13. INTERSTITIAL WATER STUDIES, LEG 25

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ABSTRACT

Interstitial water analyses from sediments collected during Leg 25 of the Deep Sea Drilling Project have revealed that in the southwest Indian Ocean, great chemical activity exists in sediments in various depositional environments. Variable sedimentation rates allow us to set some interesting boundary conditions on chemical and transport processes in these interstitial waters, particularly with regard to the distribution of dissolved sulfate. In terrigenous rapidly deposited sediments, large depletions are observed in magnesium and potassium, whereas relatively small decreases in dissolved calcium occur. In slowly deposited detrital sediments, also, large decreases in potassium and magnesium coincide with very large calcium increases. In truly pelagic sediments, a one to one replacement of magnesium by calcium is observed in the interstitial waters, presumably due to reactions in the basal sediment layers. Biogenous deposits have great influence on dissolved silica (sponge spicules and radiolarians) and on dissolved strontium (carbonate recrystallization). Otherwise, dissolved silica reflects the clay mineralogy and shows variations which seem particularly dependent on the presence or absence of kaolinite. Variable dissolved manganese values reflect reducing conditions and/or availability of manganese in the solid phases for mobilization in reducing sediments.

INTRODUCTION

During Leg 25, the *Glomar Challenger* cruise in the southwest Indian Ocean, an intensive program of sampling interstitial waters and their connate sediments was carried out. To date, such programs have been a regular feature during all legs of the *Glomar Challenger*, the results of which have been published in the various Initial Reports. During Leg 15, a more intensive geochemical program was carried out (see Part V, Geochemical Investigations in the Caribbean Sea, Leg 15 in Volume 20, 1973). During that leg, special attention was given to Sites 147, 148, and 149, with emphasis on close-spaced sampling, the study of temperature of squeezing artifacts (cf. Mangelsdorf et al., 1969; Fanning and Pilson, 1971), as well as the study of stable isotopes in both the liquid and solid phases.

These studies of the interstitial water chemistry of deep-sea sediments have often established smaller or larger deviations from the average composition of seawater, particularly with regard to some of its major constituents. The depth distribution of all the major cations and anions depends upon their reactivity in the sedimentary column as well as on the rate of supply of these ions in the case where, at a certain location in the sediment column, reactions occur that involve such ions. This rate of supply, usually controlled by molecular diffusion processes and/or upward advection of interstitial water due to compaction, also depends on the rate of sediment accumulation. Rapid sedimentation can cause the sediment-interstitial water system to become closed to exchange with the overlying seawater. The various sites investigated during Leg 25 contain a rather large variety of sedimentary sequences. Detailed descriptions of the various sites are given in the site reports (Chapters 2 through 10, this volume) as well as in the contributions of Leclaire, Moore, and Vallier (this volume). It is not deemed appropriate to repeat many of these descriptions in this report, and only the major lithologic features are recorded in the various figures giving the alkalinity distributions.

Of major interest, in addition to the mineralogical studies of Matti et al. (this volume), are the rates of sedimentation in these holes as well as the position and "duration" of the sedimentation hiatuses. This information is summarized in Figure 1. No certainty exists about the nature of these sedimentation breaks, i.e., whether they represent prolonged periods of no sedimentation or "negative" sedimentation, due, for instance, to the scouring action of bottom currents (cf. Leclaire, this volume). Whatever the cause of these sedimentation breaks, it is of importance to investigate the effect, if any, they may have had on the distribution of the various ions in the interstitial waters.

In sediments with rapid accumulation rates (usually more than 2 cm/1000 y), one often observes an increase in the alkalinity (mostly bicarbonate ions) with depth, generally as a result of sulfate reduction processes. At a certain depth, a maximum alkalinity value is often observed, followed by a rapid decrease in this parameter (see, for instance, Gieskes, 1973). In this case, diffusional supply of seawater sulfate ions or loss of bicarbonate ions is either not possible (closed system) or not fast enough to



Figure 1. Sedimentation rate diagram-Leg 25.

nullify any gradients. In slowly accumulating sediments (<1 cm/1000 y), one usually does not observe such maxima in alkalinity. However, in such sediments, one can still observe changes in the concentrations of various ions, and almost invariably one observes, below a certain depth, a gradual decrease in the alkalinity, presumably due either to the loss of carbon dioxide (or bicarbonate) by calcium carbonate precipitation or to silica reconstitution processes (cf., Siever, 1968a).

There is considerable debate about the possible significance of changes in the chemical composition of interstitial waters of deep-sea sediments, both with regard to their origin and to fluxes of elements into or out of the ocean. Little work has been done on the connate solid phases to verify postulated diagenetic mechanisms, usually because it is thought that the amounts of products of these diagenetic changes are too small to be detected. If this were so, then these studies would be irrelevant with regard to studies of overall geochemical mass balances. It is possible, however, that observed chemical changes in the interstitial waters are the result of reactions that started at or near the seawater-sediment interface and still go on after burial. This seems to be the case, for instance, at Site 149 (Leg 15), as demonstrated by Gieskes (1973), Sayles et al. (1973a), and Lawrence (1973). The latter author gave convincing

evidence for this concept in his oxygen isotope studies on pore waters and solid silicates.

Leg 25 provided a variety of holes that lend themselves excellently to investigations of the possible influence of sedimentation rates (or of sedimentation breaks) on the nature of observed chemical gradients. The various holes investigated also represent very different regimes of sedimentation, providing an excellent opportunity to study the nature of chemical changes, if any, in terms of possible diagenetic processes taking place in the sediments.

The specific aspects to which the present study will direct itself are:

1) Establishment of criteria that may serve as a guide in the determination of possible seawater contamination during retrieval of the sediment in the drilling process.

2) Further elucidation of temperature-induced effects on the chemical composition of interstitial waters; such effects arise from the retrieval of these waters under conditions of temperature and pressure different from those prevailing in situ.

3) Characterization of chemical changes, if any, in the interstitial waters that may yield information on ongoing diagenetic processes in the sediments and also on other processes affecting the interstitial water chemistry.

4) Study of the nature of chemical gradients with depth. Such information is especially important in studies of fluxes of materials in the overall geochemical system of the ocean and the sediments.

METHODS

Samples were obtained by means of so-called Manheim squeezers (Manheim and Sayles, in press). After the sediment was allowed to warm up in capped core-barrel sections, a "punch in" pH measurement was made (see below). Then the sediment was carefully scraped to remove the outer 5 to 10 mm and subsequently divided into two parts; one part was used in the room-temperature squeeze $(23^{\circ}C \pm 2)$ and the other was loaded into the cold squeezer, which was then stored in a refrigerator at 5°C for 1 to 2 hours. Any remaining sediment was stored for further laboratory examination.

Alkalinity and pH measurements were carried out immediately upon retrieval of the samples. The acidified sample was then sealed in a PVC tube for further analysis in the home laboratory.

Most analytical methods used in this study have been published in the Leg 15 Initial Reports (Gieskes, 1973). Modifications are discussed below.

Alkalinity: Potentiometric titration (Gieskes, 1973; Gieskes and Rogers, 1973). No sodium chloride was added to the 0.1 N HCl solution so that titrated samples could be investigated for chlorinity as well as for other constituents. Whatman No. 50 filters were used for the squeezing operations. As discussed previously (Gieskes, 1973), some residual acid is retained in these filters, which makes measured alkalinity and pH values slightly low. Errors due to this procedure can be as large as 0.25 meg/1 in alkalinity and about 0.2 pH units (cf. also Fanning and Pilson, 1971; Gieskes, 1973). We now have found that Whatman No. 1 filter paper has no such adverse effects (Jim Pine, personal communication). The present data, therefore, may be somewhat lower than the "real" values. The precision, however, remains better than 1 percent. The author, therefore, cautions against using the data of this report for calculating the degree of saturation of the interstitial waters with respect to calcite, but would like to stress their usefulness for comparative purposes.

pH: The *p*H was measured using "punch in" electrodes, "flow through" electrodes, and, finally, a combination electrode in the alkalinity titration vessel (Gieskes, 1973). For reasons discussed above, "flow through" and "vessel" *p*H values may be 0.1 to 0.2 *p*H units too low. A good measure of the effect of the filter paper will be any large discrepancy between these values and the "punch in" *p*H value, though differences can also be due to CO₂ losses, etc. (cf. Gieskes, 1973).

Calcium: Complexometric titration with EGTA (Tsunogai et al., 1968) as modified by Gieskes (1973) was used. Copenhagen IAPSO standard seawater was used as the standard. Corrections for strontium were made using the experimental Sr values.

Magnesium: The values of magnesium were obtained from EDTA titrations (Ca + Sr + Mg) and subtraction of (Ca + Sr) from these titrations. Again, *n*-butanol was used as an extractant, but we did find that this procedure affects the end point to a small degree (1% using 0.5-ml standard seawater aliquots, 0.5% using 1-ml aliquots). This is due to a shift in the equilibrium constants of Eriochrome Black-T with H⁺ and Mg⁺⁺ ions as a result of the change in the dielectric constant. We found, however, that if the sample size and the size of the standard seawater aliquot were equal, errors became negligible. Reproducibility was better than 0.2 percent. Again, IAPSO standard seawater was used for the standardization of the EDTA solution using the new Mg/Cl ratio of Carpenter and Manella (1973).

Dissolved Silica: An appropriate version of the method of Strickland and Parsons (1968) was used.

Chloride: Chlorinity was determined on samples previously titrated (onboard ship) for alkalinity using a Mohr titration with $AgNO_3$ and K_2CrO_4 as indicator. Corrections (less than 1%) were made for the added HCl. Whenever nonacidified samples were available, chlorinity values agreed within 1 percent.

Salinity: Total dissolved solids ("salinity") were measured using a Goldberg refractometer. Sayles, et al (1970) found that this "salinity" agreed well with their measured ion sums.

Ammonia: The method of Solorzano (1969), as modified by Presley (1971) and Gieskes (1973), was used. We found that nonacidified samples showed considerably less dissolved ammonia than did those that were titrated for alkalinity and subsequently stored at $pH \approx 3.0$. There is no guarantee that some ammonia is still not lost (presumably due to inorganic oxidation and/or biochemical consumption, since sometimes molds were found to grow in the samples), but the data should serve as a relative indicator of the sulfate reduction process.

Sulfate: The titration method of Cescon and Macchi (1973) was used. IAPSO standard seawater was used as a standard.

Manganese: 1 ml of sample was diluted with 4 ml of distilled water, and 0.1 ml of a 50,000 μ g/ml Lanthanum (La) solution was added. Standards were made in La Jolla pier water (range 0-10 ppm Mn in undiluted samples). Analysis was done by means of atomic absorption (AA) spectrometry, using a Perkin-Elmer Model 403 spectrometer.

Strontium: 2 ml of the manganese solution was further diluted with 8 ml of a 5000 ppm La solution. Analysis was carried out by AA spectrometry. Standards were prepared by making solutions of 10 to 100 ppm Sr in distilled water and diluting them in a manner similar to the dilution of the samples.

Potassium: 0.5 ml of the manganese solution was diluted with 10 ml of a 5000 ppm La solution. Analysis was carried out with the Perkin-Elmer Model 403 spectrometer in the emission mode. Standards were made of 100 to 500 ppm K in a background of 10,000 ppm Na, carrying through the dilutions as for the samples. Copenhagen IAPSO standard seawater was used as an additional standard.

Accuracies of the various measurements are affected not only by the precision of the methods but also by the handling of the samples. Also, errors are inevitably introduced in the squeezing process. In Table 1, estimates are presented of both accuracies and precisions of the various analyses. Note that the accuracy of the alkalinity and *p*H data also

	TABLE 1
Accuracy	and Precision of Analyses

Method	Accuracy (%)	Precision (%)
Alkalinity ^a	10	0.5
pH^{a}	0.2 (pH)	0.1 (pH)
Ca	2	0.2
Mg	2	0.2
so ₄	2	0.5
CI	2	0.5
NH4	10	5
SiO ₂	5	2
Mn	10	5
Sr	5	2
K	5	2

^aAccuracy affected by Whatman No. 50 paper.

depends on the variable filter paper effect. The estimated error is a maximum error.

RESULTS

Results of the various analyses are presented in Tables 2 through 7, as well as in Figures 2 through 45. The advantage of using these figures is clear as they give an instantaneous impression of the distributional trends of the various parameters.

The pH data are reported at 25° C, assuming a temperature coefficient of 0.01 pH/° C. Measurements were always carried out in the range of 20° to 26° C (laboratory temperature) so that corrections never exceeded 0.06 pH units. The cold squeeze pH values (5° C), therefore, must be augmented by 0.2 pH units to yield the value at 5° C. The data for pH and alkalinity are presented in more significant figures than seem justified; I have retained this notation for ease in comparing the various measurements.

In the lower parts of the holes, very small amounts of interstitial water sometimes were retrieved (2-3 ml). Such samples were subsequently diluted with distilled water. Some of the laboratory analyses suffered in accuracy by this procedure, and these data are bracketed in the accompanying figures.

The validity of some of the pore water data can always be questioned because of the ever-present chance of seawater contamination. Often cores show large drilling disturbances and sometimes so-called "drilling breccias," i.e., small chunks of sediment loosely aggregated in the core barrel. Also, as a result of the coring procedure, the outside of the core is in contact with seawater. Thus, even though care is taken to scrape off the contaminated outside of the core section and to avoid squeezing disturbed drilling breccia, the chance of contamination is always present.

During the course of this investigation, I found that there exists a very strong linear correlation between dissolved magnesium and dissolved calcium in holes with slow rates of sedimentation (Sites 239, 245, and 249; cf. Figures 6, 31, and 43) and a rather uniform correlation between these parameters in holes with rapid rates of accumulation (Site 242; cf. Figure 24). Very few points do not fall on these smooth curves, and those points also show anomalies in the depth distribution (cf., Figures 5, 23, 30, and 42). In addition, these anomalies are usually accompanied by similar anomalies in dissolved sulfate (Figures 21 and 41). It is the author's opinion that such anomalies can best be explained as a result of slight seawater contamination (usually less than 20%). Reaction rates, especially for reactions involving sulfate and magnesium ions (silicate reconstitution or dolomite formation), are usually sufficiently slow to cause rather smooth curves in the depth distribution of these parameters. Only a very few samples are subject to this suspicion of contamination; so, in general, the data do represent true compositional trends in the interstitial waters.

Site 241 presents a somewhat more complex problem. Here, rather irregular changes occur in the distributions of magnesium and sulfate. At 150 and 180 meter depths, somewhat unexpected values of alkalinity, dissolved silica, dissolved sulfate, and dissolved magnesium occur which are suggestive of 20 percent or less seawater contamination. Changes in the smoothness of the depth distribution of magnesium below 300 meters are not as easily explained, but I cannot assert that these are not due to slight amounts of seawater contamination. For that reason, I have drawn a smooth curve through the magnesium distribution in Figure 16. Also, the secondary extrema in the SO₄⁻⁻ and NH₄⁺ distributions in Figures 14 and 15 may not be entirely realistic.

In general, the depth distributions of the various ions seem realistic, and not withstanding some possible contamination problems, the trends are well established. An interesting problem involves the components that appear to depend on very rapid reequilibration processes, i.e., alkalinity, silica, and perhaps dissolved calcium. The temperature dependence of the alkalinity and dissolved silica will be discussed presently, but the large temperature dependence of these parameters suggests that pressure effects may not be entirely negligible. The total changes in dissolved calcium are very large; yet, even though changes alkalinity with temperature are relatively large, in temperature effects on dissolved calcium are small. Loss of CO2 during the retrieval of the cores cannot lead to large enrichments in calcium because no large changes in alkalinity are observed and also because loss of CO2 should lead to decreases in dissolved calcium, not to increases. I believe, therefore, that the observed calcium changes are real.

On a future cruise, attempts will be made to sample some interstitial waters in situ in order to test the above suggestion and also to provide an estimate of the relative effects of pressure on the distribution of the various chemical parameters, particularly those of alkalinity, dissolved silica, and dissolved calcium.

TEMPERATURE EFFECTS

Temperature of squeezing effects has been well documented by the investigations of Mangelsdorf et al. (1969), Bischoff et al. (1970), Fanning and Pilson (1971), Sayles et al. (1973a), and Gieskes (1973). It appears that for the ions Mg^{++} and K^+ , these effects are mainly caused by cation exchange equilibria with the clays, but for alkalinity, dissolved silica, and perhaps calcium, the situation may be complicated by solubility equilibria. Hammond (1973) attempted to unravel the temperature effects on alkalinity and pH on the basis of the observations made during Leg 15. He suggested that, upon warming, the clay minerals can release hydrogen ions and cause a subsequent dissolution of calcium carbonate. Observed decreases in dissolved calcium could then still be explained by temperature effects on ion exchange equilibria with the clays (cf. Gieskes, 1973).

Temperature effects on magnesium and potassium are, in general, similar to those observed in previous studies (e.g., Sayles et al., 1973a) with the possible exception of Site 249, where reverse effects are noted. Temperature effects on dissolved strontium are negligible, at least within the precision of the data. It is important to note that none of the gradients in Mg⁺⁺, K⁺, or Sr⁺⁺ are obscured by these temperature artifacts. One observation is remarkable, and that is the essential parallelism of the warm squeeze and the cold squeeze values (see, for instance, Figures 31 and 32). This is not necessarily proof that the observed irregularities in the depth distributions are real, but rather that the core section under investigation, contaminated or not, was reasonably homogeneous.

Thus, interstitial water data obtained only from room temperature squeezes will not obscure any gradients in concentrations, and, in fact, the slopes of these gradients will be little affected by the temperature effects. For surface cores, of course, the temperature problem is much more important because, in such cases, one desires to extrapolate the gradients to the sediment-seawater interface (Sayles et al., 1973c).

In the present study, alkalinity values are always lower in the low temperature squeezes. The magnitude of the effect is variable and usually ranges from 0.3 to 1.2 meg/1. Particularly pronounced effects occur in the chalk section of Site 249 (Figure 39). An interesting problem is posed by the data of Site 242. At the actual prevailing bottom (or surface of sediment) temperatures of about 1°C, the alkalinity maximum will almost disappear! Of course, it is possible that pressure effects may act in the reverse direction. In the near future, it is hoped to employ an in situ interstitial water sampler to check on such effects in rapidly accumulating sediments. Changes in pH are almost always such that pH values (measured at room temperature) are higher in the cold squeezes than in the warm squeezes. These pH values will be even higher (i.e., roughly by 0.2 pH units) after appropriate correction to the squeezing temperature of 5°C. These observations are in qualitative agreement with those made during Leg 15 (Gieskes, 1973; Hammond, 1973), but the observed effects are of greater magnitude. This can be explained from the longer equilibration time allowed for in the present study. The observations lend strong support to the tentative conclusions of Hammond (1973) about the involvement of hydrogen ion exchange with the clays and subsequent increases in alkalinity due to calcium carbonate dissolution. This may indeed explain the temperature effect on dissolved calcium. Whereas previous studies, including those of Leg 15, always showed higher cold squeeze calcium values, this is not so in the case of the Leg 25 samples. It is probably not too farfetched to speculate that if longer temperature adjustment had been allowed during Leg 15, trends in the temperature effects on dissolved calcium might have reversed. Again, no gradients in dissolved calcium are obscured, but those of alkalinity are extremely sensitive to temperature effects.

Effects of temperature on dissolved silica are very similar to those observed in previous investigations, e.g., Fanning and Pilson (1971) and Sayles et al. (1973a). The magnitude of the effect depends slightly on the lithologies; it is highest in sediments with relatively high clay and detrital mineral contents and lowest in the highly calcareous section of Site 249. This suggests that clay minerals are chiefly responsible for these temperature effects. This subject deserves further investigation. Again, the temperature effect is never large enough to obscure definite trends in the depth distribution of dissolved silica.

CHEMICAL CHANGES IN INTERSTITIAL WATERS

In this section, observations on the chemical changes observed in the interstitial fluids will be briefly described for each individual site. These changes will be related to observations made on changes in the lithologies (see site reports and the reports of Leclaire and Vallier, this volume) as well as to those on the mineralogies (Matti et al., this volume).

Site 239

This hole shows generally low rates of sedimentation, i.e., less than 2 cm/1000 y (cf. Figure 1). In such holes, usually no maxima are observed in the alkalinity, as is confirmed for this hole by the data presented in Figure 2. Disregarding the sometimes large variations in the depth distribution of this property in the upper part of the hole, the data suggest a gradual decrease in the alkalinity downwards. This decrease is related to the decrease in alkalinity that often is postulated to coincide with silicate reconstitution reactions (MacKenzie and Garrels, 1965; Siever, 1968a).

Dissolved silica values follow closely the lithologies of this hole. Between 70 and 120 meters, sponge spicules are reported to be present in fairly large quantities (Leclaire, this volume). The presence of opaline silica maintains the high dissolved silica values in this depth range. The gradient in dissolved silica from 10 to 120 meters is not necessarily a simple diffusion gradient between two zones of fixed dissolved silica concentrations. Rather, the dissolved silica is likely to be maintained at some steady state concentration which depends on the relative abundance of clay minerals versus that of sponge spicules.

The depth distribution of dissolved sulfate shows an interesting shape and suggests two principal zones where sulfate reduction occurs at higher rates than elsewhere. These zones range between 70 and 120 meters and in the hole segment below the sedimentation hiatus (cf. Figure 4). Indeed, in the range from 100 to 140 meters, pyrite was observed, especially in foram tests. Much of this pyrite, of course, may have formed shortly after the deposition of

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sediment in this segment of the hole (Berner, 1970; Sholkovitz, 1973).

Changes in dissolved calcium and magnesium are very large in this hole, as is shown in Figure 5. The gradients in the depth distributions of these ions are almost linear to a depth of 150 meters, but below that there is a very distinct curvature. From the X-ray data of Matti et al. (this volume), we observe that in the section below 150 meters the mineral palygorskite (attapulgite) increases in the <2µ-size fraction, particularly in the section below the sedimentary hiatus (Figure 1). This mineral is a high magnesium alumino silicate which often has been postulated to be a product of the diagenetic alteration of montmorillonite (von Rad and Rösch, 1972; Vallier, this volume). Much of the palygorskite in the deeper part of the hole may have formed shortly after the deposition of these sediments, but it is not possible to rule out detrital contributions of palygorskite (Goldberg and Griffin, 1970). If the palygorskite is, indeed, of diagenetic origin, then its formation may still be a continuing process and it will provide a sink for the magnesium. If this is so, then no especially highly dissolved silica or magnesium concentrations seem to be required for this reaction. Of course, these layers also contain a small amount of chlorite in the mineral assemblage which could also take up Mg++ ions, especially if this chlorite has been deposited in a degraded crystalline form (Griffin and Goldberg, 1963). Of importance is the pronounced correlation between the dissolved calcium and magnesium data (Figure 6). Changes show a ratio $\Delta Ca^{++}/$ ΔMg^{++} = 1.8. If different reactions, not related to each other, were responsible for these changes, such a relationship would not be expected unless by coincidence. I suggest that this presents strong evidence that one diagenetic process is responsible for the observed changes in calcium and magnesium. Though I have no proof that further formation of palygorskite¹ in the deeper parts of the hole constitutes the main sink for magnesium ions, I submit that this is a likely candidate.

The data for dissolved potassium (Figure 7) show a considerable decrease in concentration with depth. The shape of the depth profile is very different from those of Mg⁺⁺ and Ca⁺⁺. Of course, the curvature in Figure 7 is not well defined, and the dashed straight line equally well represents the data. If this is the case, then the main reaction site for K⁺ would be in the deeper sediment layers (perhaps involving reconstitution reactions with chlorite).

Of interest is the distribution of dissolved sodium (not shown here). If dissolved sodium is calculated from an anion-cation balance, using the data of Table 2, we observe depletions in Na⁺ of about 2 percent at 90 meters, 5.5 percent at 220 meters, and 10.4 percent at 302 meters. These depletions are significant and much larger than could be explained from temperature-of-squeezing artifacts (about 1%, Sayles et al., 1973a). Such decreases have been observed previously in holes containing detrital sediments, e.g., Hole 137 of Leg 14 (Waterman et al., 1972). Again, diagenetic changes in clays are the most likely causes for these sodium depletions. Another possibility is that changes in dissolved sodium are purely due to ionic migration caused by conditions of electroneutrality in the interstitial water column (Ben-Yaakov, 1972). However, the mechanics of such a process are difficult to visualize.

Dissolved strontium is high in the calcareous section of this hole, i.e., from 70 to 120 meters, and, in fact, shows a maximum at about 100 meters. Manheim and Sayles (1971) suggest that this is mainly due to the recrystallization of calcareous microfossils (forams and/or coccoliths). The present data support that conclusion, but the situation is complicated by the presence of fairly large amounts of tunicate spicules (Leclaire, this volume) which are aragonitic in their crystal structure (Matti et al., this volume). Leclaire assumes that these tunicate spicules were brought in by turbidity currents from the nearby continental slope of Madagascar. Conversion of aragonite to calcite would undoubtedly also release strontium to the interstitial fluids. The presence of small amounts of microcrystalline carbonates can also be considered as evidence for this recrystallization process.

The distribution of dissolved manganese in this hole was studied to only about 220 meters. This was because of a lack of samples from the two lower levels. Thus, the distribution presented in Figure 9 is incomplete. This is most unfortunate because the lower part of the hole showed the presence of small manganese nodules (Core 15, 272-281 m). From the distribution of dissolved sulfate, however, it appears that reducing conditions prevail in the lower part of the hole. Lynn and Bonatti (1965), Li, et al. (1969) and Bischoff and Sayles (1972) suggest that under reducing conditions the concentration of dissolved manganese is maintained by carbonate equilibria. Indeed, a comparison of Figure 9 (manganese) and Figure 2 (alkalinity) does suggest a vague correlation between Mn++ and HCO₃⁻, but, of course, this correlation could be refined if true pH data were available. Also, in Hole 149 of Leg 15, the correlation between the alkalinity (Gieskes, 1973) and manganese (Sayles et al., 1973a) is striking. Although manganese nodules are present in Core 15, this is not necessarily proof of present oxidizing conditions. Upon deposition of these brown clays, the conditions were undoubtedly oxidizing, and only after deep burial did they become reducing. It is possible that these nodules dissolve very slowly.

In summary, changes in the chemical composition of the interstitial waters of Site 239 are very large. Most of the hole is "reducing" (cf. the distribution of sulfate, ammonia, and manganese). Decreases in Mg^{++} , K^+ , and Na⁺ with depth are significant and are probably related to diagenetic changes in the clay minerals. Such "reverse" weathering processes are also responsible for the slight decrease in alkalinity with depth, and the dissolved calcium increases may be due to the dissolution of calcium carbonate during the clay mineral diagenesis.² To prove such a mechanism is a difficult but necessary task in this type of study.

¹Possibly from further alteration of volcanic ashes or their products.

²One serious problem here is that in such a proposed coupled silicate reconstitution and carbonate dissolution process, either alkalinity or molecular CO₂ will be produced. Such changes should be considerable, yet observed changes in alkalinity and pH are only small. Loss of CO₂ during core recovery is possible, but losses should be large. This makes the above conclusions somewhat tentative.

A final remark should be made regarding the sample from Core 16 (Table 2). A rather low chlorinity is observed in these samples, confirmed by low salinities (measured on board). The reasons for this phenomenon are not well understood, particularly because the other anions and cations do not show any anomalous values.

Site 241

Site 241, with a water depth of 4054 meters, is situated at the lower end of the continental rise in the Somali Basin. This site is characterized by very high rates of sedimentation (Figure 1). The sediments show both biogenous and terrestrial contributions (Leclaire, this volume).

Contents in organic carbon are very high in the upper zone of this hole. This, in conjunction with the high rates of sedimentation, is responsible for the large depletion in sulfate (Figure 14), the increase in alkalinity (Figure 10), and the increase in ammonia (Figure 15). These parameters are all intimately linked in the process of bacterial sulfate reduction (Berner et al., 1970; Gieskes, 1973; Hartmann et al., 1973; Sholkovitz, 1973). In general, the decrease in dissolved sulfate appears to be a function of the rate of sulfate reduction and the rate of sedimentation, and only in holes that are completely closed to diffusional communication with the overlying seawaters is complete reduction of sulfate observed (e.g., in Site 147, Leg 15; Sayles et al., 1973a). The depth distribution of alkalinity shows a classical curve, that is, a maximum followed by a gradual decrease with depth. Whereas in holes such as Site 148 of Leg 15 (Gieskes, 1973; Lawrence, 1973), such distributions can be explained from changes in alkalinity due to silicate reconstitution reactions and carbonate equilibria, the situation at Site 241 is more complicated. The distributions of dissolved sulfate and ammonia both show extrema (Figures 14 and 15). As discussed in a previous section, concentrations of between 200 and 600 meters may, to a small degree, be subject to slight seawater contamination (<20%), but this does not obscure the observed trends. From Figure 1, it follows that sedimentation rates below 220 meters are much lower than in the upper part of the core. Interstitial water-dissolved sulfate values during the Miocene, therefore, were probably much higher because of an enhanced diffusional replenishment from the overlying seawater. The fast sedimentation rates during the Pliocene and Quaternary, coupled with highly organic sediments, then led to greater isolation from the ocean.

The distribution of chlorinity is interesting and shows a decrease of 3 $^{\circ}/_{\circ\circ}$ Cl from the surface to the bottom of the hole at 1200 meters. Such changes have been observed previously in Deep Sea Drilling Project holes (Sayles et al., 1972; Presley et al., 1973). This observation can be explained either by the influence of freshwater intrusions at great depth, which must occur at least more than 5000 meters below sea level (the distance from shore is a few hundred miles), or by some unexplained diagenetic process. This latter process would involve either the uptake of chloride or the production of water. Sayles et al. (1972) prefer the explanation that some unknown diagenetic process is responsible for the uptake of chloride, and they cite the gradual increase in the Na/Cl ratio as evidence.

Calculations by charge balance from Table 3 indicate that sodium values at 258 meters differ by 0 percent from those calculated from the chlorinity (using the oceanic ratio of 0.5556; Culkin, 1965). At 532 meters, this difference is 1 percent, at 840 meters it is +3 percent, at 980 meters it is +6 percent, and at 1070 meters it is +8 percent. The data at greater depth are subject to fairly large errors, due to the small volume of pore water available (samples underwent greater dilutions before analysis). Thus, only small variations in the sodium/chloride ratio occur. This, in my opinion, does not contradict the freshwater intrusion hypothesis. Perhaps isotopic studies on these interstitial waters will shed some light on this problem.

Salinity values (Figure 12) decrease gradually with depth. In the deeper parts, these data correlate well with the chlorinity data, but between 4 and 400 meters, the shape of the depth distribution curve is influenced by the rapid changes in dissolved sulfate, magnesium, and calcium. Whenever refractometer values are below 31 °/₀₀ "salinity," depletions in chlorinity can be suspected.

Dissolved silica (Figure 13) in the upper 300 meters reflects the presence of opaline silica in the form of diatoms and radiolarians (cf. Leclaire, this volume). Below 300 meters, a rapid decrease in dissolved silica occurs, and values of 100 to 200 micromoles/1 may reflect the mixed clay mineral content of the sediment (Matti et al., this volume).

Dissolved calcium (Figure 16) follows a pattern familiar in sediments in which sulfate reduction is relatively large; that is, it shows an initial decrease followed by an increase. Values never exceed 17.5 mmoles/1. Dissolved magnesium decreases continuously downhole, which, again, may be due to clay mineral diagenesis of both the type suggested by Drever (1971) and Sayles et al. (1973a, b), i.e., exchange of Fe⁺⁺ for Mg⁺⁺ with nontronite (the Fe⁺⁺ subsequently forms pyrite, FeS₂), and the type suggested for Site 239, i.e., the continuous formation of palygorskite. The palygorskite content of this hole (<2µ fraction; Matti et al., this volume) is rather uniform and is perhaps of detrital origin. Recrystallization of this mineral, however, could provide a sink for magnesium ions. Also, sporadic occurrences of dolomite are reported by Matti et al. (this volume), but, again, some of these occurrences may be of detrital origin. Below 850 meters however, dolomite occurs in association with sand and claystone (Moore, this volume) and is probably of diagenetic origin. This, then, would constitute an additional sink for magnesium ions. Interestingly, below 800 meters the ratio Ca++/Mg++ is roughly equal to one. Whether or not this might be related to an equilibrium situation with respect to dolomite deserves further investigation.

Potassium values decrease gradually down the hole (Figure 17). This must be related to clay mineral uptake processes. Again, chlorite (present below 550 m) may be a major sink for these cations.

Dissolved strontium (Figure 18) shows a maximum at 250 meters, almost at the base of the rapidly deposited biogenous section. The rather gradual increase in dissolved Sr^{++} from 4 to 250 meters may be due to either a gradual increase in the recrystallization of calcium carbonate or a combination of this process with diffusional transport processes.

Dissolved manganese values are almost always below the detection limit of 0.1 ppm. In rapidly accumulating reducing sediments, this is a common phenomenon (Presley et al., 1967). These investigators did find total manganese contents of the bulk sediments in rapidly accumulating terrigenous sediments to be much lower than in pelagic sediments. At the same time, such sediments usually show much sulfate reduction and high alkalinity values. Thus, it appears that dissolved manganese concentrations in reducing sediments depend not only on the alkalinity, which, essentially, reflects the carbonate equilibria, but also on the form of manganese and its concentration in the solid phases.

To summarize, Site 241 is characterized by rapid sedimentation rates, and this is reflected in the extrema that occur in the depth distributions of alkalinity, sulfate, and ammonia. Reversals in the depth profiles of the latter two constituents are partly related to lower sedimentation rates below 250 meters. Upward advection of freshwater from the lower strata also affects these distributions. Dissolved calcium, magnesium, and potassium reflect changes typically observed in terrigenous hemipelagic sediments and are due to both clay mineral and carbonate reactions.

Site 242

Rates of sedimentation in this hole are very similar to those of Site 241, with a marked decrease in the Miocene. Leclaire (this volume) describes the sediments as hemipelagic, i.e., a nanno ooze mixed with a high amount of clay and some heavy mineral input. According to Leclaire, the pelagic part is generally dominant. Organic carbon contents are much lower than in the upper, biogenous part of Site 241. Radiolarians and diatoms also are very rare and are found only in the Quaternary. Below 610 meters, anomalous values were measured for the thermal conductivity and the acoustic impedance (Marshall, this volume), but no clear mineralogic change that would explain this phenomenon has been observed.

The extent of sulfate depletion in this hole is much less than at Site 241 (Figure 21). Similarly, less extensive changes occur in the alkalinity and ammonia values (Figures 20 and 22). These changes, of course, are again related to the process of bacterial sulfate reduction. Despite the fact that the rates of sedimentation of Sites 241 and 242 are very similar in the upper parts of the holes, the extent of sulfate depletion is much less. I believe this to be primarily a result of the much smaller quantities of biologically refractive organic matter in the Hole 242 sediments. Again, a minimum of sulfate is observed at about 250 meters, coinciding with a maximum of ammonia. Below 250 meters, sulfate shows a linear increase with depth. (Note that the sulfate values below 600 meters are subject to large errors, due to the small sample sizes available for sulfate analyses). From Figure 1, one observes a large change in the rate of sedimentation below about 300 meters depth. For reasons similar to those discussed under Site 241, there is good reason to believe that at the time of deposition of the sediments during the Miocene the decrease in interstitial sulfate was much less. I suggest that the linear gradient below 250 meters is essentially a diffusion gradient. Thus, the site of maximum sulfate

depletion at 250 meters serves as a sink for sulfate from both the upper strata and the lower ones. This should put some interesting limitations on sedimentary sulfate reduction models.

Dissolved silica (Figure 20) is rather uniform with depth and may reflect the clay mineralogy of this hole (Matti et al., this volume). No important change is observed below the acoustic reflector (Marshall, this volume) at 610 meters.

Dissolved calcium (Figure 23) reveals a distribution that is expected in holes that show rapid sedimentation and sulfate reduction. The observed decrease with depth in the alkalinity is probably related to diagenetic processes involving silicate minerals and magnesium and potassium ions. The profile of dissolved magnesium (Figure 23) suggests two major areas where the diagenetic reactions are proceeding at more rapid rates. First, in the zone of maximum sulfate depletion and secondly, in the zone below the acoustic reflector, i.e., below 610 meters, Matti et al. (this volume) report the presence of chlorite below 600 meters, as well as a slight increase in the amounts of palygorskite. The latter constituent is present throughout the hole and is probably largely detrital in origin. Though no clear evidence is available from X-ray data of diagenetic changes which might be related to the reported anomalies in the physical properties below 610 meters (Marshall, this volume), the dissolved magnesium distribution suggests the presence of some diagenetic process that constitutes a major sink for magnesium ions (recrystallization of chlorite and/or palygorskite?). Closer investigations of the solids have been planned.

Dissolved potassium (Figure 25) shows a rapid decrease with depth to about 300 meters, after which only a small change occurs. The shape of this curve suggests that the main uptake of K^+ occurs in the upper portions of the sediments and relates to the uptake of K^+ by detrital clay minerals. Changes in sodium, calculated from a charge balance, are less than 4 percent throughout the hole and are considered to be within the analytical error.

Dissolved strontium (Figure 26) increases gradually with depth, and this reflects the continuous recrystallation of the nanno ooze to nanno chalk. There is no relationship between Ca^{++} and Sr^{++} data. This is mainly due to the fact that calcite recrystallization occurs independently of the carbonate equilibria regulated by the silicate reconstitution reactions.

Dissolved manganese (Table 4) shows erratic variations for reasons similar to those suggested for Site 241.

In summary, Site 242 is characterized by rapid sedimentation of a hemipelagic clay and nanno ooze sediment. The lesser sedimentation rates in the Miocene (below 300 m) are reflected in reversals in the profiles of sulfate and ammonia. Dissolved silica suggests a rather uniform type of clay mineral deposition. Changes in dissolved magnesium in the sediment layers below the acoustic reflector indicate the presence of a diagenetic reaction involving magnesium ions that may be responsible for the observed changes in the heat conductance and acoustic impedance.

Site 245

Hole 245 was probably the only hole drilled during Leg 25 that has principally truly pelagic characteristics

(Leclaire, this volume). The sedimentological aspects of this hole are discussed in more detail by Leclaire, Vallier, and Warner and Gieskes (this volume). Also of importance is the mineralogical description of Matti et al. (this volume). In Figure 46, the mineralogical data on this hole ($<2\mu$ fraction) are presented. Included in this figure are some data on the carbonate-free fraction of these sediments, analyzed in a qualitative manner, without regard to the size of the fraction. Some typical observations can be made. Below the brown clay portion of this hole (upper 100 m), kaolinite disappears from the clay mineral assemblage and, also, mica becomes a less important constituent. Below 100 meters, palvgorskite becomes an important constituent. constituting more than 60 percent of the $<2\mu$ -size fraction. Often this palygorskite is associated with the zeolite clinoptillolite. This suggests that at least a fraction of the palygorskite may be of authigenic origin. Below 360 meters, palygorskite becomes a less important constituent. At greater depths, montmorillonite becomes the dominant clay mineral and is mainly derived from volcanic ash by devitrification. Based on these mineralogical data, the hole can be divided into three zones: 0-100 meters-brown clay characterized by a mica-kaolinite-montmorillonite assemblage; 100-260 meters-carbonate ooze and chalk, with cherts and a predominant montmorillonite-palygorskite clay mineral assemblage; basal nanno ooze and chalk, characterized by volcanic ash layers and a predominantly montmorillonitic clay fraction. In addition, these basal sediments are characterized by a high iron and manganese content (Warner and Gieskes, this volume).

The alkalinity profile shows rather constant values to about 200 meters, after which a gradual decrease occurs (Figure 27). The sedimentation rates in the upper 50 meters were slow (<0.5 cm/1000 y), and, therefore, this observation is in general accord with observations made during previous legs.

Dissolved silica shows a very interesting distribution (Figure 28). In the brown clay section of the hole, the values appear to be maintained by the mixed mica-kaolinite-montmorillonite clay assemblage. Below this depth, the dissolved silica goes to values of about 600 μ moles/1, a value that seems to be maintained by the montmorillonite-palygorskite clay minerals. Similar values were obtained by Sholkovitz (1973) in the interstitial waters of the Santa Barbara Basin sediments, which are predominantly montmorillonitic in their clay fraction.³ No opaline biogenous material was observed in Hole 245. Such highly dissolved silica concentrations may have been favorable for the formation of zeolites and perhaps also palygorskite shortly after deposition.

Dissolved sulfate shows a decrease to the lowest sampling depth in the hole (Figure 29). Below 100 meters, the gradient is essentially linear. This means that sulfate reduction still occurs in the deeper parts of the hole. It could be argued, of course, that with the higher sedimentation rates during the Eocene, the sulfate depletion was much higher, but, at the very low sedimentation rates during the last 40 m.y., it is most likely that if no further reduction took place below 100 meters depth, diffusional processes would have eradicated any gradients.

Data for calcium and magnesium (Figures 30 and 31) suggest essentially linear gradients with depth, as well as an exact 1:1 correspondence between the concentration changes. Deviations from the linear gradients are usually less than 5 percent and, thus, are likely to be experimental. The 1:1 ratio in the changes in dissolved calcium and magnesium has often been interpreted as an indicator of dolomite or high magnesium calcite formation. I do not subscribe to this contention but would rather prefer a mechanism in which magnesium is used up in a silicate reconstitution reaction. The basal layers of Hole 245 show high montmorillonite content, as well as many volcanic ash layers. If these layers should be the main sink for magnesium, then a silicate reconstitution reaction involving the uptake of Mg++ ions and the simultaneous release of calcium ions at a more or less constant alkalinity would explain the observed interstitial water changes in Ca++ and Mg++ concentrations. This would imply that the gradients in calcium and magnesium are primarily diffusional gradients. I interpret the decrease in alkalinity below 200 meters as due to the suggested silicate reconstitution process. I should emphasize that it will be difficult to prove this mechanism. Further experimental work has been planned.

Changes in potassium concentrations are very small in this hole (Figure 32), so that, apparently, there is no significant sink for these K^+ ions in the deeper parts of the hole. Changes in sodium concentrations, calculated from the data of Table 5, reveal an exact correspondence (if expressed in meq/1) with the dissolved sulfate concentrations. It is well possible that dissolved sodium depletions are not caused by diagenetic reactions but, rather, are the result of migration as a result of overall charge balance requirements (cf. Ben-Yaakov, 1972).

Concentrations in dissolved strontium (Figure 33) increase linearly with depth. This linear increase corresponds with the linear increase in calcium, but this does not necessarily imply a causal relationship (cf. data for Site 239). Rather, the linear profile may indicate a steady state maintained by a diffusional transport gradient and an increased amount of recrystallization of calcium carbonate with depth (cf. Manheim and Sayles, in press). Typically, the nanno ooze turns into a nanno chalk with depth.

The distribution of dissolved manganese (Figure 34) is puzzling. In the upper 100 meters, in almost all recovered cores, the presence of Fe/Mn oxides, either in the form of micro-modules or opaque streaks, has been noticed (Chapter 7, this volume). Such occurrences are also reported in Cores 245-3 (121-130 m) and 245-4 (159-168 m). Below that, the presence of iron and manganese oxides becomes apparent only in the basal sediments. The dissolved sulfate profile shows curvature down to about 100 meters after which it becomes linear

³Couture (personal communication) noticed similar relationships from an analysis of published Deep Sea Drilling Initial Reports.

(cf. also, Sayles and Manheim, 1971). Such a profile suggests that sulfate reduction takes place throughout the first 100 meters, but, of course, part of the curvature can be caused by the upward advection of pore waters in these more porous layers. This is contradicted by the linear gradients in Ca++ and Mg++. The reducing conditions caused by such sulfate reduction processes and the subsequent formation of pyrite (not observed in smear slides) would provide the proper medium for electron transport necessary to bring about the reduction of manganic oxides to manganous ions. If sulfate reduction were to occur at a maximum at about 100 meters, then this would cause maximum formation of Mn++. The distribution of dissolved manganese above and below 100 meters would then be due mainly to diffusional transport gradients. More quantitative work on these cores is planned, in order to verify this suggestion.

In summary, Hole 245 is the most typical pelagic hole drilled during Leg 25. Rates of sedimentation during the Quaternary through the Oligocene were relatively slow (<0.5 cm/1000 y), but below that, high sedimentation rates correspond to fast deposition of nanno-fossil oozes. Sulfate reduction occurs in this hole, with highest rates probably at depths around 100 meters and below 350 meters. Reducing conditions at 100 meters are reflected in maximal dissolved manganese values. Magnesium decreases linearly with depth, with a corresponding increase in dissolved calcium $(\Delta Mg^{++}/\Delta Ca^{++} = 1.0)$. This is possibly related to authigenic reactions occurring in the basal sediments, which are characterized by volcanic ash layers and high montmorillonite clay fractions. The most likely process is the formation of authigenic silicates in these layers, involving uptake of Mg⁺⁺ ions and simultaneous release of Ca⁺⁺ ions. We hope to verify some of these contentions by more detailed chemical work, as well as isotopic O¹⁸/O¹⁶ studies on interstitial waters, carbonates, and silicates (cf. Lawrence, 1973).

Site 248

This site is characterized by the presence of silts and sands, especially in the upper 300 meters (Chapter 9, this volume). This makes the squeezing operation, in many cases, rather futile because of obvious, visible seawater contamination. For these reasons, very few samples were obtained, and even those samples are somewhat suspect, as follows clearly from Sample 248-12-5 (cf. Table 6 and Figures 35 to 38). The lower part of the hole is geochemically interesting, as is shown by the data of Marchig and Vallier (this volume), and, therefore, it is unfortunate that it does not possess high quality interstitial water data.

Qualitatively, the data are representative of observations made in rapidly depositing detrital sediments. The alkalinity appears to have a "maximum" (undefined; cf. Figure 35), and the sulfate a "minimum" (Figure 36). The higher sulfates in the deeper part of the hole are probably, again, related to the corresponding lower rates of sedimentation (cf. Sites 241 and 242). Changes in calcium, magnesium, and potassium are also as expected in rapidly depositing detrital sediments. Again, I emphasize that the data are too scarce to make any conclusions about where maximum changes may occur.

There seems little point in a further discussion of the nature of these changes. Of some interest, however, is the rather small (if at all significant) increase in dissolved strontium (Table 6). Calcium carbonate contents are very low in this hole (cf. Marchig and Vallier, this volume), and this confirms the idea that observed changes in dissolved strontium principally reflect carbonate recrystallization processes, be it aragonite (cf. Site 239), or calcite (Manheim and Sayles, in press). Increases in dissolved calcium can be due to calcium release during silicate reconstitution reactions involving magnesium ions.

Dissolved manganese values are high throughout the hole, indicating reduced conditions. Presumably, the dissolved manganese concentrations are maintained by carbonate equilibria, causing minimum Mn^{++} concentrations at high alkalinities (Sample 248-4-5, 125 m). Matti et al. (this volume), in fact, report the presence of rhodocrosite at 363.4 meters. Much of this mineral may have formed shortly after deposition or may be due to hydrothermal effects; further investigation of the geochemistry of these deeper strata would be very interesting, as is also evident from the data of Marchig and Vallier (this volume).

Site 249

The sedimentation history of Hole 249 is very complicated (see Chapter 10, this volume). Quaternary and Pliocene deposits are very thin, whereas the Miocene section is rather thick. This is followed by a large sedimentary hiatus, from middle Miocene to Late Cretaceous (Figure 1). The upper part of the Cretaceous section consists mainly of clay-rich nanno chalk (170-285 m) followed by another hiatus. The lower part of the hole consists of olive-black claystone and volcanic siltstone (cf. Marchig and Vallier, this volume). This lower part of the hole is characterized by high contents of organic matter and generally low calcium carbonate contents. The mineralogy of this unit is characterized by high contents of pyrite, cristobalite, and tridymite, as well as clinoptilolite. The clay mineralogy is dominated by montmorillonite, presumably derived from the devitrification of volcanic ash. The mineral palygorskite is present only in sediments above 305 meters and may well be of detrital origin.

The alkalinity data (Figure 39) show a large scatter as well as a large temperature-of-squeezing effect. Yet a gradual decrease in the alkalinity is apparent, suggesting the gradual removal of bicarbonate from the interstitial waters with depth. The fairly constant pH values suggest also that the total CO₂ content decreases in a similar way (cf. Gieskes, 1973; Takahashi et al., 1973).

Dissolved silica values (Figure 40) are rather constant in each lithological unit, and, interestingly, the temperatureof-squeezing effect increases with the amount of clay in the sediment assemblage. This, of course, as has been discussed before, strongly suggests that clay minerals have a large effect on dissolved silica, be it due to ion exchange phenomena (doubtful, because at a pH of 7.5, only a small percent of the dissolved silica is ionized) or to solubility effects. In the lower lithological unit, values are much higher, and, again, this may be related to the very different lithology.

The dissolved sulfate profile is most intriguing. From the surface of the hole to about 260 meters, the sulfate shows an essentially linear gradient (Figure 41) with only very small and random variations. I interpret this as purely a diffusion gradient without any significant consumption of sulfate by sulfate reduction processes in the upper 270 meters of the hole. Any pyrite present in the sediment (cf. Marchig and Vallier, this volume) must have formed shortly after deposition of these sediments. In the lower sedimentary layers, it appears that larger decreases occur in the dissolved sulfate, and, in my opinion, this indicates that in these highly organic sediments, bacterial sulfate reduction processes are still important.

Gradients of calcium and magnesium are linear in the upper 170 meters. Below that, slight curvature occurs in the chalk unit, but large changes occur in the deeper sedimentary layers. Again, there is a strong linear correlation between these changes (Figure 43), with $\Delta Ca^{++}/\Delta Mg^{++} = 1.6$. As at Site 239, where the ratio was 1.8, this correlation suggests a coupled process involved in these changes. Uptake of magnesium, probably in the reactive parts of this deep volcanogenic sediment, and simultaneous release of calcium, is apparently still an ongoing process. The linear gradients in the upper lithological unit may, therefore, again represent essentially diffusional gradients.

Dissolved potassium data (Figure 44) are erratic. There appears to occur a small depletion with depth, but the profile, in general, cannot serve as an indicator of probable sites of significant removal.

Of interest again, is the distribution of dissolved strontium (Figure 45). The depth profile suggests that in the upper portion of the hole, i.e., the nanno ooze section, extensive and increasing recrystallization of calcium carbonate takes place. The maximum at 150 meters is due to the simultaneous removal of strontium to the lower and higher strata by diffusion. In fact, some of the released strontium may be taken up in the lower units by selective absorption by clay minerals (cf. Marchig and Vallier, this volume).

In summary, Site 249 is characterized by a sedimentary sequence with highly variable sedimentation rates and sedimentation hiatuses. Except for dissolved strontium, it appears that for most other constituents (sulfate, magnesium, and calcium) the lower volcanogenic section acts as a sink or source, whereas the distribution of these constituents in the upper 250 meters is mainly determined by a linear diffusional gradient, extrapolating to seawater values at the sediment-seawater interface.

SUMMARY AND CONCLUSIONS

The results of the interstitial water studies carried out on samples collected during Leg 25 are in general agreement with observations made during previous Deep Sea Drilling cruises. Much of this previous work has been summarized recently by Manheim and Sayles (in press).

During Leg 25, various types of sediments were drilled; these range from mostly detrital sediments on a continental slope (Site 241) to almost truly deep-sea pelagic deposits (Hole 245). In the following, results for these various categories are briefly summarized.

1) The first category is terrigenous hemipelagic sediments, i.e., sediments with both large detrital and large biogenic contributions, characterized by fast sedimentation rates, which are represented by Sites 241, 242, and 248. At Site 241, the biogenous contributions are large in the upper 300 meters and consist of nanno-fossil oozes with large contributions of siliceous organisms (diatoms and radio-larians). The biogenous contributions at Site 242 are found throughout the hole and consist mainly of foram-bearing nanno oozes and chalks. Biogenous contributions at Site 248 are very small and are mainly restricted to the upper part of the hole.

Each of these holes is characterized by fairly large depletions in SO_4^- , small depletions in Ca^{++} in the upper part (followed by more or less large increases), large depletions in Mg^{++} and K^+ , and increases (again in the upper parts) in alkalinity (HCO₃⁻) and NH₄⁺. All three holes show a minimum in the depth distribution of dissolved SO_4^- , which is related to lower sedimentation in the deeper parts of the holes.

2) The second category is hemipelagic sediments with generally slow sedimentation rates, characterized by large detrital silt and clay inputs originating from turbidites. Site 239 is typical here, and even the biogenous part is characterized by some shallow-water components, such as aragonitic tunicate spicules. A hole of rather similar nature is Site 137 in the Atlantic Ocean (Waterman et al., 1972), although, there, the biogenous components show a different depth distribution.

Relatively small depletions occur in SO_4^{--} , which is not unexpected in sediments with accumulation rates of lower than 2 cm/1000 years. No maximum occurs in the alkalinity, but large depletions occur in Mg⁺⁺ and K⁺, accompanied by very large increases in Ca⁺⁺. Strong linear correlations between Ca⁺⁺ and Mg⁺⁺ suggest that the changes in these concentrations are coupled, probably related to processes involving silicate reconstitution. Such processes, if coupled, would result in only minor changes in the alkalinity.

3) The third category is pelagic deep-sea sediments that are deposited both above and below the calcium carbonate compensation depth (Hole 245). In such holes, usually characterized by low sedimentation rates, often no changes are noted in any of the major constituents of interstitial water, i.e., the overlying seawater composition is maintained. In some holes, however, large gradients in Ca++ and Mg⁺⁺, usually in a 1:1 relationship (i.e., $\Delta Ca^{++}/$ $\Delta Mg^{++} = 1$), are observed, not necessarily reflecting larger or smaller sedimentation rates. In fact, Holes 70, 71, and 72 in the equatorial Pacific (Manheim and Sayles, 1971) show the largest gradients in Ca⁺⁺ and Mg⁺⁺ in the hole with the slowest rate of accumulation. Only Sr⁺⁺ values did show a good correlation between the gradient and the sedimentation rate (Manheim and Sayles, 1971). In Hole 245, it appears that the main reaction site for Mg⁺⁺ and Ca⁺⁺ is in the basal sediments, which are characterized by volcanic ash inputs (cf. Vallier, this volume; Warner and Gieskes, this volume). I suspect that the gradients in Holes 70, 71, and 72 can be due to similar basal beds of "reactive" sediments, or they may be due to differences in volcanic contributions to these holes. None of these holes were drilled to basement, so these observations are, necessarily, speculative. Only small changes are observed in SO_4^- and alkalinity, and changes in K^+ are negligible, i.e., within the error limits.

Site 249 could be classified under this category, but only with hesitation because of the rather irregular sedimentation history of the hole.

It is important to note that in many of the holes reported on here the biogenous calcareous and opaline contributions are localized in parts of the hole. For instance, sponge spicules in Site 239 are mainly found from 70-120 meters, in association with calcitic (nanno plankton) and aragonitic (tunicate spicules) skeletons. Radiolarians are abundant at Site 241 from 0-300 meters, in association with nanno-fossil oozes. Nanno-fossil oozes and chalks characterize the entire Site 242, whereas in Hole 245 they are present from 100 meters to the basaltic sill. Biogenous material is virtually absent at Site 248, and at Site 249, a Miocene nanno-fossil ooze 160 meters thick overlies a Cretaceous chalk section 110 meters thick, below which a rapid decrease occurs in biogenous components.

The presence of these biogenous components has large effects on dissolved silica values (Sites 239 and 241). Also, the distribution of dissolved Sr^{++} clearly correlates with the presence of carbonate oozes and chalks, whether such biogenous material is aragonitic or calcitic in origin. The Sr^{++} profiles relate to calcium carbonate recrystallization processes (cf. Manheim and Sayles, in press) in the sediment column. Only in holes which show contributions of calcareous organisms throughout, or at least in the deeper parts, are linear gradients in Sr^{++} found (Site 242 and Hole 245). In all the other holes, nonlinear profiles with extrema in the calcium carbonate sections of the holes support this recrystallization concept.

Dissolved silica values seem to reflect the lithologies of the sediments. Though the well-known temperature-ofsqueezing effect will cause an uncertainty of $\pm 100 \ \mu moles/1$ SiO2, the present study suggests that for sediment assemblages with nonexistent or very small biogenous silica contributions, the dissolved silica reflects the clay mineralogy. In holes where the clay assemblages, especially the $< 2\mu$ fraction, contain mica, kaolinite, montmorillonite, and palygorskite, a value of 200 µmoles/1 SiO₂ ±100 is common; when kaolinite is absent (cf. Hole 245), but mica, palygorskite, and montmorillonite are present, values of 650 µmoles/1 SiO₂ ±100 are observed. Couture (personal communication) found similar relationships from an analysis of previously published Deep Sea Drilling data. MacKenzie et al. (1967) and Siever (1968b) carried out equilibration studies between pure alumino silicates (e.g., kaolinite and montmorillonite) and seawater at various pH values. Especially, Siever's (1968b) experiments indicate that inter alia pH is a controlling factor. I conclude, therefore, that the dissolved silica values are regulated by the clay mineral assemblage, as well as by the particular chemistries (i.e., contents in Mg++, Ca++, K+, and HCO3) of the interstitial water sediment system. More experimental work of the type performed by Siever (1968b), but in clay mixtures of low water content, should verify some of these tentative conclusions.

Whenever opaline silica is present in appreciable amounts, the dissolved silica seems to be regulated by this sedimentary component (cf. Sites 239 and 241).

Dissolved SO4" and NH4⁺ are direct reflections of sulfate reduction processes. Apparently, such processes still take place in deeply buried sediments, and, presumably, such processes are still essentially bacterially controlled. In holes that show rapid sedimentation rates, sulfate depletions are usually accompanied by maxima in the alkalinity values. At rates slower than 2 cm/1000 y, the alkalinity maximum disappears. The depth and the intensity of the alkalinity maximum seems to be a function of the rate of sedimentation as well as the amount of organic matter present in the sediment. Larger amounts of organic matter also probably imply larger fractions that are easily metabolized by bacteria. This would explain the observations at Sites 241 and 242, where sedimentation rates are very similar but where different amounts of organic matter are incorporated in the sediments. The maximum in the alkalinity is usually thought to be the direct result of sulfate reduction processes. This phenomenon has been discussed in some detail by Gieskes (1973) and by Lawrence (1973). The latter author assumed that the maximum corresponded to the depth in the sediment where the precipitation of CaCO₃ proceeds at a maximum rate. Indeed, this maximum in alkalinity corresponds to a minimum in Ca++. Below this, the relative importance of sulfate reduction processes and the coinciding production of HCO3⁻ diminishes, whereas silicate reconstitution reactions become more important, resulting in decreasing values of Mg⁺⁺ and HCO₃⁻ and increasing Ca⁺⁺ values.

Of interest in the present study is the clear minimum that occurs in dissolved SO_4^- at Sites 241, 242, and 248. Generally, during periods of slower sedimentation, dissolved sulfate depletions can be expected to have been less, so that, upon the onset of faster sedimentation, SO4 depletion would become larger, thus leading to the observed minima. The rate of the sulfate reduction process is sufficiently fast for such a minimum to develop. Diffusional supply of SO_4^- from above and below would be too slow to eradicate the minimum. Depletions in Mg⁺⁺ and K⁺ take place throughout the core at such rates that extrema are not observed, even though at Site 241, the slightly higher Mg⁺⁺ values at 325 meters than those at 258 meters may be caused in a similar manner. However, as discussed in the section on the validity of the data, we cannot assert whether this does, indeed, occur, or whether the differences are due to small seawater contaminations. At Site 242, no anomalous reversals in the Mg++ gradient are observed.

Although the present studies are not conclusive about the nature of the reactions that are responsible for the changes in the composition of interstitial waters observed, I feel that some tentative conclusions can be drawn. These, of course, still warrant further verification. In the following, a brief summary is given of the possible reactions related to the observed changes.

Dissolved Silica: This component seems to reflect the mixed clay mineral assemblages or, whenever fairly large amounts of opaline biogenous silica are present, the solubility of this latter solid component.

Alkalinity: Increases are usually due to the production of HCO_3 ions in the bacterial sulfate reduction processes. Decreases are related both to the precipitation of carbonates and the "consumption" of alkalinity in silicate reconstitution reactions.

Sulfate and Ammonia: These changes are related to bacterial sulfate reduction processes.

Calcium: Changes are mostly related to calcium carbonate precipitation processes (during sulfate reduction) or due to release of calcium during silicate reconstitution. The latter process, however, is not entirely certain and has not been tested rigorously.

Magnesium: Changes are due to formation of authigenic silicates (palygorskite?); formation of intermediate montmorillonites during the alteration of volcanic ash (Hole 245); uptake in recrystallized detrital clay minerals, e.g., chlorite.

Strontium: Changes are due to recrystallization of carbonates, aragonitic (tunicate spicules) or calcitic (nannoplankton).

Potassium: Changes are due to reconstitution of clay minerals and uptake in detrital poorly crystallized clays, e.g., chlorite. Potassium depletions are usually observed only in rapidly depositing detrital sediments.

Manganese: Dissolved manganese values higher than 0.5 ppm usually imply reducing conditions and are due to the reduction of manganese dioxide phases. In rapidly accumulating detrital sediments, dissolved manganese values are low, in spite of reducing conditions. This is probably due to the great dilution in manganese in the solid phases.

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Samp (Core Section	ole e, on)	Subbottom Depth (m)	рН ^а	<i>p</i> H ^b	pH ^c	Alk ^d	Cle	so4 ^f	Caf	Mg ^f	Kf	Srf	Mn ^g	si02 ^h	NH4 ^h	se
1-4	w	4		7.55	7.60	2.39	19.6	27.9	10.4	53.6	11.4	0.21	0.3	335	9	35.2
3-2	w	20		7.72	7.63	1.86	19.8	27.3	11.0	53.6	10.5	0.39	0.0	218	64	35.2
4-3	w	70	7.59	7.36	7.31	2.06	19.75	25.1	15.7	50.9	8.8	0.55	0.5	485	160	35.2
5-3	w	80	7.57	7.39	7.35	1.48	19.8	26.4	14.9	50.1		0.55	0.6	506	208	35.2
5-3	c	80			7.65	1.23	19.8	26.1	15.0	51.0	8.8	0.55	0.3	424	203	
6-5	W	90	7.38	7.38	7.31	2.65	20.0	25.2	19.0	49.1	7.5	0.59	0.0	645	151	35.2
8-4	w	135	7.59	7.39	7.41	2.27	19.9	25.0	23.0	45.0	7.5	0.56	2.2	800	137	35.2
8-4	с	135		7.82	7.71	1.61	19.8	25.3	23.2	45.9	6.9	0.56	1.5	550	183	
9-4	w	145	7.40	7.39	7.34	2.03	19.7	25.8	22.1	46.0	7.4	0.49	2.2	460	183	35.2
12-3	w	209	7.44	7.25	7.26	1.62	19.7	24.4	30.3	41.8	5.1	0.43	9.3	260	83	35.2
12-3	с	209		7.49	7.26	1.40		25.0	31.8	45.1	5.3	0.43	8.3	161	186	35.5
13-3	w	220		7.51	7.31	1.21	19.6	24.2	35.5	39.9	4.4	0.40	8.3	198	145	35.2
16-3	w	285			7.35	<0.5	19.0	(21.4)	53.8	33.2	3.7	0.33		198		34.1
16-3	с	285				0.17	19.0	102211	57.9	28.4				62		34.1
18-2	w	302			7.22	0.62	20.3	22.2	62.0	25.5	3.7	0.33		294		36.3

TABLE 2 Site 239 (21°17.67'S, 51°40.73'E; 4971 m)

Note: w = $23^{\circ}C \pm 2$; c = $5^{\circ}C \pm 1$. Parenthesis around figures indicates doubts as to accuracy.

^a Punch in values. ^bFlow through values. ^c Vessel values. ^dIn Meq/1. ^eIn $^{\circ}/_{\circ\circ}$ ^fIn m mole/1. ^gIn ppm. ^hIn μ mole/1.

Sample (Core, Section)	Subbottom Depth (m)	рНa	<i>p</i> H ^b	pHc	Alkd	Cle	SO4 ^f	Caf	Mgf	Kf	Srf	Mng	SiO2 ^h	NH4 ^h	Se
1-4 w	5		7.22	7.32	6.22	19.7	26.0	9.0	54.1	12.4	0.10	0.9	860	262	35.2
2-2 w	12	7.10	7.10	7.19	10.03	19.7	21.3	7.6	53.0	13.4	0.14	0.2	932	428	34.9
2-2 c	12				9.90	19.6	20.3	7.4	52.7	11.6	0.15	0.0	820	374	35.2
3-4 w	50	7.05	7.03	7.12	14.80	19.6	12.4	6.6	49.9			0.0	980		34.1
4-3 w	60	7.05	6.98	7.10	15.45	19.6	10.8 11.9	6.1	46.1	12.5	0.21	0.0	960	700	34.1
5-3 w	68	6.95	6.99	7.07	16.10	19.6	8.8 9.0	5.8	45.1	12.5	0.23	0.0	940	740	33.6
5-3 c	68		7.10	7.24	14.70	19.5		5.1	46.6	11.1	0.24	0.0	900	700	
6-5 w	110	6.82	6.94	7.05	17.75	19.5	5.9	6.3	41.9	10.9	0.27	0.0	1060	830	33.0
7-3 w	145	7.00	7.17	7.27	12.95	19.5	10.0	7.0	44.6	10.0	0.30	0.0	520	825	
8-3 w	182	6.89	7.08	7.18	15.00	19.3	7.2	7.2	41.2	10.5	0.33	0.2	740	770	33.0
8-3 c	182		7.28	7.58		19.4	5.8	5.8	43.2				650	790	
10-3 w	220	6.78	6.88	7.02	13.75	19.1	(4.2)	8.5	38.9	8.6	0.37	0.0	790	650	32.2
11-3 w	258		6.95	7.06	10.50	19.4	4.9	10.2	36.8	7.8	0.38	0.0	906	525	32.4
13-3 w	325		7.25	7.31	4.00	19.2		9.9	38.6	6.2	0.32	0.4	180	540	32.7
13-3 c	325		7.96		<1.3	19.8	7.4	9.5	38.7	5.1	0.30	0.3	55	470	32.2
15-3 w	400			7.20	3.20	18.8	11.5	15.2	35.9				326		31.9
19-1 w	532			(7.15)	2.32	18.5	11.7	17.6	32.9			0.0	242	340	31.4
21-4 w	582				3.25	18.8	17.0	18.0	26.5	3.3	0.27	0.0	182	294	31.1
23-3 w	686				<1.2	18.6	14.0	16.8	24.1	3.8	0.24	0.0	172	450	30.2
23-3 c	686				0.48	17.5	12.0			2.5	0.24	0.0	52	360	28.6
25-4 w	840				2.60	17.5	8.2	16.6	20.8	2.9	0.25	0.0	100	280	29.7
27-3 w	980				1.93	15.8	6.0	14.2	12.8	1.8	0.18	0.0	79	410	26.5
28-2 w	1070				1.75	16.8	10.5	15.0	14.2	2.5	0.24	0.0	79	420	27.8
29-2 w	1168				3.10	16.6	9.5	14.7	17.3			0.0	108	380	28.6

TABLE 3 Site 241 (02° 22.24'S, 44° 40.77'E; 4054 m)

aPunch in values. bFlow through values. cVessel values. dIn Meq/1. $e_{In} \circ_{/00}$ fIn m mole/1. gIn ppm. hIn μ mole/1.

Sample (Core, Section)	Subbottom Depth (m)	рНа	pHb	pHc	Alkd	Cle	SO₄f	Caf	Mgf	Кf	Srf	Mng	SiO2h	NH4h	Se
				(******	1.5 brown			17.57.0	0						
1-3 w	4	7.26	7.29	7.36	3.59	19.4	28.1	9.8	52.3	11.5 12.1	0.11	1.0	238	84	35.2
1-3 c	4		7.80	7.76	2.90	19.5	27.8	9.0	53.6	10.3	0.11	0.9	157	100	35.5
2-3 w	55	7.32	7.30	7.31	5.50	19.6	20.0	7.3	48.7	10.3	0.21	0.8	178	275	35.2
3-3 w	132	7.46		7.29	5.40	19.6	13.6	6.7	44.3	7.8	0.32	0.0	183	425	33.8
4-5 w	152	7.41	7.28	7.35	5.53	19.6	12.7	6.4	43.4	6.8	0.32	0.1	156	390	33.6
4-5 c	152		7.63	7.72	4.00	19.7	12.9	6.1	44.2	7.3	0.33	0.1	87	420	
5-3 w	235	7.48	7.34	7.40	3.85	19.6	10.8	7.4	39.9	5.4	0.47	0.1	170	515	33.3
6-2 w	310		7.32	7.37	2.79	19.8	12.1	7.8	39.2	5.3	0.47	0.0	125	455	33.3
6-2 c	310		7.86	7.98	<<2	19.7	12.6	7.2	39.6	5.8	0.46	0.0	46	515	
7-5 w	407		7.49	7.43	2.50	19.6	12.8	11.7	36.2	07037L	(0.59)		142	440	33.8
8-4 w	483			(7.03)	<1.7	19.7	16.8	16.0	36.7		(0.76)		188		34.1
9-3 w	560			(7.65)	< 0.8	19.9	15.0	16.6	31.9	3.4	0.75	0.6	85	370	34.4
10-5 w	607			1.1. 8 -1.1.1.1.1.1.1.1.1.1.1.1.1.1.1.1.1.1.1.	0.85	(20.0)	14.0	20.1	26.2		0.79	0.5	87	285	34.1
12-2 w	622				0.55	(19.6)		21.2	20.9	4.3	0.94	0.0	114		34.1
13-5 w	635				0.65		15.4	21.8	23.2		0.81	0.0	106	350	34.6
15-2 w	652				< 0.35		12.3	22.9	20.1	4.3	0.80	0.7	187	270	34.1

TABLE 4 Site 242 (15° 50.65'S, 41° 49.23'E; 2275 m)

aPunch in values. bFlow through values. cVessel values. dIn Meq/1. eIn °/... fIn m mole/1. gIn ppm. hIn µmole/1.

TABLE 5 Site 245 (31° 32.02'S, 52° 18.11'E; 4857 m)

Sample (Core, Section)	Subbottom Depth (m)	p Ha	pH ^b	p Hc	Alkd	Cle	so4t	Caf	Mg ^f	Kf	Srf	Mng	SiO2 ^h	NH4 ^h	Se
245-1-4 w	10	7.33	7.34	7.30	2.65	19.5	29.0	10.9	(52.0)	10.0 11.8	0.11	0.0	226		35.5
245-1-4 c	10		7.35	7.26	2.44	19.6	29.0	11.0	54.6	11.1	0.09	0.1	177	52	35.2
245-2-CC w	70	7.40	7.27	7.26	2.95	19.5	27.3	13.1	52.3	10.7	0.14	1.6	205	90	35.2
245-2-CC c	70		7.14	7.13	2.56	19.5	26.7	13.7	54.7	8.6	0.13	2.1	148	155	35.2
245-3-5 w	125	7.30	7.13	7.20	3.03	19.5	(23.9?)	17.6	47.6	10.5	0.19	3.9	390	89	35.2
245-3-5 c	125			7.33	2.79	19.7	25.2	18.0	49.0	9.0	0.19	3.9	368	78	35.2
245-4-4 w	165		7.22	7.23	2.48	19.7	24.8	19.0	47.4	10.7	0.19	2.8	565	115	35.2
245-4-4 c	165		7.24	7.18	2.33	19.8	24.8	19.1	48.0	8.6	0.23	2.7	533	113	35.3
245-5-4 w	212			7.21	2.71	19.6	24.2	21.6	45.4	9.7	0.24	1.3	611	156	35.2
245-5-4 c	212				<2.0		24.9	21.6	45.0				472	114	
245-6-2 w	246			7.10	2.44	19.6	23.8	22.4	43.8	9.2	0.25	0.7	620	180	35.2
245-8-1 w	284			7.15	2.11	19.8	22.1	24.3	42.8	8.8	0.30	0.5	656	250	35.5
245-9-2 w	313			7.18	<1.1		21.9	27.1	38.5	7.2	0.32	0.4	622	220	34.9
245-11-4 w	333			7.07	1.24		22.1	28.1	37.5	8.8	0.35	1.2	642	165	34.1
245A-1-5 w	30	7.44	7.39	7.31	3.06	19.5	28.0	12.3	52.2	10.1	0.12	0.7	179		35.2
245A-1-5 c	30		7.38	(7.44)	2.70	19.4	27.5	12.4	54.3	8.9	0.12	0.7	131	74	35.5
245A-2-4 w	58	7.33	7.30	7.29	2.71	19.7	27.1	13.3	52.0	10.4	0.13	2.8	209	123	35.8
245A-2-4 c	58				2.38		26.8	14.0	53.1	9.6	0.16	2.6	163	123	35.5
245A-4-5 w	76	7.33	7.33	7.22	2.55	19.6	26.9	13.5	52.1	10.0	0.14	3.7	190	106	35.5
245A-4-5 c	76		7.41		2.38	19.6	27:3	14.3	54.2	8.9	0.14	3.5	142	72	35.2
245A-6-2 w	104		7.27	7.03	2.82	19.5	26.0	16.2	51.0	9.0	0.17	5.6	330	134	
245A-6-2 c	104		7.35		2.53	19.7	26.7	16.7	53.2	7.6	0.18	4.9	256		
245A-7-5 w	145		7.15	7.16	2.88	19.6	25.2	18.4	48.1	10.5	0.19	3.5	530	102	35.2

aPunch in values. bFlow through values. cVessel values. dIn Meq/1. eIn °/... fIn m mole/1. gIn ppm. hIn.µmole/1.

Subbottom Sample (Core, Depth pHa pHb Section) (m) pHc Alkd Cle SO4f Caf Mgf Kf Srf Mng SiO2h NH4^h se 2-2 w 5 7.35 7.44 7.39 4.53 19.4 27.4 11.0 52.6 11.4 0.10 9.8 535 106 35.2 2-2 c 5 7.84 7.80 3.88 19.4 27.4 10.8 54.6 10.3 0.11 6.6 362 87 35.2 4-5 w 125 7.68 7.76 7.76 6.50 19.6 17.5 9.5 50.2 8.3 0.14 0.9 169 322 34.1 4-5 c 125 8.37 8.35 9.4 5.88 19.5 17.7 51.7 7.7 0.2 374 34.1 71 10-1 w 325 21.0 0.18 7.66 7.45 2.06 19.3 22.0 44.9 5.3 6.5 198 159 34.4 10-1 c 325 8.20 1.84 19.6 23.2 22.6 46.1 4.9 0.17 4.4 94 203 34.4 11-1 w 365 25.6 7.3 655 34.4 7.25 1.96 19.7 21.0 40.4 0.16 6.5 228 11-1 c 365 (7.63)1.62 19.7 21.3 26.4 40.1 6.3 0.16 3.9 388 270 12-5 w 395 1.78 19.7 35.2 7.36 25.0 37.2 36.4 6.5 0.16 3.5 735 117 14-3 w 412 20.8 35.6 35.9 4.7 1.36 19.6 5.7 0.19 433 18 34.1

TABLE 6 Site 248 (29° 31.78'S, 37° 28.48'E; 4994 m)

Note: $w = 23^{\circ}C \pm 2$; $c = 5^{\circ}C \pm 1$.

aPunch in values. bFlow through values. cVessel values. dIn Meq/1. eIn °/_{oo} fIn m mole/1. gIn ppm. hIn μmole/1.

Sample (Core, Section)	Subbottom Depth (m)	рНa	p Hb	pНc	Alkd	Cle	so4t	Caf	Mgf	Kf	Srf	Mng	SiO2 ^h	NH4 ^h	Se
1.5	7	7.44	7.50	7.50	2.69	(10.0)	27.0	10.1	52.5			0.0	210		25.2
1-5 W	/	(17°C)	1.52	7.50	2.68	(18.9)	27.8	10.1	52.5			0.0	218		35.2
1-5 c	7		7.47	7.53	2.52	19.3		10.2	54.6	10.2	0.10	0.0			35.2
2-2 w	15	7.44 (18°C)	7.47	7.46	2.73	19.2	27.8	10.5	52.6	11.0	0.17	0.0	128	3	35.2
2-2 c	15	(10 0)	7.47	7.51	2.39	19.4	27.6	10.6	54.4	11.0	0.17	0.3	123		35.2
4-5 w	33	7.50 (18°C)	7.39	7.41	2.74	19.6	26.9	11.5	52.1	10.7	0.26	0.0	107		35.5
4-5 c	33	5.000	7.58	7.69	2.07	19.2	27.1	11.1	52.4	9.9	0.24	0.0	86		
6-5 w	50	7.52 (18°C)	7.32		2.64	19.5	26.9	11.8	51.8	11.1	0.32	0.0	105		35.2
6-5 c	50	(7.58		(1.85)	19.6	26.8	11.3	52.1	10.4	0.30	0.0	87		35.4
8-5 w	70		7.36	7.39	2.55	19.6	25.6	12.2	51.2	10.7	0.35	0.0	102		35.2
8-5 c	70		7.59	7.70	1.84	19.3		11.6	51.6	10.3	0.35	0.1	75		35.2
10-5 w	90		7.40	7.40	2.20	19.6	26.2	12.9	51.7	10.4	0.41	0.0	98		35.2
10-5 c	90		7.58	7.67	1.63			12.1	50.9	9.8	0.38	0.0	73		34.1
12-5 w	109		7.39	7.38	2.55	19.4	25.5	13.5	50.8	9.6	0.42	0.0	105		35.2
12-5 c	109		7.67	7.69	1.83	19.2	25.0	12.9	50.2	9.8	0.42	0.0	74		35.2
14-5 w	136		7.29	7.37	1.98	19.6	24.9	14.4	49.9	9.3	0.42	0.0	99		35.2
14-5 c	136		7.83	7.82	<1.0	19.7	25.0	13.7	50.2	10.1	0.41	0.2	52		35.2
15-5 w	157			7.27	1.75	19.2	24.2	15.1	48.2	9.5	0.41	0.0	140		
15-5 c	157			7.61	<<1.0	19.7	25.8	14.0	50.3				57		
16-1 w	168			7.43	1.16	19.6	25.0	14.7	49.4		0.45	0.0	102		35.2
16-1 c	168			7.57	0.64	19.3		13.9	47.5	9.5	0.39	0.0	62		34.9
17-5 w	185			7.36	2.12		24.6	16.6	47.4	9.7	0.41	0.0	180		35.2
17-5 c	185			7.62	1.50	19.4		18.2	46.8	8.0	0.34	0.0	98		35.2
19-3 w	225			7.34	1.70	19.5	23.2	18.8	47.1	8.1	0.35	0.1	205		35.2
19-3 c	225			(7.42)	< 0.3										35.2
21-5 w	263			7.37	1.10	19.4	22.4	21.0	45.4	7.5	0.32	0.2	187		35.2
21-5 c	263			7.30	0.2	19.45	23.0	21.1	45.2	7.7	0.32	0.2	71		35.2
23-3 w	290			7.43	1.90	20.0	24.2	25.6	47.0				625		
23-3 c	290			7.96	1.52	19.5	23.0	24.4	45.6	7.2	0.27	0.5	410		
25-2 w	310			7.47	1.36	20.1	.21.5	30.2	39.8				333		35.5
26-1 w	320			7.19	0.68	20.1	18.3	32.0	39.5	7.5	0.23	0.1	426		35.5
28-1 w	337			7.33	0.76	19.1	15.4	37.0	35.5	12211201	3.233	12022	426		34.4
30-2 w	375				0.78		16.3	42.5	31.7	(8.9)	0.25	0.5	436		36.3

TABLE 7 Site 249 (29° 56.99'S, 36° 04.62'E; 2088 m)

^aPunch-in Values. These values not corrected to 25°C.

^bFlow through values.

cVessel values.

dIn Meq/1.

eIn °/00

 $f_{In m mole/1.}$

gIn ppm.

 $h_{In \ \mu mole/1.}$



Figure 2. Site 239-alkalinity.





Figure 4. Site 239-sulfate.



Figure 5. Site 239-calcium and magnesium.

Figure 3. Site 239-silica.



Figure 6. Site 239-calcium vs. magnesium.



Figure 7. Site 239-potassium.



Figure 8. Site 239-strontium.

Figure 10. Site 241-alkalinity.

Figure 9. Site 239-manganese.

NANNO OOZE DIATOM & RAD. OOZE * SILTY CLAY & CLAYEY SILT

x

meq./1

NANNO OOZE * SILTY CLAY & CLAYEY SILT

CLAYSTONE

CLAYSTONE

CLAYSTONE + SILT

CLAYSTONE

CLAYSTONE

• = 23°C X = 5°C



Figure 12. Site 241-"salinity."

Figure 14. Site 241-sulfate.

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Figure 18. Site 241-strontium.



Figure 20. Site 242-silica.

Figure 22. Site 242-ammonia.







Figure 24. Site 242-calcium vs. magnesium.





Figure 25. Site 242-potassium.

Figure 27. Hole 245-alkalinity.





Figure 26. Site 242-strontium.

Figure 28. Hole 245-silica.



Figure 29. Hole 245-sulfate.

Figure 30. Hole 245-calcium and magnesium.



Figure 31. Hole 245-calcium vs. magnesium.





Figure 32. Hole 245-potassium.

Figure 34. Hole 245-manganese.



Figure 33. Hole 245-strontium.

Figure 35. Site 248-alkalinity.



Figure 36. Site 248-sulfate.



Figure 37. Site 248-calcium and magnesium.







Figure 39. Site 249-alkalinity.





Figure 40. Site 249-silica.



Figure 42. Site 249-calcium and magnesium.



Figure 41. Site 249-sulfate.

Figure 43. Site 249-calcium vs. magnesium.



Figure 44. Site 249-potassium.

Figure 45. Site 249-strontium.



