Proceedings, Third International Coral Reef Symposium
Rosenstiel School of Marine and Atmospheric Science
University of Miami
Miami, Florida 33149, U.S.A.
May 1977

EARLY DIAGENESIS OF DISSOLVED SULFUR AND NITROGEN SPECIES IN JAMAICAN REEF SEDIMENTS (DETERMINED BY IN SITU SAMPLING)

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ABSTRACT

Interstitial waters of the fore-reef and back-reef carbonate sands in the vicinity of Discovery Bay, Jamaica, were sampled underwater from interstitial water wells. This new method of interstitial water withdrawal is unique in that it is reproducible, does not involve coring or squeezing sediments, and enables transfer of samples in hypodermic syringes back to a laboratory without oxidation or contamination. Chemical analyses of SO_4^{2-}, $H_2S + HS^-$, NO_3^-, NO_2^-, and NH_4^+ indicate that a thermodynamic equilibrium distribution is approached by sulfur and nitrogen species. Sulfate reduction is the principal control of hydrogen sulfide generation, whereas deamination can account for the ammonia concentrations. Decrease of oxidized reactants and increase of reduced reactants are generally not uniform with sediment depth; local maxima and minima occur at intermediate depths between the surface and bottom of the wells (0-70 cm). The non-steady state diagenesis of reef sediment pore waters is probably due to heterogeneous sediment textures, enormous activity of benthic macrofauna, and erratic distribution of organic carbon with depth. However, diffusion or bioturbation are not rapid enough to prevent microbial activities that trend toward thermodynamic equilibrium within micro-environments.

KEY WORDS: Diagenesis, Sedimentary Geochemistry, Denitrification, Sulfate Reduction, Interstitial Waters, Reef Sediments, Carbonates, Analytic Techniques, Eh-pH

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I. Introduction

The investigation of interstitial solutions by numerous workers since the pioneering study of Murray and Irvine (1) has revealed much information about fluvial, lacustrine, estuarine, and oceanic sediment pore waters. However, contamination through anaerobic collection and aerobic analyses and degassing caused by mechanical agitation (i.e., squeezing cores) yield results which are difficult, if not impossible, to relate to the original composition of the pore waters in contact with the sediments (2). In situ samplers such as the one designed by Sayles et al. (3) for collecting deep-sea sediment pore waters and analyses under pure nitrogen such as those of Emerson (4) help to minimize many of these problems. This investigation employed diver-operated interstitial water wells. These are unique in that they retrieve reproducible solution samples in hypodermic syringes back to the laboratory without the artifacts of oxidation, contamination, or excessive mechanical agitation.

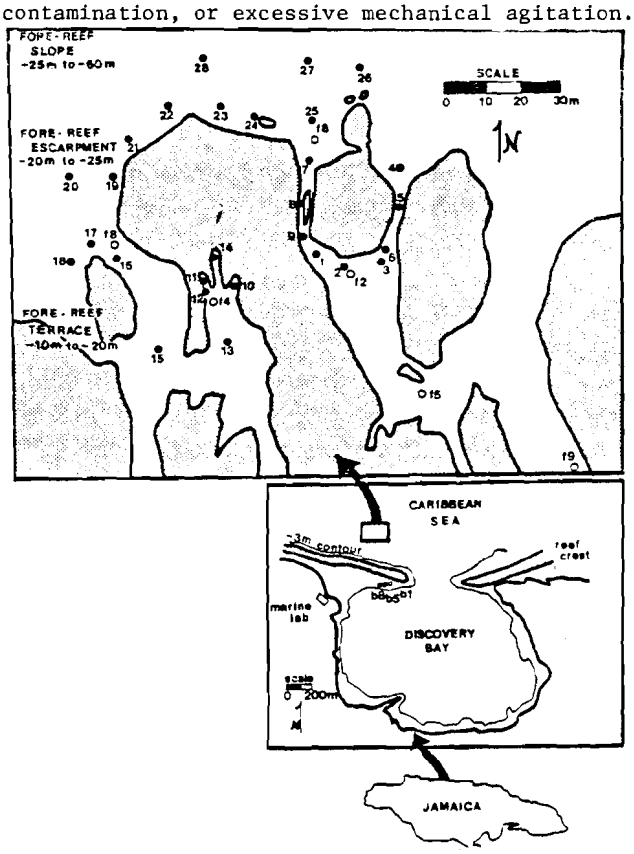

Fig. 1. Map of the reef off Discovery Bay, Jamaica. O Cores. O Interstitial water wells. Shaded areas indicate coral-coralline algal biolithites. Clear areas indicate carbonate sands. Map after Goreau and Land (11), aerial photographs, and underwater mapping.

The analytic results obtained from methods outlined below offer pertinent information on the dissolved sulfur and nitrogen geochemistry of reef sediments, a setting which has been greatly neglected in pore-water studies. Though reef sediments are of known geologic and biologic importance, the phobia of coring with oceanographic vessels proximal to reef crests has precluded their effective study. By using the interstitial water wells on a Jamaican fringing reef and the facilities of the nearby Discovery Bay Marine Laboratory, this problem was circumvented (see location map, Fig. 1).

II. Methods and Materials

Economy of time and materials resulted in the design of the interstitial water well. Shown in Figure 2 is the assembled device, consisting of a 2.54 cm diameter, 1.52 m section of rigid P.V.C. tubing. To the sides are attached a number (3 or more) of 1.82 m lengths of flexible 5 mm diameter plastic aquarium tubing via a bolted clamp at the base and waterproof tape at the midsection and top. The plastic tubing is color-coded and respectively punctured at various individual lengths. After the well is embedded into the sediment, requiring SCUBA and a sledge hammer underwater, water samples may be withdrawn at the differing depths of substrate penetration into hypodermic syringes which mate to the aquarium hoses. By discarding the first 50 ml of solution, the tubing-stored water is expelled. After subsequent withdrawal, the hypodermics are then capped underwater and transported back to the laboratory. The plunger on the syringe effectively compensates for ambient pressure changes when surfacing. The reproducibility was tested by repeated withdrawals up to a month apart from the same wells at the same interstitial depths. The results were always well within analytic error. For this study, well penetration was limited to a maximum of 70 cm because of subsurface reef debris and submarine hard grounds.

Cores were taken by SCUBA-diver-operated sledge hammering of 6 cm diameter, 1.52 m P.V.C. tubes. These were extruded in the laboratory and stored at -25°C. Samples were subsequently analyzed for organic carbon by the ignition methods of Dean (5). Analytic precision,

± one standard deviation, is ± 1.74 weight percent organic carbon.

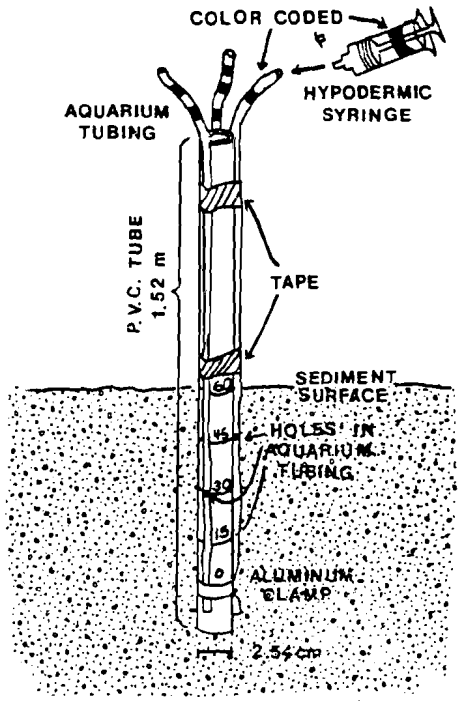

Fig. 2. Interstitial water well for *in situ* sampling.

Grain size analyses for 5 cm core sections were determined according to the methods of Fol (6). After careful washing to reduce aggregate artifacts, the samples were dry-sieved on 0.5 ∅ interval screens using an Endecott Test Sieve Shaker.

Sulfate was analyzed turbidimetrically using a dilution of 0.1 ml of 0.45 μ Millipore-filtered sample to 25 ml of distilled water, introduction of Hach SulfaVer III reagent in preweighed amounts of 0.970 g, and agitation for exactly 30 seconds. After precisely 10 minutes had lapsed, this solution's net absorbance was determined on a Zeiss PMQ II Spectrophotometer using 5 cm cells at 420 mu. The error, ± one standard deviation, was determined as a standard error of the estimate by a least squares fit to a suite of standards (7). For sulfate the precision was determined to be ± 6.87 X 10^{-6} moles per liter of solution. Hydrogen sulfide reported as $H_2S + HS^-$ was similarly determined turbidimetrically as sulfate after oxidation of an aliquot with 2 ml of 30% hydrogen peroxide for exactly 30 minutes, yielding a final dilution of 0.1 ml of sample in 27.1 ml of solution. Precision of this method was slightly less, ± 3.37 X 10^{-5} moles per liter of solution. For both methods, sensitivity occasionally required less sample dilution.

Dilutions were not required for analyses of the nitrogen species. After similar filtration, nitrite was determined by mixing preweighed 0.759 g amounts of Hach 1-naphthylamine-sulfanilic acid for exactly one minute and determining the net absorbance of 520 mu precisely 15 minutes later using 1 cm cells on a Beckman DU-2 Spectrophotometer. Precision was determined to be ± 1.11 X 10^{-7} moles per liter of solution. Nitrate was determined after cadmium reduction with preweighed 0.310 g of Hach NitraVer VI reagent added to 30 ml of sample and mixed for exactly 3 minutes. After the sample was allowed to stand undisturbed for precisely 1 minute, 25 ml of the supernatant fluid were pipetted off for nitrite determination in the previous manner. Precision was determined to be ± 4.35 X 10^{-7} moles per liter of solution. Ammonia reported as NH_4^+ was analyzed by oxidation to nitrite according to the methods outlined by Strickland and Parsons (8) but modified to determine nitrite by the spectrophotometric methods outlined above. Precision was determined to be ± 4.47 X 10^{-7} moles per liter of solution.

The redox potentials of the interstitial solutions were determined to the nearest 1 mv using a Fisher saturated calomel electrode for reference. A Fisher platinum electrode was used to measure Eh after standardization with + 430 mv ZoBell's solution at 25°C (9). Measurements were made immediately after sample collection without unnecessary agitation. The advantage of using hypodermic transportation of the solution from the interstitial water wells was shown by the extremely low drift of readings (stabilizing within 5 minutes and with a drift usually less than 5 mv) when compared with Eh measurements taken in the typical fashion on nearby cores with the electrodes inserted directly within the sediment (these readings were much more positive and drifted badly, sometimes more than 50 mv). The Eh readings were not corrected to an arbitrary pH; instead they are presented in their uncorrected form as propounded by Baas Becking, *et al.* (10).

Electrode potentials were measured to the nearest 1 mv with a Beckman Zeromatic pH meter using a saturated Fisher calomel electrode as reference and a Fisher glass electrode to determine pH. Before and after every measurement the electrodes were standardized with Beckman pH = 4.008 and pH = 7.00 (25°C) buffers. The sample solutions were stirred by a teflon coated magnet rotated by a magnetic stirrer. The temperature variations were monitored and the ph was corrected to 25°C, slightly lower than the approximate average water temperature for the July-August investigation (measurements at 1 meter intervals from the surface to 11 m on the fore-reef above water well f5 at 0800 hrs. on 5 August 1976 averaged 27.94°C with a standard deviation of ± 0.05°C, and at 1430 hrs. on the same day they averaged 28.01°C with a standard deviation of ± 0.10°C).

III. Summary of Results

A. Sediment textures and organic carbon

The loci of cores and interstitial water wells are shown in Figure 1. Though the sand channels of the fore-reef were of primary interest, ancillary stations in the back-reef were chosen for comparison. The subaqueous gemorphology and active depositional processes of the Discovery Bay fringing reef have been discussed in detail by Goreau and Land (11); the petrography has been described by Moore, et al. (12).

Grain size analyses of these sediments taken from cores at the well stations f2, f5, b1, and b8 show textural variations with depth. The average of the 19 fore-reef samples of 5 cm core sections including $\pm$ one standard deviation can be described according to the terminology of Folk (6) as poorly sorted (σ_I = 1.2 Ø, $\pm$ 0.5 Ø), near symmetrical (Sk_I = 0.09, $\pm$ 0.32), mesokurtic (K_G = 1.03, $\pm$ 0.21), slightly gravelly coarse sands (M_z = 0.34 Ø, $\pm$ 1.14 Ø). By contrast, the 14 back-reef samples can be described as poorly sorted (σ_I = 1.73 Ø, $\pm$ 0.95 Ø), strongly coarse skewed (Sk_I = -0.35, $\pm$ 0.25), leptokurtic (K_G = 1.31, $\pm$ 0.58) slightly gravelly medium sands (M_z = 1.36 Ø, $\pm$ 0.95 Ø). These sediments are made up predominantly of Halimeda species, mollusc, foram, coralline algal, and coral fragments (if lithified, could become unsorted biosparites). The heterogeneous textures observed within the cores are largely due to the mechanical agitation of the sands by intense activity of benthic macrofauna. This textural variability may control some of the erratic organic carbon distributions within these sediments.

When 101 samples taken at 5 cm intervals from 24 fore-reef cores were analyzed for weight percent organic carbon, the distribution shown in Figure 3 resulted. The extreme variability within and among the cores is similar to that found by Bunt, et al. (13) among surface sediments in the Caribbean. This large variability in organic matter can explain some of the observed nonuniform distributions with depth of the sulfur and nitrogen species: it serves as the electron donor for sulfate reduction and denitrification, and as a nitrogen source for deamination.

B. Sulfate and hydrogen sulfide: some limiting factors

When the concentrations of sulfate and hydrogen sulfide are plotted as a function of depth within the sediment as in Figure 4, the well-defined concave downward curves of sulfate characteristic of steady state diagenesis (14) are lacking. Instead, as with organic carbon, a large scatter is observed. However, by comparing sulfur species one may notice that maxima in sulfate often correlate to minima in hydrogen sulfide and vice versa. In Figure 5 this inverse relationship becomes readily apparent. The correlation coefficient is -0.67, highly significant ($p < 0.01$). From this regression the increase in hydrogen sulfide and decrease in sulfate is 45% mutually accounted for (r^2 = 0.45). Interestingly, this shows a nonstoichiometric production of hydrogen sulfide, about two orders of magnitude less than theoretically predicted (see the following equation). This might be explained by any of the following: 1) analytic error, 2) active biosynthesis of elemental sulfur or of sulfur-containing organic molecules from hydrogen sulfide, 3) differences in diffusion rates, or 4) formation of sulfide minerals. L. S. Land (personal communication, 1976) has recorded 860 p.p.m. total iron in these back-reef sediments, or about 1.54 X 10^{-2} moles per kg of wet sediment. If this iron is assumed to exist for the minimum case of sulfide mineral formation entirely as FeS (i.e., mackinawite), it could account for at most about three orders of magnitude more hydrogen sulfide

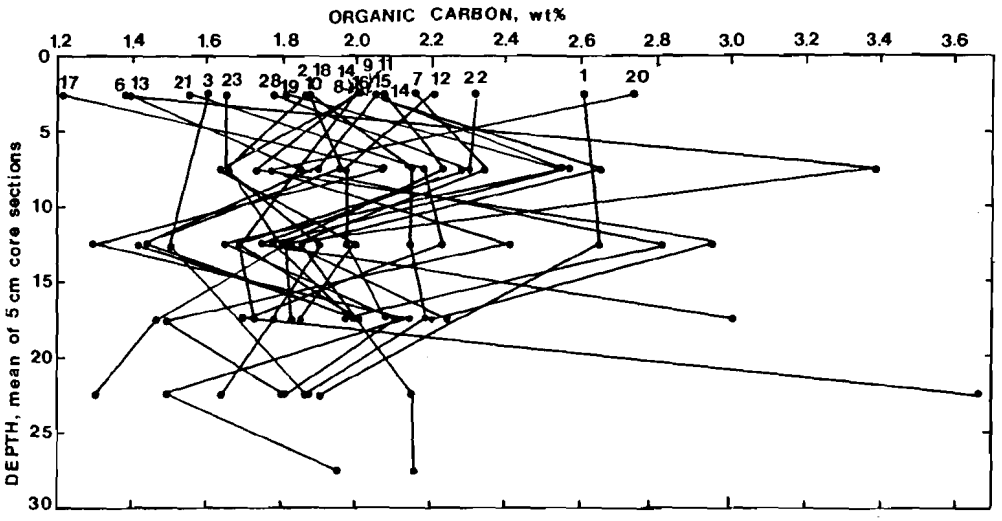

Fig. 3. Distribution of organic carbon with depth in Jamaican reef sediments.

than the maximum observed in these sediment pore waters (1.22 X 10^{-4} moles $H_2S + HS^-$ per liter of solution X 0.252 liters of solution per kg of wet reef sediment of 50% porosity = 3.07 X 10^{-5} moles $H_2S + HS^-$ per kg of wet sediment). Thus, it appears that the formation of iron sulfides is more than sufficient to account for the observed nonstoichiometric amounts of hydrogen sulfide due to sulfate reduction.

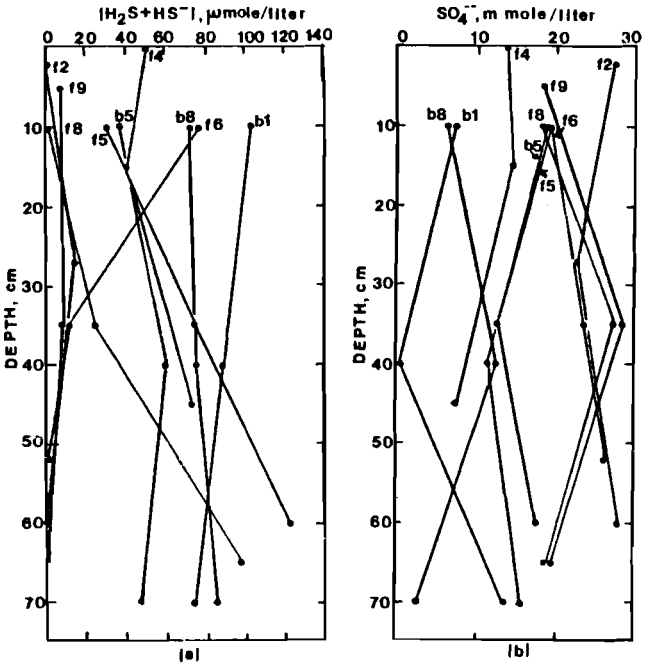

Fig. 4. Dissolved hydrogen sulfide (a) and sulfate (b) vs. depth in Jamaican reef sediment pore waters.

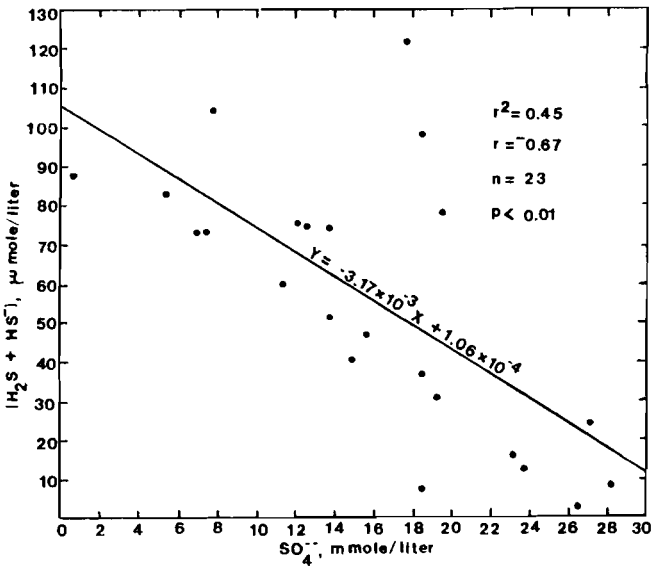

Fig. 5. Dissolved hydrogen sulfide vs. dissolved sulfate in Jamaican reef sediment pore waters.

The bacterial reduction of sulfate within these sediments by Desulfovibrio species can be represented by the following equation with organic carbon approximated as carbohydrate, CH_2O:

$$2CH_2O + SO_4^{2-} \quad 2HCO_3^- + HS^- + H^+. \qquad (I)$$

Therefore, one mole of sulfate is required to oxidize two moles of carbohydrate by sulfate reduction. These reef sediments can contain up to 129 times as many moles of carbohydrate as sulfate, much in excess of that required to completely reduce the sulfate within the interstitial waters. If 1 kg of wet reef sediment with 50% porosity contains 252 cm^3 of aragonite sand and 252 cm^3 of seawater, then organic carbon is at most 3.66 weight percent (maximum value observed) X 743 g (P aragonite = 2.95 g/cm^3) = 27 g or about 0.91 moles of CH_2O per kg of wet sediment. Still, dissolved sulfate is 252 cm^3 per kg of wet sediment X 0.028 moles of sulfate per 1000 cm^3 (maximum value observed) = 7.1 X 10^{-3} moles per kg of wet sediment. This is about two orders of magnitude less than the 4.55 X 10^{-1} moles of sulfate needed for complete oxidation of the carbohydrate by sulfate reduction. Thus, if a closed system, sulfate is the limiting reactant. However, if the system is partially open to seawater, as suggested by intense bioturbation, nonstratified sediments, and non-steady state diagenesis, organic carbon could become limiting. As the open seawater ratio of sulfate to carbohydrate is about 1.3 X 10^7 (data of particulate carbon from Reiswig, 15, for these fore-reef waters is 63.9 mg per cubic meter or about 2.13 X 10^{-9} moles per liter), the particulate carbon could become completely oxidized by sulfate reduction if seawater is flushed through in great enough amounts. An intermediate case appears to apply here as the minimum amount of organic carbon found in these sulfate-reducing sediments is 1.218 weight perc cent or 0.426 moles of carbohydrate per kg of wet sediment. This indicates that the organic material within these reef sediments is greatly in excess of the ability of sulfate-reducing bacteria to completely oxidize it. Therefore, only in marine environments where organic carbon content is much less or pore water circulation is greater is sulfate not a limiting factor.

C. Nitrate, nitrite and ammonia

When nitrate, nitrite, and ammonia are graphed as a function of depth in the interstitial water wells as shown in Figure 6, extreme variability within and among the water wells is apparent. Again, as with the sulfur species, maxima and minima occur sporadically throughout the wells. But in contrast, correlations among the observed nitrogen species are insignificant ($p >> 0.05$). Thus, a loss of nitrate and nitrite by denitrification cannot explain the gain in ammonia. The ammonia concentrations can, instead,

be explained by the bacterial deamination of nitrogenous organic matter.

Organic nitrogen within the top 2.5 cm of these reef sediments at 16 m water depths averaged 1.14×10^{-4} g N/cm^3 (data interpreted from Bunt, et al., 13). If 1 kg of wet sediment has 252 cm^3 per kg of wet sediment X 1.14×10^{-4} g N/cm^3 = 2.87×10^{-2} g N per kg of wet sediment, then about 2.04×10^{-1} moles of potential N are available for a one-to-one mole deamination to ammonia. This is greatly in excess of the 252 cm^3 per kg of wet sediment X 2.22×10^{-6} moles NO_3^-/l (maximum observed) = 5.59×10^{-4} moles NO_3 per kg of wet sediment available for a one-to-one mole conversion of nitrate to ammonia by denitrification. Thus, organic matter is in sufficient concentration to potentially yield by deamination the excess ammonia observed in these reef sediment pore waters.

IV. Discussion of thermodynamic equilibria

The preceding data demonstrate that the early diagenesis within these reef sediment pore waters do not exhibit the features representative of the steady state models found in many other environments (see 16). This non-steady state diagenesis may still be checked for internal thermodynamic equilibrium for sulfur and nitrogen species by calculating and comparing the pe for the respective oxidation-reduction couples (17). The pe may be defined as:

$$pe = \frac{EH\ F}{2.303\ RT} \quad . \qquad (II)$$

Eh is the reversible redox potential, F is the faraday (23.06 kcal per volt-gram equivalent), R is the gas constant (0.987 cal/deg-mole), and T is the absolute temperature. The following equations for the calculation of pe_S and pe_N are from the study of Thorstenson (17):

$$pe_S = 4.6 - 1.125\ pH + 0.125 \log \frac{m\ SO_4^{2-}}{m\ HS^-} \quad . \qquad (III)$$

$$pe_N = 5.25 - 1.333\ pH + 0.167 \log \frac{m\ N_2}{m^2\ NH_4^+} \quad . \qquad (IV)$$

The pe for all pairs should be the same if there is homogenous solution equilibrium. The molality of the dissolved sulfide anion is calculated using the apparent dissociation constant K'_1 (H_2S) = $10^{-6.79}$ (18). The molality of dissolved nitrogen is assumed to be 3.96×10^{-4} based on saturation of seawater with air at 25°C (interprete from the data of Rakestraw and Emmel, 19). The assumption of constant dissolved nitrogen introduces at most an error of $\pm$ 0.2 in the pe units (17).

When the pe_S is compared to the pe_N for these reef sediment pore waters as shown in Figure 7, a significant correlation results ($r = 0.59$, $p < 0.05$). The thermodynamic equilibria of the sulfur species correlate to the nitrogen species. But though the data indicate an approach to internal equilibrium, equilibrium is not complete. This might result because of the nitrogen or sulfur species not readily exchanging electrons with one another inorganically at these temperatures (14). However, these redox couples tend to be consistently below the line representing internal equilibrium. This could be due to either a persistent excess of sulfide ion or insufficient ammonia for complete equilibrium. Possible explanations for this problem are differences in reaction kinetics or errors in the analyses, the thermodynamic calculations, or the assumed thermodynamic constants. If analytic and computational errors are insignificant, then an interesting unsolved thermodynamic problem exists.

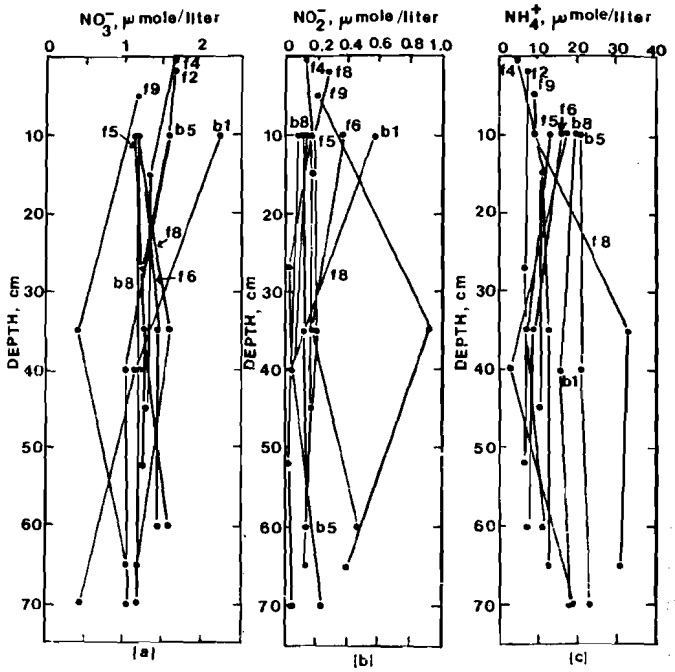

Fig. 6. Dissolved nitrate (a), nitrite (b), and ammonia (c) vs. depth in Jamaican reef sediment pore waters.

The observed Eh does not reflect the Eh expected for any of these half-cell couples because these species are not rapidly reactive at an electrode surface (14). An Eh-pH diagram can, however, accurately portray the interstitial environments for these reef sediments. Figure 8 indicates that the oxidation and electrode potentials of both the sampled back-reef and fore-reef interstitial environments occur within a narrow range. The back-reef sediment pore waters appear to be significantly more acidic

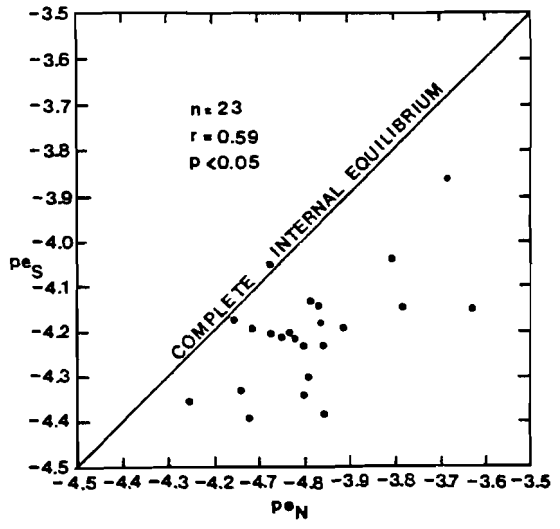

Fig. 7. Correlation of pe_S and pe_N for Jamaican reef sediment pore waters.

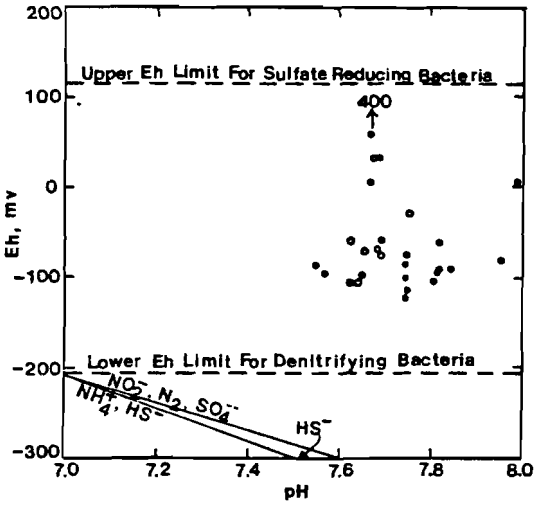

Fig. 8. Eh - pH diagram for Jamaican reef sediment pore waters. Microbial activity ranges adapted from Baas Becking, et al. (10). Thermodynamic stability fields adapted from Berner (14). f Fore-reef sample. b Back-reef sample.

($t = 2.18$, $p < 0.05$), but no more reducing ($t = 0.032$, $p >> 0.05$). Microbially, these reef sediments are well within the combined activity limits of the ubiquitous deaminating heterotrophic, the denitrifying, and the sulfate reducing bacteria, between +115 and -205 mv (10). These activities additionally have been indicated by our diagenetic observations.

Though the intense bioturbation of these reef sediments inhibits steady state diagenesis, microbial activities are rapid enough to bring the system within small microenvironments close to thermodynamic equilibrium.

Acknowledgments

This study, Contribution Number 133 of the Discovery Bay Marine Laboratory, was made possible by the financial assistance of the Geological Society of America with a Penrose Bequest Research Grant generously contributed by the Mobil Oil Corporation. Logistical support was furnished by the D.M.B.L. staff and students. Patricia K. Bettis provided excellent laboratory assistance. This research, which forms part of the author's Master's thesis, was creatively supervised by Lynton S. Land and Robert L. Folk. James T. Sprinkle, Charles W. Kreitler, Kitty Lou Milliken, Susan D. Hovorka, and Brandt F. Henningsen were helpful in their discussion of the manuscript. Illustrations were prepared by Susan D. Hovorka. The author would also like to thank God, the moral support offered by his grandmother, Mrs. Johnnie Mac Poe, and all those micro-organisms, too numerous to mention individually, but without whose aid these diagenetic observations would surely not have been made.

References

1. Murray, J. and R. Irvine. 1895. On the chemical changes which take place in the composition of sea water associated with blue muds on the floor of the ocean. Trans. Roy. Soc. Edin., 37: 481-508.

2. Garrels, R.M. and C.L. Christ. 1965. Solutions, Minerals, and Equilibria. Harper & Row, N.Y., N.Y. 450 pp.

3. Sayles, F.L., T.R.S. Wilson, D.N. Hume and P.C. Mangelsdorf, Jr. 1973. In situ sampler for marine sedimentary pore waters: evidence for potassium depletion and calcium enrichment.

4. Emerson, S. 1976. Early diagenesis in anaerobic lake sediments: chemical equilibria in interstitial waters. Geochim. Cosomochim. Acta, 40: 925-934.

5. Dean, W.E., Jr. 1974. Determination of carbonate and organic matter in calcareous sediments and sedimentary rocks by loss on ignition: comparison with other methods. Jour. Sed. Pet., 44: 242-248.

6. Folk, R.L. 1974. Petrology of Sedimentary Rocks. Hemphill Publishing Co., Austin, Tex. 182 pp.

7. Spiegel, M.R. 1961. Schaum's Outline of Theory and Problems of Statistics. Schaum Pub. Co., N.Y., N.Y. 359 pp.

8. Strickland, J.D.H. and T.R. Parsons. 1968. A practical handbook of seawater analysis. Fish. Res. Bd. Can., 167: 311 pp.

9. Zobell, C.E. 1946. Studies on redox potential of marine sediments. Bull. Amer. Ass. Pet. Geol., 30: 477-513.

10. Baas Becking, L.G.M., I.R. Kaplan and D. Moore. 1960. Limits of the natural environment in terms of pH and oxidation-reduction potentials. Jour. Geol., 68: 243-284.

11. Goreau, T.F. and L.S. Land. 1974. Fore-reef morphology and depositional processes, North Jamaica. In: Reefs In Time and Space, L.F. La Porte (ed.) Soc. Econ. Paleont. Miner. sp. publ., 18: 77-89.

12. Moore, C.H., Jr., E.A. Graham and L.S. Land. 1976. Sediment transport and dispersal across the deep fore-reef and island slope (-55m to -305m) Discovery Bay, Jamaica. Jour. Sed. Pet., 46: 174-187.

13. Bunt, J.S., C.C. Lee and E. Lee. 1972. Primary productivity and related data from tropical and subtropical marine sediments. Mar. Biol., 16: 28-36.

14. Berner, R.A. 1971. Principles of Chemical Sedimentology, McGraw-Hill, N.Y., N.Y. 240 pp.

15. Reiswig, H.M. 1972. The spectrum of particulate organic matter of shallow-bottom boundary waters of Jamaica. Lim. and Ocean., 17: 341-348.

16. Berner, R.A. 1976. The benthic boundary layer from the viewpoint of a geochemist. In: The Benthic Boundary Layer, I.N. McCave (ed.) Plenum Pub. Corp., N.Y., N.Y. 33-55.

17. Thorstenson, D.C. 1970. Equilibrium distribution of small organic molecules in natural waters. Geochim. Cosomochim. Acta, 34: 745-770.

18. Thorstenson, D.C. and F.T. Mackenzie. 1974. Time variability of pore water chemistry in recent carbonate sediments, Devil's Hole, Harrington Sound, Bermuda. Geochim. Cosomochim. Acta, 38: 1-19.

19. Rakestraw, N.W. and V.M. Emmel. 1938. The solubility of nitrogen and argon in sea water. Jour. Phys. Chem., 42: 1211-1215.