26. PRELIMINARY GEOCHEMISTRY

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INTRODUCTION

This section deals primarily with evaluation of the water samples collected and the shipboard analyses. Details of the analytical procedures employed are given in the introduction ot the site reports. The complete set of chemical data is given in Table 1 and is discussed in the respective site report. This section is an evaluation and synthesis of the Leg 4 shipboard data.

SAMPLING

The methods of sampling are discussed in the Deep Sea Drilling Project core manual. Great effort was made to sample undisturbed material. In fine-grained sediments the occurrence of contamination does not appear to be a problem. Contamination in coarser sediments is far more likely, and should be considered in more detail. At Site 26, silty clays and sandy silts were sampled. The samples were only slightly disturbed in coring and represent nearly perfect coarse samples. The *p*H and total salinity data are significantly different from sea water, and indicate that little or no contamination has occurred as this should have obliterated these differences. At Site 29 a large section of radiolarian ooze was cored. This material is fairly coarse with clay contents commonly 50 per cent or less. The material appeared highly disturbed in most core sections. Despite the apparent disturbance during coring, the chemical data suggests that contamination was not severe if it occurred at all (see Site 29, Site Reports). On the basis of the observations and shipboard data from Leg 4, it appears that contamination can be largely eliminated, even in relatively coarse-grained deep ocean sediment, by judicious selection of samples.

SALINITY

Salinities were measured with a temperature compensated refractometer. The reproducibility of the readings is ±0.2 per cent. The values reported for the sites in the Atlantic are, with few exceptions, slightly below the expected bottom water salinity of 34.7 per cent (Wüst, 1936; Fuglister, 1960). At Site 26, abnormally low salinities were found (as low as 31.0 per cent). In the Caribbean, the salinity values scatter about the presumed bottom water salinities at most sites; however, Site 30 is characterized by salinities well below any possible bottom water values. There is no characteristic trend of salinity with depth.

Data comparable to that of Leg 4 are not abundant. The earlier Deep Sea Drilling Project data indicate that for most samples from the Atlantic the salinities are about the same as expected bottom water salinities (Deep Sea Drilling Project Legs 1, 2 and 3). Samples from the Bermuda Rise yielded salinities somewhat greater than that of sea water. Most Gulf of Mexico samples show little deviation from expected bottom water salinities except where contiguous to evaporites. In the latter case, strong salinity increases with depth were found due to the upward diffusion of salts (Manheim and Bischoff, 1969; Manheim and Sayles, 1969).[1] Except for the latter cases there was no definite trend in salinity with depth. Rittenberg *et al.* (1963) have reported a very slight overall increase in chlorinity from cores from the experimental Mohole project. Most of the reported data support the conclusion that there is little change in the total salt content of interstitial solutions in oceanic sediments with depth. Salinities are generally quite close to that presumed for the bottom waters (±<1 per cent). This is the case for most of the Leg 4 samples.

It has been recognized for years that expulsion of pore waters from sediments or soils under pressure may affect the composition of these solutions making the effluent not truly representative of the original interstitial solution (see for example von Englehardt and Gaida, 1963; Kryukov *et al.,* 1963). It must be considered whether the salinity data reported for Leg 4 are representative of the interstitial solutions or simply artifacts produced during squeezing.

The experiments of Kryukov and Komarova (1956) have shown that little or no effect upon pore solutions can be detected below about 600 kg/cm^2 (8500). However, they have also shown that the type of material being squeezed and the salinity may be very important in determining the magnitude of the compositional changes in the effluent solutions. Manheim (1966) has argued that at lower pressures the effects upon pore water composition are small for the type of squeezer employed by him in his experiments. This same type of squeezer is used aboard the *Glomar Challenger* to obtain interstitial water samples. Englehardt and Gaida (1963) report no changes in solution expressed from kaolinite (cation exchange capacity equals 3 to 5 meq/100 gm), but in montmorillonite (cation exchange

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[1] In Hole 1, in the cap rock of the salt dome drilled, very low salinities were measured and were due, apparently, to the reduction of sulfate (SO_4=) and oxidation of hydrocarbons.

TABLE 1
Chemical Data, Leg 4

Sample No.	Salinity %	*p*H	Eh (mv.)	CO_2 (µl/ml)
23-1-1 (130-145)	36.3	7.6	+460	–
23-3-2 (135-145)	34.7	6.6	+500	–
23-4-2	34.1	–	–	–
23-4-3 (54-60)	34.4	7.6	+440	–
24-4-3 (142-146)	33.3	–	–	–
24A-3-1 (122-131)	35.5	7.5	(Negative)	–
26-1-3 (81-130)	32.2	–	–	–
26-1-3 (7-10)	31.9	7.8	+440	–
26-3-2 (100-150)	31.0	–	–	–
26-3-2 (6-12)	31.1	7.6	+420	–
26-3-5 (87-131)	32.2	–	–	–
26-5-3 (4-9)	31.6	7.8	+420	–
27-2-2 (95-150)	34.1	–	–	–
27-2-3 (5-8)	34.1	7.5	+495	164.7
27-3-2 (5-11)	33.0	8.3	+431	93.5
27-3-2 (0-64)	33.3	–	–	–
27-4-1 (140-145)	33.4	7.9	+450	85.9
27-4-3 (84-150)	33.4	–	–	–
27-5-2 (95-149)	34.1	–	–	–
27-5-2 (141-145)	34.1	7.2	+490	17.4
27A-1-5 (139-145)	34.7	7.9	+470	109.3
27A-1-5 (93-140)	35.2	–	–	–
27A-2-3 (127-134)	34.7	7.9	+480	125.9
27A-2-3 (90-138)	35.8	–	–	–
27A-3-3 (130-134)	34.1	8.0	+460	133.6
27A-4-3 (70-86)	34.7	8.0	+420	95.8
27A-4-3 (33-37)	34.7	8.0	+440	129.1
28-2-3 (82-150)	34.7	–	–	–
28-2-3 (140-145)	34.7	7.0	+460	186.9
28-3-1 (138-145)	34.7	7.2	+460	74.5
28-3-2 (89-150)	35.2	–	–	–
29-1-3 (140-145)	35.2	7.4	+420	59.0
29-1-3 (90-150)	35.2	–	–	–
29-4-3 (140-145)	34.4	7.5	+450	57.0
29-4-3 (85-140	34.9	–	–	–
29-9-2 (140-145)	34.9	7.5	+500	66.6

TABLE 1 – *Continued*

Sample No.	Salinity %	pH	Eh (mv.)	CO_2 (μl/ml)
29-9-3 (80-136)	34.9	–	–	–
29-12-6 (143-148)	34.7	7.3	+510	107.0
29-14-3 (135-140	34.7	7.4	+490	55.8
29-17-1 (136-143)	35.2	7.4	+495	60.8
29B-1-6 (139-148)	34.7	7.3	+470	57.8
29B-2-2 (94-150)	34.7	–	–	–
29B-44 (48-53)	34.1	7.3	+500	53.8
29B-5-2 (99-150)	34.7	–	–	–
29B-8-2 (70-77)	34.7	7.3	+500	71.8
29B-9-4 (71-77)	35.2	7.7	+500	54.2
30-2-4 (122-131)	32.7	7.9	+490	257.8
30-2-4 (90-150)	32.7	–	–	–
30-3-3 (144-150)	31.9	7.9	+450	197.8
30-5-2 (90-146)	31.6	–	–	–
30-6-2 (139-144)	31.6	7.6	+460	50.8
30-11-2 (71-73)	31.9	8.1	+490	9.8
30-13-1 (145)	–	7.6	+450	–
30-15-4 (8-12)	32.7	8.0	+410	25.8
31-3-6 (142-147)	34.4	7.0	+520	51.8
31-9-2 (105-108)	35.2	7.2	+370	68.2
31-10-2 (142-145)	35.2	7.4	+470	89.8

capacity equals 40 to 150 meq/100 gm) noticeable changes were observed. Warner (1964) has clearly shown the difference in the effect of montmorillonite and illite (cation exchange capacity equals 10 to 40 meq/100 gm) upon expressed pore waters. Much lower porosities were required in illites than in montmorillonites before any compositional effects were noted. In all cases the noted effect was a decrease in dissolved salt content of the effluent. Manheim (1966) points out that normal sediments can be expected to affect compositions to a lesser degree than montmorillonites as the overall surface activity is far less. The Leg 4 sediment can be expected to behave more like kaolinite or illite than like montmorillonite; however, one can only say that the large salinity fluctuations are probably not due primarily to squeezing effects. Such a process cannot be ruled out entirely.

To investigate the possibility of alteration of actual salinities by the squeezing procedure, two of the most clay-rich, carbonate poor samples were squeezed at successively higher pressures and the salinity of the effluent at each pressure measured.[2] The samples were first mixed with a solution of sodium chloride (29.4 gm/l) with a mechanical blender. They were then centrifuged and the salinity of the supernatant solution measured. The solid was then placed in a squeezer and the salinity of the effluent at successively higher pressures measured. The results are presented in Figure 1.

It is obvious that there is a difference in the effect produced by the two different squeezers employed (there is no evidence of a significant mineralogical difference in the two samples). The small area piston squeezer produced no effect upon the pore water composition even at pressures of nearly 10,000 psi. The squeezer with the larger piston area did produce a decrease in the salinity at the higher pressures employed (1500 psi and 2300 psi). The total quantity of effluent produced at these

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[2] By virtue of the high clay content and low carbonate content, these samples should show a greater effect upon measured salinities during squeezing than a great majority of the samples collected.

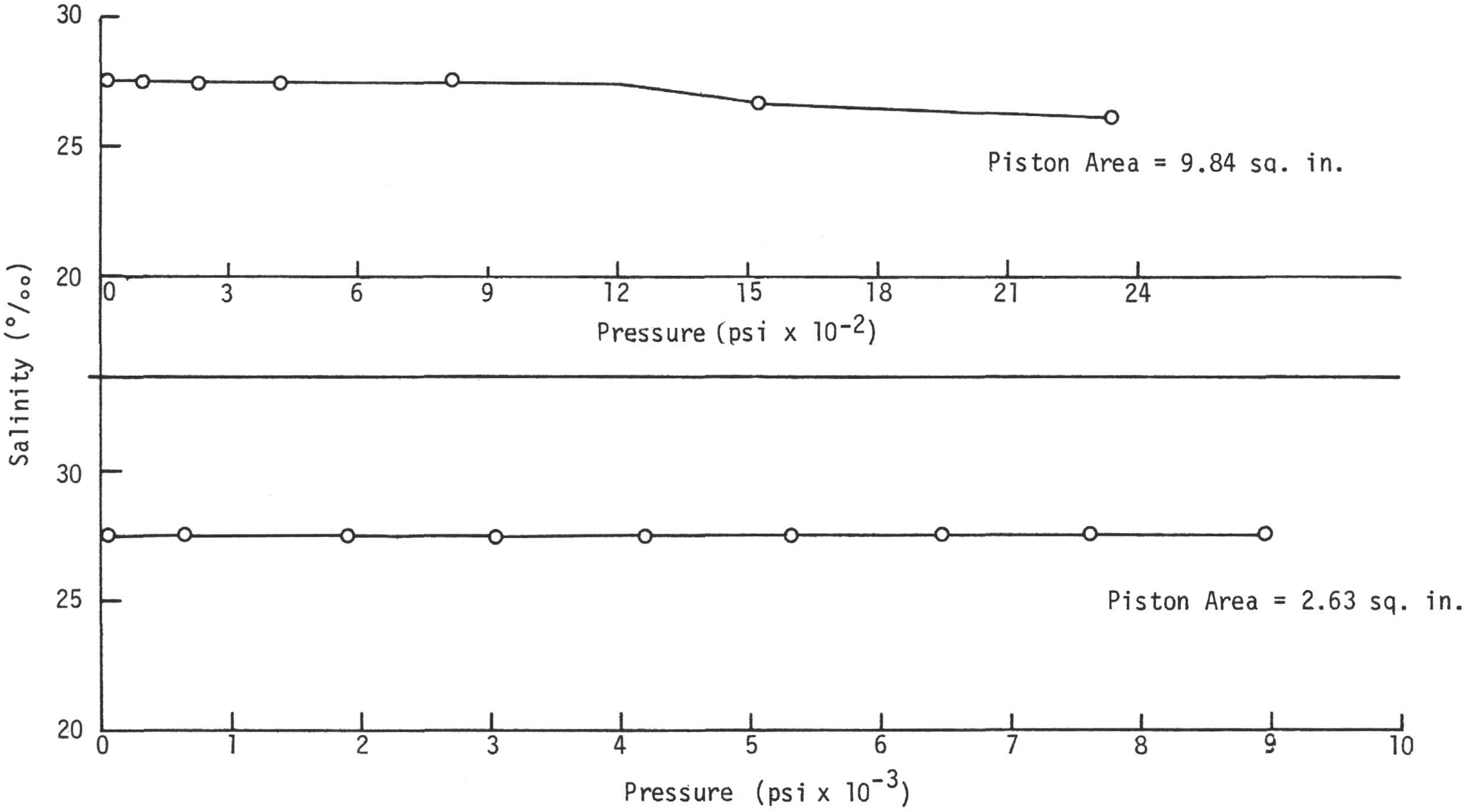

Figure 1. *Effect of pressure on effluent salinity.*

higher pressures was about 1 milliliter. The lowest yield of solution from samples collected on Leg 4 was 6 milliliters from an amount of sediment equivalent to that used in these experiments. If only one part in six has a lower salinity, then the effect upon the total effluent collected will be approximately the error in the measurement (±0.2 per cent). Few samples produced as little as 6 milliliters of solution, most yielded eight to ten; in these samples squeezing effects will be below the analytical sensitivity. Further, few samples are as clay-rich (90 to 92 per cent) and squeezing effects in a great bulk of the samples can be expected to be significantly less than those shown in Figure 1.

These experiments have utilized a sodium chloride solution for determining squeezing effects. It is possible that the doubly charged ions Ca^{++} and Mg^{++} may be more strongly affected than Na^{+}. The experiments of Kryukov *et al.* (1963) indicate that there is little specific ion effect. On this basis only the changes in sodium chloride would be large enough to significantly affect the salinity determination, and the behavior of the sodium chloride solution can be considered comparable to that of the interstitial solutions.

The above experiments have utilized samples which should exhibit maximum changes in salinity resulting from squeezing. In these extreme cases, the effects do not exceed the analytical uncertainty of the salinity determinations; changes in most samples will be still less. The salinities measured are representative of the interstitial solutions; the low salinities measured are real.

The two different squeezers employed differ noticeably in their effects upon the effluent. Despite lower pressures (by a factor of 6.5) the large volume squeezer is the one which produces a detectable decrease in the salinity, though it is only slight. This merely reflects the fact that the effectiveness of the given clay in altering the salinity of solutions expressed from such a clay sediment is primarily a function of the geometry of the particles in the sediment (see Warner, 1964). The large volume squeezer is far more effective at reducing the void space of the entire sample than is the small volume squeezer.

The deviations of pore water salinity from expected bottom water values that have been reported for Leg 4 are, with few exceptions, towards lower values. At two sites (26 and 30) these deviations are relatively large (up to 3.6 per cent). Ion migration under the influence of a variety of forces has been suggested by Mangelsdorf *et al.* (1969) as a possible mechanism for altering the composition and total salt content of interstitial solutions. Changes introduced during compaction of clays (induced or natural) have been mentioned previously. A third possible mechanism is by chemical reaction. The observed changes with depth, where they are large—as at Sites 26 and 30, are a dilution of the presumed original solution. The first two mechanisms mentioned above (ion migration and compaction) will lead to an overall increase in the salt content of pore water with depth. This is a trend opposite to that observed even in clay-rich samples which should maximize effects introduced by compaction (see Figure 2). The observed salinity changes most probably result from chemical diagenesis; a detailed analysis of possible reactions is left to the shore laboratory reports.

EH MEASUREMENTS

The Eh of the interstitial water samples was measured utilizing a platinum electrode and calomel reference electrode. Only a single negative Eh was recorded; a great majority of the measurements fell in the range +400 to +500 millivolts. Such uniformity in the wide range of environments encountered is highly unusual. The measurement of Eh by the technique employed aboard the *Glomar Challenger* has been the subject of much controversy, centering primarily around the validity of such e.m.f. measurements. Because of this uncertainty and the narrow range of recorded values an independent view of Eh should be obtained. A qualitative or semi-quantitative estimate of the redox potential of the solutions can be gathered from a consideration of several relevant redox reactions. These values provide a check upon the validity of the Eh measurements.

The presence of the mineral pyrite ($Fe\ (Co, Ni)\ S_2$) in contact with solutions whose compositions are similar to those being dealt with in this report requires reducing conditions if any equilibrium model is presumed to be valid. Utilizing the Eh-*p*H diagrams of Garrels and Christ (1965, pp. 218-224) it can be seen that even for a solution with total dissolved sulfur as high as 10^{-1}M, the maximum Eh at which ferrous sulfate (FeS_2) is stable ($pH = 7.5$) relative to ferric oxide (Fe_2O_3) and ferrous carbonate ($FeCO_3$) is approximately -175 millivolts. In actual fact, total dissolved sulfur will generally be somewhat lower, approximately 3×10^{-2}M. The above Eh values are for 25°C and 1 atmosphere and are not strictly applicable to the conditions of the *in situ* samples. It is very doubtful, however, if even such large pressure changes can account for the discrepancies encountered. In general, pressure effects upon the partial molal volumes of aqueous and solid species are small, and thus the change in free energy with pressure can be expected to be small.

In one case (24A-3-1) a negative Eh was measured (this could not be done quantitatively due to equipment failure). This is qualitatively in accord with theory, and equilibrium is at least possible. Pyrite was also noted in Cores 3 and 4 at Site 27. Eh measurements for samples from these cores are +430 millivolts and +450 millivolts, respectively; highly unrealistic values for solutions presumably in equilibrium with pyrite. Pyrite was also found in samples from Core 3 at Site 31. The Eh

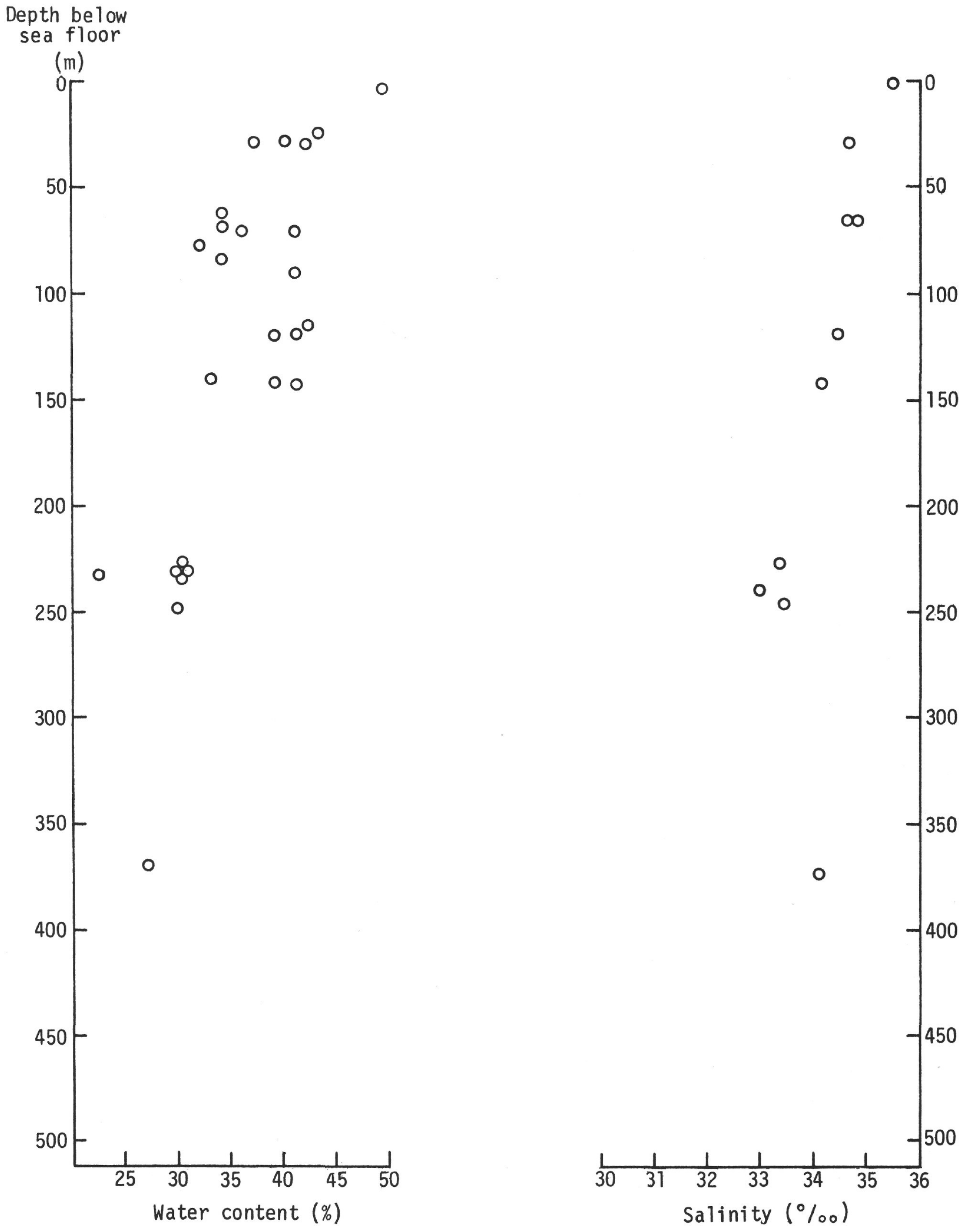

Figure 2. *Water content and salinity as a function of depth for clay-rich (≥ 85%), organic poor (< 0.2%), carbonate poor (< 5.0% samples.*

measured in this instance was +520 millivolts; it should be noted, however, that in the latter case the pyrite occurred as isolated aggregates rather than being disseminated throughout the core as in the previous cases.

Glauconite is generally thought to be indicative of mildly reducing conditions (Deer *et al.,* 1962) because of the presence of both divalent and trivalent iron substituting in the octahedral Al^{3+} lattice sites. At Site 23 in Core 4 glauconite was reported as common, yet the pore water yielded an Eh of +440 millivolts. The same results were found in glauconitic samples from Sites 27 and 30. At the latter site three samples from glauconitic sediments yielded Eh values of +410 to +490 millivolts. All of these data are incompatible with an equilibrium model.

Another reaction having bearing upon the question of the validity of the Eh measurements is the reduction of sulfate ($SO_4^{=}$) by bacteria. Reducation of $SO_4^{=}$ to $S^{=}$ is well documented in the waters of anoxic basins (Richards, 1965). Such a reaction has been reported in several pore water studies (see Manheim and Bischoff, 1969 and references cited therein). Sulfate reduction will only occur when all or nearly all of the oxygen, nitrate ions and nitrite ions have been consumed. Wheatland (1954) concluded on the basis of experimental work that reduction is negligible in the presence of 0.11 ppm (V/V) oxygen. Sulfate reduction can only be expected to occur under negative Eh conditions. According to Garrels and Christ (1965) at 25°C and 1 atmosphere $[HS^-] = [SO_4^{=}]$ at a *p*H of 7.5 at approximately -225 millivolts. To further remove sulfate ($SO_4^{=}$) would require still more negative values; as noted previously, the 25°C, 1 atmosphere pressure values are not directly applicable, but pressure effects should not produce a drastic change in stability relations. The reduction of the amount of sulfate at Site 26 has been to 0.06 gm/kg; at Site 30 it has been reduced to 0.11 gm/kg (unpublished data from Deep Sea Drilling Project, Leg 4 Samples). Various determinations for sea water range from 2.69 to 2.74 gm/kg (Culkin, 1965). It is possible that the removal of sulfate ($SO_4^{=}$) has been accomplished by precipitation, but the association with relatively high organic content makes sulfate ($SO_4^{=}$) reduction much more likely.

If the low sulfate ($SO_4^{=}$) concentration at Sites 26 and 30 is due to the reduction of sulfate as seems most likely, then negative Eh values should have been measured in the interstitial solution samples from these sites. This was not the case; the range of values for both sites is +410 to +490 millivolts.

Efforts were made to clean the electrode frequently, but this had no effect. The squeezer was thoroughly flushed with N_2 just prior to squeezing to eliminate oxygen (O_2) contamination with no detectable effect. A second platinum electrode was used with equal lack of change. Measurements were made as rapidly as possible after drift had ceased.

On the basis of the chemical considerations presented above, it must be concluded that the measured Eh values appear to have little relevance to the oxidation potentials of the solutions. For the three redox reactions investigated, measurement of e.m.f. with the platinum electrode yielded impossible values almost without exception. This has been a cursory and qualitative investigation, but it seems doubtful if more detailed efforts will significantly alter the picture presented. The Eh data must be considered unreliable.

PH MEASUREMENT

The measurement of *p*H was accomplished with a combination glass-calomel electrode. The range of values was 6.6 to 8.3; a great majority of the samples fell between 7.3 and 8.0. No consistent trend of *p*H with depth was observed; the fluctuation within a single hole is commonly greater than the fluctuation from site to site. Not surprisingly, the control of *p*H appears to be highly local and determined by complex equilibria which vary greatly over short distances. One feature has been superimposed upon all or nearly all of the samples: increased acidity. Sea water at about 5000 meters can be expected to have a *p*H of on the order of 7.8 or at 25°C and 1 atmosphere, 8.0. Nearly all of the samples are more acid than the expected bottom water by up to 0.6 *p*H units. The most probable origin of the lower *p*H values is increased carbon dioxide (CO_2) from organic matter oxidation by available oxygen and/or sulfate ($SO_4^{=}$) reduction.

The values given in the Site Reports are at 25°C and 1 atmosphere. It is presumed that the aqueous distribution of species reaches equilibrium rapidly, and hence the recorded *p*H values are quite different from *in situ* values. By extrapolating and interpolating the data of Culberson and Pytkowicz (1968) and Harvey (1966), correction for pressure and temperature changes may be made. The apparent dissociation constants given in the above two references are not true thermodynamic equilibrium constants and are sensitive to ionic strength; the sensitivity is not high, however. As the sample salinities are, with few exceptions (excluding Sites 26 and 30), within 1 per cent of the salinity studied by Culberson and Pytkowicz (1968), their data are directly applicable to the Leg 4 samples. Harvey's (1966) data cover a range of salinities. No attempt has been made to recalculate all of the data; only the range of corrections has been estimated. The temperatures of the samples from near the sediment-water interface will be close to 2°C; for the Atlantic the pressures will be on the order of 500 atmospheres for these samples. Almost all of the measured *p*H values fall in the range 7.4 to 8.0. For a *p*H of 7.4 the correction to 2°C and 500 atmospheres is -0.23 *p*H units; for a *p*H of 8.0 it will be -0.20. Pressure effects increase the dissociation constants of the carbon dioxide (CO_2) species of concern and the borate as well. Temperature increases will decrease the dissociation constants. For the pressure and temperature gradients within the sediments the net effect is small. The deepest samples were collected approximately 550 meters below the sea floor. The temperature increase of some 16°C and pressure increase of about 100 atmospheres produce a net change in *p*H from that calculated for the sea floor of only about -0.03 *p*H units;[3] such a change is not significant in terms of the accuracy of the data. A re-calculation of the laboratory values of *p*H to *in situ* values will employ an essentially constant correction. Consequently, any trends exhibited by the *p*H vs. depth plots in the site reports are directly translatable to *in situ* trends.

The buffer solutions used to standardize the *p*H readings were standard dilute buffers; the samples are characterized by ionic strengths similar to that of sea water (0.7). This discrepancy will introduce an error in the *p*H measurement relative to an absolute scale, i.e., in the interpretation of *p*H as hydrogen ion activity. This error arises through a change in the liquid junction potential (buffer $|$ $KCl_{(sat.)}$ and solution X $|$ $KCl_{(sat.)}$) when exchanging unknown for buffer in the cell. The error so introduced in the solutions considered here may amount to as much as 0.04 *p*H units (see Garrels and Christ, 1965).

The change in junction potential mentioned above causes drift of the measured potential as the cell equilibrates; this will introduce still another error. It may take up to twenty minutes in extreme cases for drift to cease. Many of the solutions have carbon dioxide (CO_2) contents differing from the equilibrium values at 25°C and 1 atmosphere by factors of 1/6 to 4. Carbon dioxide loss will lead to drift in the same direction as the junction potential drift. It is impossible to distinguish between the two, and hence prolonged drift is arbitrarily cut off and the *p*H measured. In such a case carbon dioxide loss may have led to a different *p*H than in the original solution or a stable value may not have been reached. While carbon dioxide equilibration is presumed to be slow, errors introduced in the manner just described may be very significant. Considering the errors resulting from junction potential and drift uncertainties, it is felt that the *p*H data are not accurate to more than the nearest 0.1 *p*H unit.

While the calculation of hydrogen ion activity may be in error, the errors in most samples will be similar for the simple reason that there are only small differences in the chemical compositions of the samples. Consequently, the *p*H values recorded have greater accuracy relative to each other than in absolute terms; i.e., they accurately record hydrogen ion activity changes, but this is not directly translatable to activities without the introduction of the errors mentioned previously. Because of the consistency within the group of samples, the *p*H changes with depth shown in the Site Reports have been presented to precision greater than 0.1 *p*H unit.

CARBON DIOXIDE (CO_2) MEASUREMENTS

The total carbon dioxide data are summarized in Figure 3. Although the data are sparse for some sites (28 in particular), the tendency for the carbon dioxide distribution to reach maximum values at depths between 60 and 150 meters is quite apparent. Values 2.5 to 4 times that of surface sea water were recorded. Where deep coverage is available, carbon dioxide contents as low as one-sixth of the surface sea water valve have been found. The accuracy of the chromatographic analysis does not appear to be better than ±10 per cent. As handling of the samples is inevitable there is apt to be a significant change in carbon dioxide content prior to analysis for those samples which differ markedly from equilibrium at atmospheric carbon dioxide (CO_2) pressure. It is impossible to evaluate this error.

The origin of the distribution patterns of carbon dioxide seen in Figure 3 can only be speculated upon, as adequate coverage exists only for Site 27; even in this case coverage begins at 30 meters. Carbon dioxide contents as high as ten times that of surface sea water have been reported in piston cores (see Siever *et al.,* 1965). Emery and Hoggan (1958) have reported values only slightly higher than sea water, but showing a marked increase with depth. Pushkina (1963) found a severalfold increase in total carbon dioxide within three meters of the sediment-water interface, and a decrease from this point downward. The origin of the carbon dioxide appears to be oxidation of organic matter in the sediment. It is to be expected that the carbon dioxide in the Leg 4 cores is of the same origin. One would expect to find maximum values within the first five meters as reported by Pushkina (1963) as diffusion of oxygen (O_2) for oxidation or carbon dioxide (CO_2) diffusion must be rate controlling; burial of tens of meters should lead to prohibitively slow reaction rates. The occurrence of maxima below 60 meters[4] most probably represents changes in sedimentation rates and/or organic content of the sediment, and reflects preserved features. Diffusion would tend to smooth out the carbon dioxide

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[3] In the absence of temperature data the average crustal gradient of 3°/100m has been used. The pressure increase has been calculated by assuming an average density of 1.7 gms/cc and assuming that hydrostatic pressure is equal to total load pressure (see Fyfe, Turner and Verhoogen, 1958).

[4] It should be noted that for Sites 28 and 30 maxima may occur anywhere within the upper 60 meters, as no samples are available in this interval. Only Site 27 has a thoroughly documented maximum.

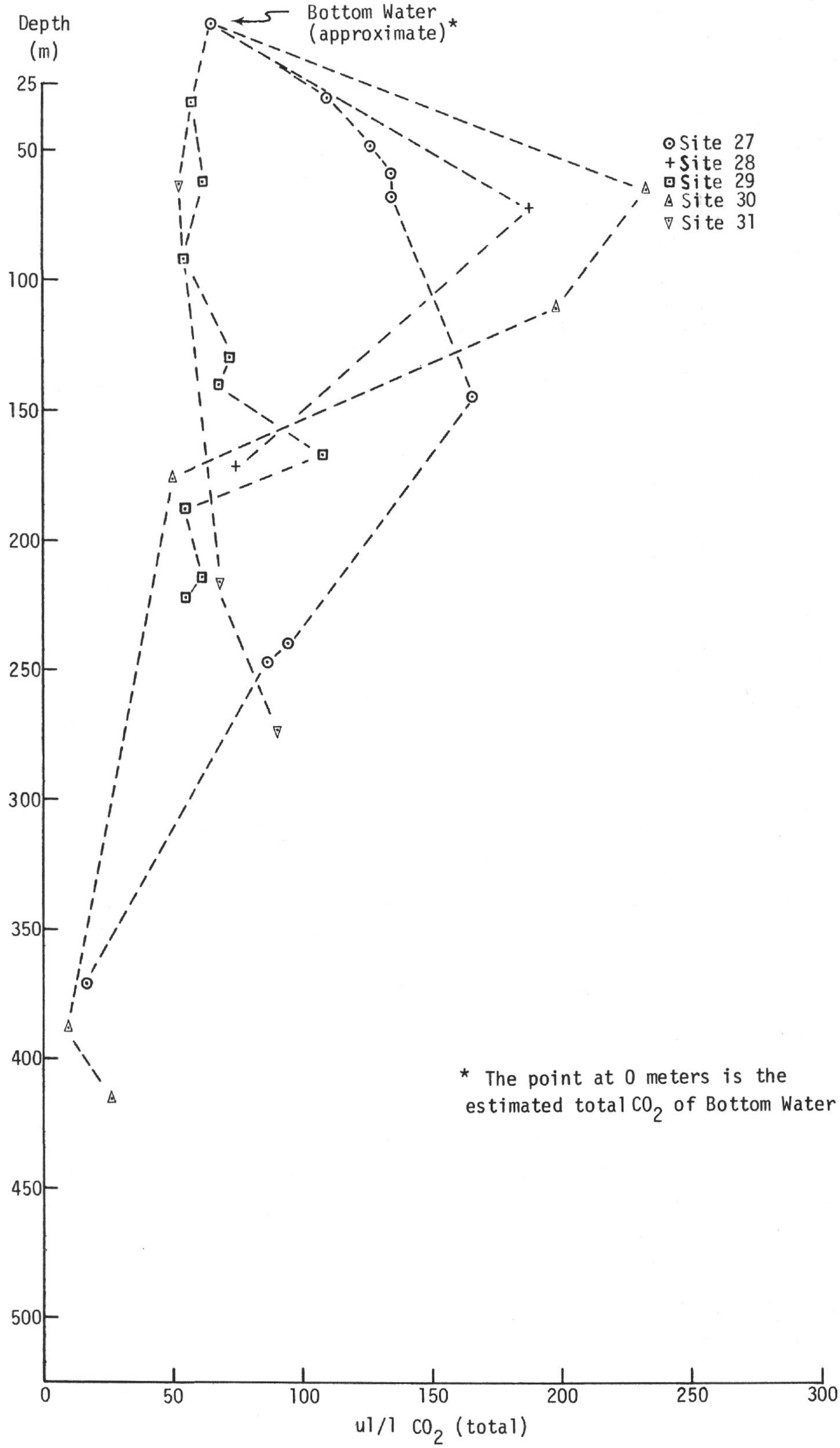

Figure 3. *Total CO_2 variation with depth for all sites measured.*

distribution and erase differences produced by small changes in organic contents and burial rate. It is also possible that this distribution is a steady-state balance between diffusion controlled carbon dioxide production and diffusion and reaction loss of carbon dioxide, but this does not appear likely.

At Sites 27 and 30, carbon dioxide contents well below bottom water values were noted. The most obvious explanation for the loss of carbon dioxide is precipitation of a carbonate phase. Adsorption of $CO_3^=$ on clay surfaces as shown experimentally by Bruyevich and Kulik (1967) is also a possibility, but as clay surfaces carry a negative charge, the mechanism of adsorption is difficult to explain. It is impossible to evaluate the carbonate equilibria with the available data, and consequently it cannot be determined whether either of the above are operative. Regardless of the manner of carbon dioxide (as $CO_3^=$) loss, if any approach to equilibrium is presumed, the loss in $CO_3^=$ must lead to an increase in H^+ activity. The pH-CO_2 data indicate that in some instances parallel variation is observed, providing qualitative agreement with the above models. Just as frequently pH increases as total carbon dioxide decreases. This is incompatible with the removal of $CO_3^=$ and the maintenance equilibrium. Such a response would be produced by the removal of carbon dioxide, perhaps by diffusion.

The above suggests ways in which the observed pH-CO_2 variations can be qualitatively explained. Data on cation concentrations are required to check these suggestions in a quantitative fashion and are not now available. If the suggested reactions are important in determining the observed carbon dioxide distributions, it is difficult to envision why the reactions are so slow. The decreases are noted only after tens of millions of years. While either adsorption or precipitation may alter the total carbon dioxide content slightly, it does not seem likely that either is the mechanism primarily responsible for the marked decreases in total carbon dioxide seen at Sites 27, 28 and 30. If the reactions are to occur, they should do so in the upper portions of the sediment, i.e., during the first several million years following burial. The basic shape of the curves most probably represents a distribution produced by differences in the organic content and more particularly oxidation of organic matter to carbon dioxide. Upon this may be superimposed processes slightly reducing the carbon dioxide or $CO_3^=$ in the original sediment and leading to low values, such as, the deep samples from Sites 27 and 30. The absence of any indication of the trend to low values in Sites 29 and 31 and at Site 24 (based on HCO_3^- data) support this view.

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