.6	6.85	0.417	0.325	0.243
2 2 1	13:35	8.09	2.455	29.7	8.52	1.327	0.961	0.228
2 2 1	15:15	8.13	2.538	28.7	7.90	3.317	1.089	0.309
2 2 1	17:25	8.02	2.118	28.5	7.85	1.169	1.583	0.274
2 2 1	19:30	7.98	2.550	28.4	8.35	1.545	0.901	0.257
2 2 1	21:50	7.98	2.432	28.4	7.18	1.900	1.200	0.300

Loc Lay & Diu	Time ----	pH --	Alk (mM/l)	Temp (C)	pO2 (ppm)	{Ca} (mM/l	{Mg+Ca} (cM/l)	{Cl} (dM/l)
2 2 1	23:40	8.06	1.498	27.7	6.92	0.939	0.397	0.171
2 2 2	1:40	8.15	2.337	27.5	6.95	1.226	0.972	0.208
2 2 2	4:45	8.14	2.272	26.5	6.46	1.090	0.561	0.199
2 2 2	7:20	8.11	1.507	27.3	6.85	0.529	0.247	0.272
2 2 2	10:40	7.98	2.094	28.5	6.97	2.581	1.504	0.341
2 2 2	13:05	8.16	2.861	29.6	6.73	2.246	1.373	0.346
2 2 2	15:30	8.11	2.589	29.2	8.48	2.383	1.450	0.341
2 2 2	18:05	8.07	2.429	28.2	7.69	2.736	1.504	0.381
2 2 2	21:40	7.91	2.829	28.0	7.49	2.528	1.560	0.427
2 3 1	11:30	8.18	2.319	28.9	6.85	1.226	1.329	0.257
2 3 1	13:35	8.12	2.434	30.0	7.48	1.507	0.864	0.250
2 3 1	15:15	8.09	2.291	28.7	7.64	0.977	0.583	0.197
2 3 1	17:25	7.99	2.637	28.5	7.53	1.486	1.082	0.237
2 3 1	19:30	7.97	2.277	28.4	7.87	1.569	0.664	0.175
2 3 1	21:50	8.02	2.433	28.5	7.07	1.640	1.122	0.261
2 3 1	23:40	8.05	2.350	27.7	6.44	1.118	0.683	0.202
2 3 2	1:40	8.15	2.302	27.5	6.90	1.254	1.410	0.236
2 3 2	4:45	8.13	2.420	26.8	6.15	1.689	1.800	0.370
2 3 2	7:20	8.10	2.818	27.5	7.04	2.126	1.966	0.318
2 3 2	10:40	7.93	2.547	27.6	7.18	1.673	1.715	0.277
2 3 2	13:05	8.06	2.721	29.7	7.04	2.159	1.207	0.313
2 3 2	15:30	8.10	2.725	29.3	8.06	1.995	1.230	0.351

Loc Lay & Diu	Time ----	pH --	Alk (mM/l)	Temp (C)	pO2 (ppm)	{Ca} (mM/l)	{Mg+Ca} (cM/l)	{Cl} (dM/l)
2 3 2	18:05	8.04	2.897	28.2	7.97	1.880	1.230	0.305
2 3 2	21:40	7.95	2.605	28.3	7.55	2.202	1.323	0.300
3 1 1	11:30	8.15	2.269	28.7	7.27	1.196	0.951	0.174
3 1 1	13:35	8.13	2.400	29.3	7.13	0.811	0.710	0.161
3 1 1	15:15	8.12	2.565	28.8	7.62	2.385	1.450	0.356
3 1 1	17:25	8.03	2.351	28.7	7.64	1.220	0.792	0.237
3 1 1	19:30	7.98	1.964	28.5	7.13	1.119	1.168	0.182
3 1 1	21:50	8.01	2.981	28.6	6.82	1.307	1.070	0.286
3 1 1	23:40	8.08	2.321	28.0	7.01	1.544	1.450	0.194
3 1 2	1:40	8.17	2.263	27.7	6.98	1.271	0.836	0.237
3 1 2	4:45	8.18	2.360	27.6	.	1.400	0.770	0.230
3 1 2	7:20	8.13	2.385	27.6	7.14	0.552	0.284	0.180
3 1 2	10:40	8.05	2.544	28.7	7.03	2.175	1.800	0.351
3 1 2	13:05	8.15	2.789	29.7	7.49	2.383	1.299	0.336
3 1 2	15:30	8.17	2.749	29.5	9.01	2.336	1.373	0.387
3 1 2	18:05	8.07	2.845	28.8	7.19	2.291	1.619	0.439
3 1 2	21:40	7.93	2.613	28.2	6.96	2.336	1.398	0.305
3 2 1	11:30	8.13	2.342	28.8	7.38	1.486	0.845	0.155
3 2 1	13:35	8.15	2.590	29.4	7.11	2.452	1.297	0.250
3 2 1	15:15	8.11	2.692	28.9	7.76	2.159	1.143	0.327
3 2 1	17:25	8.03	2.480	28.8	7.47	1.769	1.460	0.321
3 2 1	19:30	7.97	2.464	28.6	7.68	1.614	1.649	0.280

Loc Lay & Diu	Time ----	pH --	Alk (mM/l)	Temp (C)	pO2 (ppm)	{Ca} (mM/l)	{Mg+Ca} (cM/l)	{Cl} (dM/l)
3 2 1	21:50	8.02	2.372	28.6	7.04	1.653	0.888	0.250
3 2 1	23:40	8.09	2.352	28.0	6.96	1.344	1.649	0.296
3 2 2	1:40	8.16	2.200	27.9	6.98	2.376	1.649	0.256
3 2 2	4:45	8.17	2.160	27.7	.	1.200	0.600	0.210
3 2 2	7:20	8.15	2.424	27.9	7.36	1.727	0.742	0.197
3 2 2	10:40	8.03	2.509	28.7	7.03	2.043	1.402	0.355
3 2 2	13:05	8.17	2.134	29.7	7.84	2.430	1.619	0.366
3 2 2	15:30	8.16	2.847	29.4	7.92	2.336	1.299	0.366
3 2 2	18:05	8.04	2.741	28.9	7.31	2.430	1.532	0.327
3 2 2	21:40	7.98	2.565	28.2	7.32	2.383	1.424	0.346
3 3 1	11:30	8.10	2.620	29.0	7.25	3.315	0.809	0.304
3 3 1	13:35	8.17	2.465	29.5	7.68	0.921	0.549	0.208
3 3 1	15:15	8.13	2.284	28.8	7.89	2.797	1.377	0.229
3 3 1	17:25	8.00	2.735	28.5	7.58	2.175	1.329	0.313
3 3 1	19:30	7.96	2.158	28.6	7.81	1.294	0.822	0.212
3 3 1	21:50	8.02	2.636	28.5	6.83	2.198	1.616	0.365
3 3 1	23:40	8.09	2.433	28.0	7.05	0.804	0.720	0.240
3 3 2	1:40	8.11	2.650	27.7	6.45	2.562	1.682	0.346
3 3 2	4:45	8.18	2.500	27.4	.	1.700	0.800	0.250
3 3 2	7:20	8.14	2.346	27.9	.	0.745	1.202	0.232
3 3 2	10:40	8.02	2.877	28.8	7.09	2.430	1.559	0.250
3 3 2	13:05	8.19	2.737	29.9	7.93	2.430	1.450	0.346

Loc & Diu	Loc	Time	pH	Alk (mM/l)	Temp (C)	pO2 (ppm)	{Ca} (mM/l)	{Mg+Ca} (cM/l)	{Cl} (dM/l)
3	3 2	15:30	8.12	2.897	29.3	7.68	2.479	1.398	0.356
3	3 2	18:05	8.05	2.753	29.0	7.41	2.200	1.400	0.350
3	3 2	21:40	7.97	2.865	28.4	7.29	2.159	1.504	0.371
4	1 1	15:20	8.19	2.110	31.0	7.64	2.164	1.480	0.339
4	1 1	18:15	8.15	2.341	29.9	7.48	2.383	1.748	0.340
4	1 1	21:15	8.22	2.501	29.8	7.35	2.158	1.495	0.354
4	1 2	0:10	8.24	2.605	28.3	7.44	2.430	1.617	0.356
4	1 2	3:10	8.06	2.477	29.2	7.32	2.034	1.230	0.356
4	1 2	7:25	8.25	1.874	28.6	7.44	2.433	1.534	0.323
4	1 2	11:20	8.26	2.461	30.5	8.21	2.034	1.254	0.351
4	1 2	15:10	8.17	2.529	31.1	8.28	1.994	1.555	0.329
4	2 1	15:20	8.22	2.437	30.4	7.91	2.433	1.649	0.345
4	2 1	18:15	8.17	2.469	29.7	7.54	1.717	1.843	0.342
4	2 1	21:15	8.25	2.409	28.7	7.38	2.388	1.680	0.405
4	2 2	0:10	8.24	2.108	28.6	7.56	2.295	1.562	0.339
4	2 2	3:10	8.26	2.026	28.2	7.05	2.002	1.453	0.297
4	2 2	7:25	8.25	2.285	28.7	7.46	2.158	1.206	0.300
4	2 2	11:20	8.25	2.533	30.2	8.32	1.955	1.206	0.304
4	2 2	15:10	8.27	2.561	30.6	8.03	2.210	1.649	0.415
4	3 1	15:20	8.20	2.483	31.1	7.43	1.892	1.913	0.368
4	3 1	18:15	8.18	2.273	30.0	7.55	2.116	1.356	0.304
4	3 1	21:15	8.23	2.222	29.6	7.28	2.297	1.809	0.318

Loc Lay & Diu	Time ----	pH --	Alk (mM/l)	Temp (C)	pO2 (ppm)	{Ca} (mM/l)	{Mg+Ca} (cM/l)	{Cl} (dM/l)
4 3 2	0:10	8.26	2.481	28.4	7.47	2.201	1.466	0.329
4 3 2	3:10	8.24	2.541	28.9	6.83	2.034	1.466	0.314
4 3 2	7:25	8.25	2.685	28.6	7.28	2.034	1.304	0.319
4 3 2	11:20	8.24	2.034	30.1	8.15	1.397	0.899	0.290
4 3 2	15:10	8.25	2.233	30.5	8.00	2.034	1.383	0.324
4 4 1	15:20	8.21	2.513	30.4	7.51	2.126	1.649	0.351
4 4 1	18:15	8.20	2.805	29.9	7.61	2.041	1.534	0.356
4 4 1	21:15	8.25	2.341	29.3	7.58	2.290	1.383	0.340
4 4 2	0:10	8.24	2.533	28.7	7.52	1.917	1.230	0.368
4 4 2	3:10	8.25	2.893	28.5	6.98	2.126	1.743	0.396
4 4 2	7:25	8.23	2.573	28.8	7.12	2.122	1.453	0.328
4 4 2	11:20	8.22	2.230	30.3	8.09	1.900	1.400	0.280
4 4 2	15:10	8.24	2.301	31.0	8.10	1.967	1.447	0.289
4 5 1	15:20	8.20	2.640	31.1	.	2.100	1.400	0.330
4 5 1	18:15	8.20	2.797	30.1	7.54	2.100	1.400	0.340
4 5 1	21:15	8.23	2.894	29.9	7.46	2.005	1.588	0.351
4 5 2	0:10	8.25	2.589	28.5	7.40	1.994	1.279	0.362
4 5 2	3:10	8.23	2.825	29.4	6.85	1.651	1.559	0.342
4 5 2	7:25	8.23	2.545	28.8	7.02	2.201	1.466	0.329
4 5 2	11:20	8.23	2.877	30.1	7.89	2.034	1.330	0.329
4 5 2	15:10	8.24	2.757	31.4	8.01	2.245	1.383	0.319
5 1 1	15:20	8.22	2.790	30.8	7.90	2.400	1.600	0.340

Loc Lay & Diu	Time ----	pH --	Alk (mM/l)	Temp (C)	pO2 (ppm)	{Ca} (mM/l)	{Mg+Ca} (cM/l)	{Cl} (dM/l)
5 1 1	18:15	8.19	2.605	30.4	8.14	2.386	1.534	0.333
5 1 1	21:15	8.23	2.084	29.7	7.25	2.201	1.410	0.345
5 1 2	0:10	8.22	2.723	28.9	6.74	2.116	1.466	0.324
5 1 2	3:10	8.24	2.297	28.5	6.76	1.994	1.304	0.356
5 1 2	7:25	8.24	1.828	28.8	7.04	1.684	1.224	0.311
5 1 2	11:20	8.24	2.389	30.4	8.31	1.994	1.304	0.304
5 1 2	15:10	8.25	2.146	31.6	8.70	2.253	1.843	0.311
5 2 1	15:20	8.24	2.213	30.7	8.07	2.340	1.649	0.345
5 2 1	18:15	8.23	2.919	30.4	8.20	2.253	1.843	0.386
5 2 1	21:15	8.25	2.150	29.1	7.52	2.340	1.534	0.339
5 2 2	0:10	8.26	2.389	28.4	6.99	1.955	1.555	0.351
5 2 2	3:10	8.24	2.650	29.9	7.02	1.956	1.276	0.313
5 2 2	7:25	8.25	2.357	28.9	7.32	2.122	1.427	0.333
5 2 2	11:20	8.22	2.038	30.3	7.68	2.253	1.680	0.318
5 2 2	15:10	8.26	2.413	31.8	8.60	2.075	1.585	0.351
5 3 1	15:20	8.24	1.982	31.0	7.92	2.075	1.304	0.362
5 3 1	18:15	8.22	2.799	30.8	8.13	2.253	1.530	0.318
5 3 1	21:15	8.20	2.345	29.7	7.35	2.483	1.618	0.296
5 3 2	0:10	8.23	2.166	28.9	7.03	2.340	1.562	0.333
5 3 2	3:10	8.25	2.138	28.7	6.98	2.158	1.617	0.319
5 3 2	7:25	8.25	2.281	29.0	7.11	2.041	1.377	0.323
5 3 2	11:20	8.20	2.126	30.4	7.70	2.116	1.617	0.356

Loc Lay & Diu	Time ----	pH --	Alk (mM/l)	Temp (C)	pO2 (ppm)	{Ca} (mM/l)	{Mg+Ca} (cM/l)	{Cl} (dM/l)
5 3 2	15:10	8.27	2.517	31.3	8.75	1.917	1.356	0.319
6 1 1	15:20	8.35	2.349	30.7	8.21	2.336	1.279	0.340
6 1 1	18:15	8.29	2.269	30.6	8.40	2.435	1.843	0.405
6 1 1	21:15	8.16	2.621	29.5	7.12	2.383	1.410	0.379
6 1 2	0:10	8.25	2.540	28.6	7.01	2.200	1.500	0.350
6 1 2	3:10	8.15	2.292	29.1	5.85	2.075	1.681	0.314
6 1 2	7:25	8.16	2.339	29.1	6.47	1.815	1.427	0.356
6 1 2	11:20	8.27	2.166	30.2	8.58	2.295	1.590	0.339
6 1 2	15:10	8.32	2.361	32.1	7.89	1.955	1.356	0.329
6 2 1	15:20	8.24	2.761	31.0	8.14	2.290	1.383	0.319
6 2 1	18:15	8.23	2.697	30.9	8.03	2.164	1.506	0.362
6 2 1	21:15	8.15	2.577	29.6	7.42	2.342	1.649	0.377
6 2 2	0:10	8.24	2.417	29.1	6.95	1.917	1.330	0.356
6 2 2	3:10	8.25	2.877	28.8	6.96	2.290	1.206	0.319
6 2 2	7:25	8.25	2.477	29.0	7.12	2.075	1.254	0.319
6 2 2	11:20	8.21	2.110	31.1	7.87	1.955	1.230	0.319
6 2 2	15:10	8.25	2.269	31.3	8.01	1.785	1.319	0.256
6 3 1	15:20	8.26	2.361	31.0	8.17	2.207	1.506	0.351
6 3 1	18:15	8.23	2.134	30.7	7.99	2.340	1.590	0.339
6 3 1	21:15	8.11	2.623	30.1	7.30	2.336	1.438	0.314
6 3 2	0:10	8.23	2.329	28.8	6.46	2.290	1.206	0.351
6 3 2	3:10	8.24	2.669	29.5	6.97	1.955	1.438	0.324

Loc Lay & Diu	Time ----	pH --	Alk (mM/l)	Temp (C)	pO2 (ppm)	{Ca} (mM/l)	{Mg+Ca} (cM/l)	{Cl} (dM/l)
6 3 2	7:25	8.22	2.597	29.4	6.94	2.164	1.402	0.317
6 3 2	11:20	8.22	2.505	30.5	7.83	2.158	1.525	0.329
6 3 2	15:10	8.23	2.445	31.5	8.13	2.531	1.843	0.326

APPENDIX C

Measured Saturation States

SATURATION STATES

Relative to Listed Mineralogies

Loc Layer & Time	Arag	Calc	Mole Percent Magnesium 2	3	6.9	10.4	12.7	17.9
1 1 11.50	2.24	4.39	4.96	6.06	3.67	1.77	1.40	0.62
1 1 13.58	0.45	0.88	0.99	1.21	0.73	0.35	0.28	0.12
1 1 15.25	1.30	2.54	2.89	3.54	2.16	1.05	0.83	0.38
1 1 17.42	1.13	2.21	2.50	3.06	1.85	0.89	0.71	0.32
1 1 19.50	1.32	2.59	2.92	3.58	2.16	1.04	0.82	0.37
1 1 21.83	0.78	1.52	1.73	2.12	1.30	0.63	0.50	0.23
1 1 23.67	1.88	3.67	4.11	5.01	2.98	1.42	1.11	0.48
1 1 25.67	1.92	3.75	4.21	5.14	3.09	1.48	1.16	0.51
1 1 28.75	1.51	2.96	3.34	4.09	2.47	1.19	0.94	0.42
1 1 31.33	0.82	1.61	1.82	2.22	1.34	0.65	0.51	0.23
1 1 34.67	1.53	2.99	3.37	4.13	2.49	1.20	0.95	0.42
1 1 37.08	1.67	3.27	3.69	4.52	2.73	1.32	1.04	0.46
1 1 39.50	1.35	2.64	2.98	3.65	2.20	1.06	0.84	0.37
1 1 42.08	1.59	3.11	3.52	4.31	2.62	1.27	1.00	0.45
1 1 45.67	1.31	2.55	2.88	3.52	2.12	1.02	0.80	0.36

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Loc Layer & Time	Arag	Calc	Mole Percent Magnesium 2	3	6.9	10.4	12.7	17.9
1 2 11.50	2.01	3.93	4.41	5.38	3.21	1.53	1.20	0.53
1 2 13.58	1.63	3.18	3.59	4.38	2.65	1.27	1.00	0.45
1 2 15.25	2.08	4.07	4.62	5.67	3.47	1.69	1.34	0.61
1 2 17.42	1.16	2.26	2.55	3.12	1.89	0.91	0.72	0.32
1 2 19.50	1.52	2.97	3.35	4.09	2.46	1.18	0.93	0.41
1 2 21.83	1.61	3.14	3.52	4.29	2.56	1.22	0.95	0.42
1 2 23.67	1.34	2.61	2.95	3.61	2.18	1.05	0.83	0.37
1 2 25.67	1.63	3.18	3.59	4.39	2.65	1.28	1.01	0.45
1 2 28.75	1.55	3.03	3.43	4.20	2.55	1.23	0.97	0.44
1 2 31.33	1.28	2.50	2.81	3.44	2.06	0.99	0.78	0.34
1 2 34.67	1.56	3.06	3.48	4.27	2.62	1.28	1.02	0.46
1 2 37.08	2.09	4.09	4.62	5.65	3.41	1.65	1.30	0.58
1 2 39.50	1.10	2.16	2.42	2.96	1.77	0.85	0.67	0.29
1 2 42.08	1.76	3.44	3.89	4.76	2.88	1.39	1.10	0.49
1 2 45.67	1.59	3.11	3.51	4.29	2.59	1.25	0.99	0.44
1 3 11.50	1.01	1.97	2.22	2.72	1.64	0.79	0.62	0.28
1 3 13.58	1.59	3.12	3.52	4.30	2.60	1.25	0.99	0.44
1 3 15.25	1.06	2.08	2.36	2.90	1.78	0.87	0.69	0.31
1 3 17.42	1.13	2.22	2.50	3.05	1.83	0.88	0.69	0.31
1 3 19.50	1.11	2.18	2.47	3.04	1.86	0.91	0.72	0.33
1 3 21.83	0.88	1.71	1.93	2.36	1.43	0.69	0.54	0.24
1 3 23.67	1.30	2.55	2.88	3.52	2.13	1.03	0.81	0.36

Loc Layer & Time	Arag	Calc	Mole Percent Magnesium 2	3	6.9	10.4	12.7	17.9
1 3 25.67	2.12	4.14	4.67	5.71	3.44	1.65	1.30	0.58
1 3 28.75	2.04	3.99	4.54	5.57	3.42	1.67	1.33	0.60
1 3 31.33	1.52	2.96	3.34	4.08	2.46	1.18	0.93	0.41
1 3 34.67	1.89	3.70	4.17	5.10	3.06	1.47	1.16	0.51
1 3 37.08	1.60	3.12	3.51	4.29	2.58	1.24	0.97	0.43
1 3 39.50	2.02	3.95	4.45	5.43	3.27	1.57	1.23	0.54
1 3 42.08	2.09	4.08	4.60	5.62	3.38	1.62	1.28	0.57
1 3 45.67	1.48	2.90	3.26	3.97	2.38	1.14	0.89	0.39
1 4 11.50	1.73	3.39	3.86	4.73	2.90	1.41	1.13	0.51
1 4 13.58	1.49	2.91	3.28	4.02	2.43	1.17	0.92	0.41
1 4 15.25	2.01	3.93	4.44	5.42	3.28	1.58	1.25	0.56
1 4 17.42	1.03	2.01	2.28	2.80	1.72	0.84	0.67	0.30
1 4 19.50	1.28	2.50	2.83	3.47	2.10	1.02	0.80	0.36
1 4 21.83	1.37	2.68	3.04	3.72	2.25	1.09	0.86	0.39
1 4 23.67	1.51	2.94	3.35	4.11	2.52	1.23	0.98	0.44
1 4 25.67	1.16	2.26	2.57	3.16	1.93	0.94	0.75	0.34
1 4 28.75	1.42	2.77	3.14	3.85	2.34	1.14	0.90	0.41
1 4 31.33	1.38	2.70	3.05	3.73	2.24	1.08	0.85	0.38
1 4 34.67	1.78	3.47	3.91	4.78	2.87	1.38	1.09	0.48
1 4 37.08	2.18	4.25	4.79	5.85	3.52	1.69	1.33	0.59
1 4 39.50	1.74	3.41	3.83	4.68	2.81	1.35	1.06	0.47
1 4 42.08	1.80	3.51	3.96	4.85	2.92	1.41	1.11	0.49

Loc Layer & Time	Arag	Calc	Mole Percent Magnesium 2	3	6.9	10.4	12.7	17.9
1 4 45.67	1.06	2.06	2.33	2.85	1.73	0.83	0.66	0.29
2 1 11.50	2.07	4.04	4.55	5.55	3.34	1.60	1.26	0.56
2 1 13.58	2.03	3.98	4.49	5.49	3.31	1.59	1.26	0.56
2 1 15.25	1.30	2.55	2.89	3.54	2.16	1.05	0.83	0.37
2 1 17.42	1.73	3.39	3.82	4.67	2.81	1.35	1.07	0.47
2 1 19.50	1.09	2.12	2.41	2.95	1.79	0.87	0.69	0.31
2 1 21.83	1.65	3.23	3.65	4.47	2.71	1.31	1.03	0.46
2 1 23.67	1.99	3.89	4.40	5.39	3.27	1.59	1.25	0.56
2 1 25.67	2.07	4.04	4.56	5.57	3.35	1.61	1.27	0.56
2 1 28.75	2.62	5.12	5.77	7.05	4.24	2.04	1.60	0.71
2 1 31.33	1.62	3.17	3.60	4.41	2.69	1.31	1.04	0.47
2 1 34.67	1.83	3.57	4.02	4.92	2.96	1.43	1.12	0.50
2 1 37.08	2.26	4.42	4.98	6.09	3.66	1.76	1.38	0.61
2 1 39.50	2.12	4.14	4.67	5.70	3.44	1.65	1.30	0.58
2 1 42.08	0.75	1.46	1.65	2.02	1.22	0.59	0.46	0.20
2 1 45.67	1.50	2.93	3.30	4.03	2.43	1.17	0.92	0.41
2 2 11.50	0.81	1.58	1.78	2.18	1.32	0.64	0.51	0.23
2 2 13.58	1.54	3.01	3.40	4.16	2.52	1.22	0.96	0.43
2 2 15.25	1.77	3.46	3.90	4.77	2.87	1.38	1.09	0.48
2 2 17.42	0.97	1.90	2.17	2.67	1.65	0.81	0.65	0.30
2 2 19.50	1.36	2.67	3.01	3.67	2.21	1.06	0.84	0.37
2 2 21.83	1.36	2.65	2.99	3.66	2.21	1.06	0.84	0.37

Loc Layer & Time	Arag	Calc	Mole Percent Magnesium 2	3	6.9	10.4	12.7	17.9
2 2 23.67	0.95	1.85	2.08	2.54	1.52	0.73	0.57	0.25
2 2 25.67	1.81	3.54	4.01	4.91	2.98	1.44	1.14	0.51
2 2 28.75	1.73	3.38	3.80	4.64	2.79	1.34	1.05	0.46
2 2 31.33	0.57	1.11	1.25	1.53	0.92	0.44	0.35	0.15
2 2 34.67	1.34	2.63	2.96	3.62	2.18	1.05	0.82	0.36
2 2 37.08	2.21	4.32	4.87	5.95	3.59	1.73	1.36	0.60
2 2 39.50	1.96	3.82	4.31	5.27	3.18	1.53	1.20	0.53
2 2 42.08	1.82	3.55	4.00	4.88	2.93	1.41	1.10	0.49
2 2 45.67	1.37	2.69	3.03	3.71	2.23	1.08	0.85	0.38
2 3 11.50	1.55	3.03	3.45	4.23	2.60	1.27	1.01	0.46
2 3 13.58	1.63	3.18	3.59	4.38	2.64	1.27	1.00	0.44
2 3 15.25	1.38	2.71	3.05	3.73	2.25	1.08	0.85	0.38
2 3 17.42	1.48	2.89	3.27	4.00	2.42	1.17	0.93	0.41
2 3 19.50	1.54	3.00	3.37	4.11	2.45	1.17	0.92	0.40
2 3 21.83	1.45	2.83	3.20	3.91	2.37	1.14	0.90	0.40
2 3 23.67	1.43	2.80	3.16	3.86	2.33	1.12	0.88	0.39
2 3 25.67	1.65	3.23	3.68	4.51	2.77	1.36	1.08	0.49
2 3 28.75	1.49	2.91	3.32	4.08	2.51	1.23	0.98	0.45
2 3 31.33	2.14	4.19	4.77	5.85	3.58	1.75	1.39	0.63
2 3 34.67	1.27	2.49	2.83	3.48	2.13	1.04	0.83	0.38
2 3 37.08	1.81	3.55	3.99	4.88	2.93	1.41	1.11	0.49
2 3 39.50	1.72	3.36	3.79	4.64	2.80	1.35	1.06	0.47

Loc Layer & Time	Arag	Calc	Mole Percent Magnesium 2	3	6.9	10.4	12.7	17.9
2 3 42.08	1.80	3.52	3.98	4.86	2.94	1.42	1.12	0.50
2 3 45.67	1.53	3.00	3.38	4.13	2.49	1.20	0.94	0.42
3 1 11.50	1.88	3.68	4.16	5.09	3.09	1.50	1.19	0.53
3 1 13.58	1.63	3.19	3.61	4.42	2.69	1.30	1.03	0.46
3 1 15.25	1.94	3.79	4.27	5.22	3.15	1.52	1.19	0.53
3 1 17.42	1.25	2.44	2.76	3.37	2.04	0.98	0.77	0.34
3 1 19.50	1.08	2.11	2.40	2.94	1.80	0.88	0.70	0.32
3 1 21.83	1.40	2.74	3.11	3.81	2.32	1.12	0.89	0.40
3 1 23.67	1.85	3.62	4.11	5.04	3.08	1.50	1.19	0.54
3 1 25.67	1.68	3.29	3.71	4.54	2.74	1.32	1.04	0.46
3 1 28.75	1.95	3.81	4.29	5.24	3.15	1.51	1.19	0.53
3 1 31.33	1.35	2.64	2.98	3.64	2.19	1.05	0.83	0.37
3 1 34.67	1.60	3.12	3.54	4.34	2.64	1.28	1.02	0.46
3 1 37.08	2.25	4.41	4.96	6.06	3.64	1.74	1.37	0.60
3 1 39.50	2.04	3.99	4.50	5.50	3.31	1.59	1.25	0.55
3 1 42.08	1.63	3.18	3.59	4.40	2.67	1.29	1.02	0.46
3 1 45.67	1.54	3.00	3.39	4.14	2.49	1.20	0.94	0.42
3 2 11.50	2.27	4.43	4.99	6.10	3.67	1.76	1.39	0.61
3 2 13.58	2.65	5.18	5.83	7.12	4.27	2.05	1.61	0.71
3 2 15.25	1.96	3.84	4.32	5.27	3.16	1.52	1.19	0.52
3 2 17.42	1.36	2.66	3.02	3.70	2.25	1.09	0.87	0.39
3 2 19.50	1.25	2.44	2.77	3.40	2.09	1.02	0.81	0.37

Loc Layer & Time	Arag	Calc	Mole Percent Magnesium 2	3	6.9	10.4	12.7	17.9
3 2 21.83	1.45	2.84	3.20	3.91	2.35	1.13	0.88	0.39
3 2 23.67	1.30	2.55	2.91	3.58	2.21	1.08	0.87	0.40
3 2 25.67	2.32	4.53	5.12	6.27	3.80	1.83	1.45	0.65
3 2 28.75	1.69	3.31	3.72	4.55	2.73	1.31	1.03	0.45
3 2 31.33	2.38	4.65	5.22	6.36	3.80	1.81	1.42	0.62
3 2 34.67	1.43	2.80	3.16	3.87	2.34	1.13	0.89	0.40
3 2 37.08	1.68	3.28	3.71	4.54	2.74	1.32	1.04	0.47
3 2 39.50	2.19	4.27	4.81	5.87	3.53	1.69	1.33	0.59
3 2 42.08	1.92	3.76	4.25	5.19	3.13	1.51	1.19	0.53
3 2 45.67	1.56	3.04	3.43	4.19	2.52	1.21	0.96	0.42
3 3 11.50	1.45	2.84	3.20	3.91	2.35	1.13	0.89	0.39
3 3 13.58	1.58	3.10	3.49	4.27	2.57	1.24	0.98	0.43
3 3 15.25	2.68	5.24	5.88	7.18	4.29	2.05	1.61	0.71
3 3 17.42	1.70	3.33	3.76	4.59	2.77	1.33	1.05	0.47
3 3 19.50	1.11	2.18	2.46	3.01	1.81	0.87	0.69	0.31
3 3 21.83	1.54	3.02	3.42	4.19	2.54	1.23	0.97	0.44
3 3 23.67	1.18	2.30	2.61	3.20	1.95	0.94	0.75	0.34
3 3 25.67	2.22	4.34	4.90	5.99	3.62	1.75	1.38	0.61
3 3 28.75	2.23	4.36	4.90	5.98	3.58	1.71	1.34	0.59
3 3 31.33	1.24	2.43	2.78	3.42	2.11	1.04	0.83	0.38
3 3 34.67	2.32	4.53	5.12	6.26	3.78	1.82	1.44	0.64
3 3 37.08	2.34	4.58	5.16	6.31	3.80	1.83	1.44	0.64

Loc Layer & Time	Arag	Calc	Mole Percent Magnesium 2	3	6.9	10.4	12.7	17.9
3 3 39.50	2.23	4.36	4.91	5.99	3.60	1.73	1.36	0.60
3 3 42.08	1.73	3.39	3.82	4.67	2.82	1.36	1.07	0.48
3 3 45.67	1.50	2.93	3.31	4.05	2.45	1.19	0.94	0.42
4 1 15.33	1.59	3.11	3.52	4.30	2.60	1.26	0.99	0.44
4 1 18.25	1.85	3.62	4.09	5.01	3.04	1.47	1.16	0.52
4 1 21.25	2.01	3.94	4.45	5.45	3.30	1.59	1.26	0.56
4 1 24.17	2.51	4.91	5.55	6.78	4.10	1.98	1.56	0.70
4 1 27.17	1.75	3.42	3.85	4.71	2.84	1.37	1.08	0.48
4 1 31.42	1.93	3.78	4.27	5.21	3.15	1.52	1.20	0.53
4 1 35.33	1.98	3.88	4.38	5.35	3.23	1.55	1.22	0.54
4 1 39.17	1.78	3.48	3.94	4.83	2.94	1.42	1.13	0.51
4 2 15.33	2.15	4.21	4.75	5.82	3.52	1.70	1.34	0.60
4 2 18.25	1.58	3.10	3.53	4.33	2.66	1.30	1.04	0.47
4 2 21.25	2.05	4.00	4.52	5.54	3.36	1.62	1.28	0.57
4 2 24.17	1.98	3.87	4.37	5.34	3.23	1.56	1.23	0.55
4 2 27.17	2.00	3.90	4.41	5.40	3.28	1.59	1.25	0.56
4 2 31.42	2.29	4.48	5.05	6.16	3.70	1.78	1.40	0.62
4 2 35.33	2.22	4.34	4.90	5.99	3.61	1.74	1.37	0.61
4 2 39.17	1.93	3.77	4.27	5.23	3.17	1.54	1.22	0.55
4 3 15.33	1.61	3.16	3.59	4.41	2.71	1.32	1.05	0.48
4 3 18.25	1.87	3.66	4.13	5.06	3.05	1.47	1.16	0.52
4 3 21.25	2.09	4.08	4.62	5.66	3.44	1.67	1.32	0.59

Loc Layer & Time	Arag	Calc	Mole Percent Magnesium 2	3	6.9	10.4	12.7	17.9
4 3 24.17	2.43	4.74	5.36	6.55	3.96	1.91	1.51	0.67
4 3 27.17	2.30	4.51	5.10	6.24	3.78	1.83	1.45	0.65
4 3 31.42	2.48	4.85	5.47	6.69	4.04	1.95	1.54	0.68
4 3 35.33	1.43	2.79	3.15	3.86	2.33	1.12	0.89	0.39
4 3 39.17	1.89	3.69	4.17	5.10	3.08	1.49	1.18	0.52
4 4 15.33	1.94	3.79	4.30	5.26	3.20	1.55	1.23	0.55
4 4 18.25	2.09	4.08	4.62	5.65	3.43	1.66	1.32	0.59
4 4 21.25	2.18	4.26	4.81	5.88	3.54	1.70	1.34	0.59
4 4 24.17	1.94	3.80	4.29	5.25	3.17	1.53	1.20	0.54
4 4 27.17	2.33	4.55	5.16	6.33	3.86	1.87	1.49	0.67
4 4 31.42	2.30	4.50	5.08	6.22	3.76	1.82	1.44	0.64
4 4 35.33	1.92	3.75	4.25	5.20	3.15	1.53	1.21	0.54
4 4 39.17	2.01	3.93	4.44	5.44	3.30	1.60	1.26	0.57
4 5 15.33	2.04	3.99	4.50	5.51	3.33	1.61	1.27	0.57
4 5 18.25	2.19	4.28	4.84	5.92	3.58	1.73	1.36	0.61
4 5 21.25	2.27	4.43	5.02	6.15	3.74	1.82	1.44	0.65
4 5 24.17	2.13	4.17	4.70	5.75	3.47	1.67	1.32	0.59
4 5 27.17	1.99	3.89	4.42	5.42	3.32	1.62	1.29	0.58
4 5 31.42	2.33	4.56	5.15	6.31	3.81	1.84	1.45	0.65
4 5 35.33	2.38	4.65	5.26	6.43	3.88	1.87	1.48	0.66
4 5 39.17	2.45	4.78	5.39	6.59	3.98	1.91	1.51	0.67
5 1 15.33	2.44	4.78	5.40	6.61	3.99	1.93	1.52	0.68

Loc Layer & Time	Arag	Calc	Mole Percent Magnesium 2	3	6.9	10.4	12.7	17.9
5 1 18.25	2.22	4.33	4.89	5.98	3.61	1.74	1.37	0.61
5 1 21.25	1.76	3.44	3.88	4.75	2.87	1.38	1.09	0.48
5 1 24.17	2.40	4.70	5.31	6.50	3.93	1.90	1.50	0.67
5 1 27.17	1.87	3.66	4.13	5.05	3.05	1.47	1.16	0.52
5 1 31.42	1.44	2.81	3.18	3.89	2.36	1.14	0.90	0.40
5 1 35.33	2.07	4.04	4.57	5.58	3.37	1.63	1.28	0.57
5 1 39.17	1.94	3.80	4.31	5.28	3.22	1.56	1.24	0.56
5 2 15.33	1.93	3.77	4.26	5.22	3.16	1.53	1.21	0.54
5 2 18.25	2.27	4.43	5.03	6.16	3.75	1.83	1.45	0.65
5 2 21.25	2.05	4.00	4.52	5.53	3.34	1.61	1.27	0.57
5 2 24.17	2.02	3.94	4.47	5.48	3.33	1.62	1.28	0.58
5 2 27.17	2.26	4.42	4.99	6.10	3.69	1.78	1.40	0.62
5 2 31.42	2.14	4.17	4.72	5.77	3.49	1.69	1.33	0.59
5 2 35.33	1.80	3.51	3.98	4.87	2.96	1.43	1.13	0.51
5 2 39.17	1.89	3.69	4.18	5.11	3.11	1.51	1.19	0.53
5 3 15.33	1.48	2.90	3.27	4.00	2.42	1.16	0.92	0.41
5 3 18.25	2.46	4.81	5.44	6.65	4.02	1.94	1.53	0.68
5 3 21.25	2.34	4.57	5.16	6.31	3.81	1.84	1.45	0.65
5 3 24.17	2.04	3.98	4.50	5.51	3.33	1.61	1.27	0.57
5 3 27.17	2.04	3.98	4.51	5.52	3.35	1.62	1.29	0.58
5 3 31.42	2.05	4.00	4.52	5.53	3.34	1.61	1.27	0.57
5 3 35.33	1.57	3.08	3.49	4.27	2.59	1.26	1.00	0.45

Loc Layer & Time	Arag	Calc	Mole Percent Magnesium 2	3	6.9	10.4	12.7	17.9
5 3 39.17	2.08	4.07	4.60	5.63	3.41	1.65	1.30	0.58
6 1 15.33	2.48	4.85	5.46	6.67	4.00	1.92	1.51	0.67
6 1 18.25	1.93	3.78	4.28	5.24	3.18	1.54	1.22	0.55
6 1 21.25	1.97	3.86	4.35	5.32	3.20	1.54	1.21	0.54
6 1 24.17	2.31	4.51	5.09	6.23	3.77	1.82	1.44	0.64
6 1 27.17	1.78	3.47	3.94	4.82	2.94	1.43	1.13	0.51
6 1 31.42	1.51	2.96	3.36	4.11	2.50	1.21	0.96	0.43
6 1 35.33	2.02	3.94	4.46	5.45	3.30	1.60	1.26	0.56
6 1 39.17	2.03	3.97	4.49	5.49	3.33	1.61	1.27	0.57
6 2 15.33	2.52	4.93	5.55	6.79	4.09	1.97	1.55	0.69
6 2 18.25	2.10	4.10	4.63	5.67	3.43	1.66	1.31	0.59
6 2 21.25	1.88	3.68	4.16	5.09	3.09	1.49	1.18	0.53
6 2 24.17	1.87	3.66	4.14	5.07	3.07	1.48	1.17	0.52
6 2 27.17	2.90	5.66	6.37	7.77	4.66	2.23	1.75	0.77
6 2 31.42	2.28	4.46	5.03	6.15	3.70	1.78	1.40	0.62
6 2 35.33	1.60	3.12	3.52	4.31	2.60	1.25	0.99	0.44
6 2 39.17	2.04	3.98	4.51	5.52	3.35	1.62	1.28	0.57
6 3 15.33	1.99	3.89	4.40	5.38	3.26	1.57	1.24	0.55
6 3 18.25	1.85	3.62	4.09	5.01	3.03	1.46	1.16	0.52
6 3 21.25	2.01	3.92	4.42	5.41	3.26	1.57	1.24	0.55
6 3 24.17	2.08	4.07	4.58	5.58	3.35	1.60	1.26	0.55
6 3 27.17	2.25	4.39	4.97	6.09	3.69	1.79	1.41	0.63

Loc Layer & Time	Arag	Calc	Mole Percent Magnesium 2	3	6.9	10.4	12.7	17.9
6 3 31.42	2.33	4.55	5.13	6.28	3.79	1.83	1.44	0.64
6 3 35.33	2.09	4.08	4.62	5.65	3.42	1.66	1.31	0.58
6 3 39.17	2.28	4.46	5.05	6.18	3.75	1.81	1.43	0.64