

39. INTERSTITIAL WATER STUDIES, LEG 15 – INTRODUCTION AND SUMMARY

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Although many of the products of the diagenesis of deep-sea sediments have been identified, the details of the chemical processes leading to their formation are largely unknown. Attempts to unravel the sequence of events leading to the formation of minerals such as chert, dolomite, pyrite, and sepiolite have met with only the most rudimentary success. The problem is a fantastically complicated one. Marine sediments consist of widely varying proportions of many mineral phases of variable grain size and chemical composition. As has been shown by numerous kinds of isotopic studies of bulk sediment, much of the material is highly inert and retains the properties which characterized the continental soils from which it originated. Mixed with this inert debris are highly reactive organic residues, organism hardparts (calcite, opal, etc.) and authigenic materials (oxides, zeolite, etc.). We are still many years away from any meaningful description of the web of intertwined chemical processes which contribute to the gradual reconstitution of this mix. In fact, we are still searching for the appropriate empirical springboard from which to launch such studies. One of the most promising candidates appears to be the chemical gradients found in the pore fluids of these sediments. Since the fraction of any given element dissolved in these waters (compared to that present in the adjacent solid phases) is very small, any chemical processes leading to the reconstitution of the solid phases would be expected to leave a marked imprint on the pore fluid composition.

Studies of waters squeezed from the sediments recovered as part of the DSDP were initiated with the hope that the changes with depth in any given hole of the concentrations of particular chemical species would point to specific chemical reactions taking place within the sediments. The pioneering studies of Manheim and his colleagues at Woods Hole Oceanographic Institution and of Kaplan and his colleagues at UCLA demonstrated that large and systematic changes in pore water composition with depth in the sediment column are indeed present. The variations found for the major ion species (Na, K, Mg, Ca, SO_4 , and Cl) are summarized in Table I where four patterns of change are recognized. First, there are holes for which no significant chemical changes are found with depth. Second, there are holes in which the anion composition remains nearly constant (i.e., no measureable reduction of $\text{SO}_4^{=}$ and consequent increase in HCO_3^- occurs) but where the cation composition changes (Mg and K decrease and Ca increases with depth). Third, there are holes where partial reduction of the SO_4 occurs. Such columns also show Mg and K loss and Ca gain with depth in the pore fluid column. Finally, there are cores in which complete SO_4 reduction occurs. In such cores Mg, K, and Na decrease and Ca increases with depth. No means have been found to relate the pattern for any given hole to its lithology, sedimentation rate, sediment thickness or porosity.

The reason for the hole-to-hole variability in the nature of the chemical gradient with depth in the pore fluid column remains unknown. Also, other than the obvious fact that $\text{SO}_4^{=}$ ion (and consequently organic matter) is being consumed to a greater or lesser extent by anaerobic bacteria and that the $\text{S}^{=}$ ion generated is being precipitated as some sulfide mineral, little can be said about the chemical changes in the solid phases responsible for the observed gradients. It is not even clear at which depths in the sediment column these reactions occur.

Analyses for trace constituents have provided one major clue. The element Sr has been shown to experience much greater fluctuations in pore fluid concentration than might be expected if it were to follow Ca in some direct manner (i.e., via a unidirectional solution of calcites). Sayles and Manheim have suggested that the magnitude of the Sr increase observed in many holes must be the result of a rather large-scale recrystallization of the calcite present in the sediment.

A review by the JOIDES pore water panel in May 1970 (R. Garrels, SIO; W. Broecker, LDGO; I. Kaplan, UCLA; and F. Manheim, WHOI) of the data obtained for the first few legs concluded that five major improvements were needed before the next step could be taken in understanding the observed pore water gradients. First, several loose ends with regard to the major element analyses themselves had to be cleared up. These were as follows:

- 1) The accuracy of the analytical data had to be verified.
- 2) The temperature of squeezing dependence of pore fluid cation content found by Mangelsdorf had to be confirmed and its variability with sediment type analyzed.
- 3) More detailed sampling was needed in a single hole to define the exact shape of the concentration versus depth curves.

Second, it was felt that properties such as pH, ΣCO_2 , alkalinity, and SiO_2 were not being measured with sufficient accuracy. Since the concentrations of these species appear in virtually every reaction thought to take place in marine sediments, it was deemed essential that they be reliably measured.

Third, it was concluded that other properties of the pore fluid should be measured which might provide additional insight into the processes taking place. Among these were the concentrations of nutrient compounds NH_3 and PO_4 , the isotopic ratios D-H and $\text{O}^{18}\text{-O}^{16}$ in the water, $\text{C}^{13}\text{-C}^{12}$ and D-H in the methane, and $\text{O}^{18}\text{-O}^{16}$ and $\text{S}^{34}\text{-S}^{32}$ in the $\text{SO}_4^{=}$, the trace components of the dissolved pore gas (i.e., C_2H_6 , CO, H_2 , H_2S , He^3 , He^4 , Ne, Ar, Kr, Xe, etc.).

Fourth, the question of contamination of the pore fluids with drilling water (i.e., surface seawater) needed careful consideration. Since the pore water compositions generally fall on a line between the composition of some deep-end member and surface seawater, an analysis of the data

TABLE 1
Variations in Major Ion Species

Category I: Major SO ₄ ⁼ Depletion				
Site	SO ₄ ⁼	Ca/Mg	K/Na	Sr
27	26-5	0.29-0.88	0.40-0.20	6-17
30	<6	0.04-0.43	0.38-0.23	6-25
34	19-11	0.19-0.63	0.45-0.31	7-12
35	18-2	0.16-2.1	0.48-0.15-0.80	7-20
148	27-4	0.20-0.11-0.32	0.46-0.28	9±1
Category II: Moderate SO ₄ ⁼ Depletion				
32	26-21	0.19-0.25	0.51-0.32	7-9
33	27-18	0.16-0.28	0.47-0.42	7-9
64	27-19	0.19-0.41	0.44-0.39	12-70
70	27-23	0.22-1.31	0.44-0.19	8-19
71	27-21	0.21-1.0	0.41-0.34	22-100
149	28-23	0.23-1.1	0.37-0.20	9-44
Category III: Negligible SO ₄ ⁼ Depletion				
29	26±2	0.24-0.42	0.44-0.34	9-1
53	24±4	0.7-10	0.45-0.08	10-15-11
55	27±1	0.17-0.11	0.42±0.02	9-13-11
57	27±1	0.27-0.38	0.47±0.02	24-10
62	26±2	0.23-0.49	0.45-0.30	15-31-15
63	24±2	0.18-0.54	0.44-0.33	12-87
66	27±1	0.18-0.25	0.46-0.31	7-11
72	25±1	0.20-0.26	0.45-0.37	37-15-19
Category IV: No Ca/Mg Change				
10	26±1	0.23±0.02	0.43±0.02	12-13-6
36	26±2	0.20±0.01	0.48±0.03	7±1
42	26±2	0.20±0.01	0.42±0.03	8±1
54	27±2	0.20±0.01	0.48±0.04	8±1
56	27±1	0.19±0.01	0.44±0.03	21-10
65	28±1	0.21±0.01	0.40±0.01	8±1
69	28±1	0.19±0.01	0.45±0.03	9±1
73	26±1	0.21±0.01	0.43±0.01	13-17-14
74	27±1	0.20±0.01	0.44±0.03	9±1
75	27±1	0.21±0.01	0.41±0.02	9±1

themselves would reveal only gross contamination in isolated samples. Any contamination which varied smoothly with depth would go undetected.

Fifth, since molecular diffusion within the pore water column was clearly an important modifying process, it was deemed important to determine how its rate varied with depth in the sediment column. Porosity data (measured routinely) alone are not adequate for this purpose. The electrical conductivity (not measured) is also needed.

Having defined these objectives, the panel decided that they could not be accomplished under the existing format of the program. The manpower available on the ship for pore water work was just not adequate. Also, new procedures had to be developed and special equipment built. Two things were obviously required: 1) technical talent and money to develop the new procedures, and 2) a large component of shipboard personnel.

Terry Edgar, acting for the Deep Sea Drilling Project and in his capacity as co-chief scientist for the forthcoming Caribbean leg, resolved both of these problems by offering

Deep Sea Drilling funds to underwrite the development costs and to permit six pore water workers to work as a team over a period of two weeks on an intensive pore water program. The group then asked me to act as coordinator for this special program. I accepted pending agreement by Ross Horowitz of LDGO that he would take a major responsibility for designing, purchasing, and assembling the necessary gear. Horowitz agreed to do this and Lee Waterman of WHOI agreed to work with him.

The first planning session for the special Leg 15 pore water program was held in La Jolla in 1970. It was attended by Broecker, Takahashi, Barnes, Garrels, Berner, and Craig. Horowitz and Broecker then met with Berner and Garrels in Bermuda to design a punch-in and a flow-through electrode system and with Manheim, Sayles, and Waterman of the WHOI group to plan the squeezing procedure revisions, means of measuring the electrical conductivity of the sediment, and a shipboard method to measure silica. Joris Gieskes of SIO agreed to participate in the shipboard work and to take the responsibility for developing a shipboard alkalinity titration apparatus. Brian Clarke of McMaster University agreed to perform the inert gas measurements and work with Horowitz to develop a shipboard sampling procedure. Taro Takahashi of Queens College worked with Horowitz in designing a new method of tapping the gas pockets which form in CH₄-rich sediments during decompression. In the four months which followed Horowitz and Waterman worked untold hours bringing to reality all these plans. They were joined by Dave Bos and Richard Dubois in San Juan to install this gear on the *Glomar Challenger* between Legs 14 and 15. Bos, Dubois, and Waterman went with the *Glomar* from San Juan and spent the first 23 days completing the installation and overcoming many unexpected technical difficulties; Gieskes, Horowitz, and Broecker joined the *Glomar Challenger* in Curaçao on 29 December. During the seventeen days which followed, three holes—147, 148, and 149—were intensively sampled and subjected to numerous shipboard analyses. The results of this shipboard effort and of the subsequent laboratory studies made on the samples collected constitute the basis for the papers which follow in Volume 20 of the Initial Reports. The laboratory work was carried out by scientists at WHOI, Scripps, Lamont, Queens College, UCLA, Texas A&M, McMaster, Osservatorio Geogisico Sperimentale (Italy), Shell Development (Houston), and USGS (Denver). It represents a degree of cooperation rarely achieved among scientists.

The three sites chosen for this intensive program were selected to provide the greatest possible variation in pore water chemistry. The Cariaco Basin site (Site 147) promised to be one where SO₄⁼ reduction would be very rapid (the basin is anaerobic below 150 m and material obtained by piston coring is a rapidly deposited [50 cm/1000 years] organic-rich ooze). The Aves Ridge site (148) was chosen to be close to a previous drilling site (Site 30, Leg 4) in which SO₄⁼ ion was depleted and the cations Ca, Mg, and K showed their characteristic trend (i.e., Ca increasing and Mg and K decreasing with depth). Finally the Venezuelan Basin was chosen because previous drilling (Site 29, Leg 4) had shown no evidence of SO₄ reduction but did show the same cation trends. As the data reported here demonstrate, we

achieved our objective. Each of the three holes had its own distinctive chemical pattern allowing a broad range of conditions to be studied.

As the accomplishments of Leg 15 are well stated in the papers resulting, there is no need to repeat them in any detail in this introductory report. As an aid to the reader I will, however, mention a number of these and state in which of the following reports they are to be found.

(1) Major element data were measured by four different groups. Sayles et al. report Na, Mg, Ca, K, SO_4 , and Cl on both the warm (23°C) and the cold squeeze (4°C) water. Presley et al. report the same elements on cold squeeze water. Gieskes reports Ca and Mg data on both the warm and cold squeeze samples. Cescon and Macchi and Lloyd report SO_4 data for some of the samples analyzed by Sayles et al. and Presley et al. Each author comments on the degree of agreement with other analysts and Hammond (a nonparticipant in the analytical work) presents an independent analysis of the reliability of all these results. The only serious problem seems to be associated with the Ca analyses. The very low values obtained by Presley et al. and Sayles et al. on samples with high alkalinity and high CO_2 partial pressure strongly suggest that CO_2 loss and CaCO_3 precipitation occurred during storage. Gieskes was aware in advance of this problem and decided to use shipboard acidified samples for Ca analysis. Other than this, the agreement is in general quite good. It is clear, however, that any deviation from a smooth depth trend is more likely than not the result of experimental error. Diffusion very likely has smoothed out any local tendencies for deviation from this mean trend.

The objective to establish the dependence on squeezing temperature of the cation composition was largely successful (see Sayles et al.). One unfortunate deficiency in the shipboard work was that adequate time was not allowed for the warm squeeze sediment to reach room temperature. The combination of a lapse in planning and the intense time pressure on the shipboard workers was responsible for this slip-up. The exact temperature history of each sample should have been more carefully documented.

(2) Alkalinity - ΣCO_2 - $p\text{CO}_2$ - pH. Although not totally successful, the concerted effort to establish the concentration of H^+ , HCO_3^- , CO_3^{2-} , and CO_2 worked out extremely well. Gieskes clearly showed that extremely precise alkalinity titrations could be performed at sea on 10 cc pore water samples and that previously obtained results on stored samples are highly questionable (especially on those waters where the alkalinity was high). Although Takahashi's procedure for storage and analysis (glass dumbbells subsequently subjected to total acidification and IR analyses of the extracted gas) proved to be far superior to that of Presley et al. and Sayles et al. (storage in plastic tubes without acidification), there still is evidence for several percent ΣCO_2 loss during storage.

The punch-in pH measurements proved easy to make and surprisingly reliable compared to other measurements. The flow-through electrode for pore water pH measurement proved to be ideal for shipboard work on very small samples. The finding that calcite is close to saturation (see Gieskes) is a very important one. Since virtually all deep sea cores contain some calcite, it means that pH estimates can

be made from alkalinity data alone (the pH in any calcite-saturated water of known alkalinity is fixed).

The results of this study suggest that pre-Leg 15 pH and ΣCO_2 (or alkalinity) data on pore water are, at least in some cases, not reliable. The pH measurements are suspect both because very small samples exposed to the air were used and because the operators or the gear were not adequately trained in pH technology. The ΣCO_2 (and alkalinity) estimates are suspect due to the possibility of CO_2 loss and CaCO_3 precipitation during storage. In the future a shipboard alkalinity titration and either or both a shipboard punch-in pH measurement or shipboard pore water pH measurement using the flow-through electrode technique should be made.

(3) Silica. The comparison between the shore and shipboard results suggests that the results on stored samples are correct and hence that results obtained prior to Leg 15 are reliable.

(4) H_2S and HS^- . Much preparation was devoted to designing a means of adequately measuring reduced sulfur species in the pore waters. The loading of the squeezers was performed in an inert atmosphere. Plans were made to precipitate and recover the sulfide from the extracted pore water. These efforts were rewarded by the finding that virtually all the waters (even those free of SO_4^{2-} ion) contained no measurable reduced sulfur. Only in the upper few meters of the highly reduced Cariaco Basin sediment was it encountered. Thus the oxidation of reduced sulfur species in the pore waters of sediments proves to be of little hazard, at least for work on deep-sea sediments. It is doubtful whether any of the pre-Leg 15 results have been affected by such oxidation. Repetition of the precautions we took (i.e., the use of an argon-filled dry box) on future legs appears to be unnecessary.

(5) Gas pocket studies. The new gas pocket sampling device paid off. The previously used device suffered from many inadequacies (fragile, air contamination, CO_2 contamination). As discussed by Hammond et al., the new device yielded samples which had only 3 percent air contamination. Whether this represents contamination of the pore water samples with air-bearing drilling fluid or leakage during injection into the chromatograph, is not clear. An improved version of the Horowitz-Takahashi sampler should be used on all subsequent studies.

As shown by Hammond et al., there is much to be learned from gas pocket studies. The question of N_2 utilization could be resolved. Also boundary conditions could be placed on the existence of CH_4 clathrate compounds (Stoll et al., 1971). The main problem is a more adequate measurement of the ratio of gas pocket to sediment volume and a means of determining whether lateral loss of gas along the core liner occurs prior to gas sampling.

(6) Isotope studies. The power of isotopic data in unraveling the complex sequence of events in the diagenetic history of marine sediments is made clear by the results given by Friedman and Hardcastle (H-D on H_2O), by Lyon ($\text{C}^{13}/\text{C}^{12}$ and H-D on CH_4), by Lloyd ($\text{O}^{18}/\text{O}^{16}$ on SO_4^{2-}), and by Lawrence ($\text{O}^{18}/\text{O}^{16}$ on H_2O and $\text{O}^{18}/\text{O}^{16}$ and $\text{C}^{13}/\text{C}^{12}$ on the CaCO_3 and the non- CaCO_3 fraction). As pointed out by Lawrence, this approach is especially

fruitful when both the solid phases and the pore fluids are measured. Lloyd's finding that the O^{18}/O^{16} ratio in the $SO_4^{=}$ ion remains constant with depth at Site 149 adds a very important boundary condition to the thinking on a question which has puzzled isotope geochemists for some years. The latter is an example of how pore waters can be used to yield information on subjects other than sediment diagenesis.

In this connection it is absolutely essential that H-D and O^{18}/O^{16} analyses be carried out on the previously collected pore water samples now stored at the USGS in Denver. This information is needed for the interpretation of isotope analyses of the solid phases from these holes.

(7) Trace constituent analysis. The results for Sr, Li, B, and Br on Leg 15 confirm the value of these measurements in the interpretation of pore water data. On the other hand, the value of results on elements such as Mn, Co, Cu, etc., is yet to be demonstrated. Other than getting more analyses per hole and some temperature effect data, the Leg 15 exercise contributed little to this aspect of the program.

(8) Rare gases. The results obtained by Clarke et al. demonstrate a new line of information that can be obtained from DSDP cores. The gradient of 3He with depth in the sediment column can be used as an index of the rate of local mantle outgassing and perhaps as a means for reconstructing temporal variations in the ratio of global 3He input from the earth's mantle to 3He loss from the atmosphere to outer space. If this is to be accomplished, however, a more suitable method of rare gas sampling must be found. On Leg 15 a normal pore water squeezer was used to transfer water from the sediment to Clarke's copper storage tubes. This procedure resulted in serious loss of gas. Work is under way to test a procedure which involves trapping the sediment itself (rather than the squeezed pore water) in copper storage tubes.

(9) Diffusion rate determination. The graphite electrode unit provided by Manheim for conductivity measurements malfunctioned. Because of the press of other activities no serious attempt to remedy the trouble was made. Consequently no conductivity data are available. In retrospect more emphasis should have been placed in selecting, testing, and trouble-shooting this apparatus. In the future diffusivity measurements must be made.

(10) Drilling fluid contamination. The fact that many sections of the core liner are badly pocketed with blobs of drilling water makes clear the problem of contamination. Even though visual examination through the core liner allows these sections to be avoided and even though a double check can be made when the sample is removed from its core liner for processing, there still is no guarantee that visually acceptable samples are contamination free. Virtually every sample is coated by a thin water-rich layer adjacent to the liner. Although this coating is scraped away before squeezing, diffusional and mechanical intrusion into the interior of the core must to some extent occur.

Two ways have been thought of to check this. One is to assume that any residual $SO_4^{=}$ ion deep in cores showing a rapid $SO_4^{=}$ depletion with depth is an artifact of contamination. Such estimates provide only an upper limit on the extent of contamination. The $SO_4^{=}$ results for the deep portions of Holes 147 and 148 suggest that contamination

of this sort is less than 5 percent (with surface sea water used as a drilling fluid).

The other way is to use a tracer. We tried two approaches on Leg 15 — dye and fresh water, both have serious drawbacks. The use of fresh water seems to have an adverse affect on the drilling conditions. The sediment is badly churned and is in the visually unusable category. Why this is the case, no one knows for sure. Possibly the drillers are unable to obtain a pressure balance between the water column inside (drilling fluid) and outside (seawater plus sediment) the pipe. Another possibility is that exposure to fresh water causes the sediment to disaggregate. In any case, fresh water tests are probably very misleading.

Dye suffers from strong uptake by the clay minerals in the sediment. We used rhodamine B. Experiments showed that dispersion of sediment in dyed water followed by settling removed more than 99 percent of the dye. Thus, although dye might give a visual estimate of what portions of the sediment have been contaminated, no quantitative estimates of the degree of contamination are possible. Tritium would be the best tracer. Its high price and the impracticability of shipboard measurement make it undesirable. Thus we did little more than eliminate two obvious tracer techniques from the running.

One of the sections on which fresh water was used was squeezed and analyzed as shown in Table 2. The results as compared with the average of the overlying and underlying samples point to a 12 percent contamination with fresh water. As mentioned above, this result cannot be taken as typical.

One sample from Site 147 (147-2-2) proves to be a great mystery. In Table 3 its composition is compared with that for the sample just above and the sample just below it. The SO_4 , Ca, and Mg data on the sample from 15 meters depth suggest that it has been contaminated with about 85 percent sea water. The alkalinity, ΣCO_2 , and K content suggest a much lower degree of contamination (~60%). Nothing unusual about the visual character of the sample was noted during the sampling or squeezing operations. These facts, taken together, might indicate that the results are valid and that drilling fluid contamination is very unlikely. On the other hand, taking the ion diffusivity to be 3×10^{-6} cm²/sec and the age of the 15 meter level in the hole to be 30,000 years, the mean diffusion path, \sqrt{Dt} , would be 16 meters. If so, the maintenance of such a high SO_4 ion content at the 15 meter level is very difficult to believe. The results obtained on this sample thus remain an

TABLE 2
Results for the Fresh Water Drilling Fluid Test (Cold Squeeze)

Sample	Depth	Cl ⁻ ppt	SO ₄	Alk.	Mg	Ca	K	pH
			10 ⁻³ moles/Kg					
149-11-4		19.3	23.7	1.71	48.49	16.40	6.98	7.26
149-12-5 ^a	90	17.1	21.2	1.29	36.98	17.33	5.72	7.14
149-14-3	116	19.5	24.1	1.77	45.15	20.55	5.84	7.26
Approx fresh water								
contamination (%) ~12: ~12 ~26 ~21 ~7 ~11 —								

^aFresh water used as drilling fluid.

TABLE 3
The 15 Meter Anomaly at Site 147

Sample	Depth (m)	Cl ppt	← 10 ⁻³ moles/kg →					pH	
			SO ₄	Alk.	ΣCO ₂	Ca	Mg		K
147-2-3/4	8.5	19.91	4.7	17.7	—	3.21	47.8	7.58	7.51
147-2-2	15.	19.97	23.6	8.2	8.2	9.14	55.2	8.95	7.32
147-2-6	15	20.2	0.3	13.8	12.5	4.17	43.5	6.90	7.38
Approx. seawater con- tamination (%)									
		—	~85	~55	—	~85	>80	~60	—

enigma. The temptation to pass them off as the result of some freak process is strong. However, as they may carry a clue to some as yet unrecognized phenomena, more thought should be given to their possible mode of origin. A $^{230}\text{Th}/^{234}\text{U}$ age measurement on the solid from which this sample was squeezed shows it to be less than 3000 years old and hence "fall in" material.

So much for the specific accomplishments of Leg 15. Let us turn our attention to the overall scientific question. As a result of this exercise have we made a great leap forward in our understanding of the processes contributing to the diagenesis of deep-sea sediments? The answer has to be "no." Although we have fortified the results of previous work by clearly demonstrating that the major features they yielded are valid, we made no startling new findings. Although we have demonstrated that these are additional measurements that can provide valuable information about not only diagenetic changes but also the paleoceanography, meteorology, and mantle outgassing, these results raise more questions than they answer.

What, then, did we accomplish? First, we recorded for future study the first set of data detailed and accurate enough for serious diagenetic modeling. I suspect that this

set of data will be the basis for many years of thought and speculation. Little serious modeling has been attempted to date; hopefully these results will prove to be a shot in the arm to the theoretical aspects of diagenesis. Until working models are developed, there is little hope that a big advance in understanding will be made. Second, our detailed results and our evaluation of procedures will enable others to make much better use of previously collected DSDP pore water data. Its strengths and pitfalls are now apparent. Third, this exercise largely removed a serious communication gap which had developed among workers in this field. Because of the complexity of the scientific problem and because only one collection facility exists (the *Glomar Challenger*) it is important that interested scientists join forces rather than work in isolation. Hopefully, the fine atmosphere of cooperation which characterized the Leg 15 venture will become an integral part of future deep drilling pore water work.

REFERENCES

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