28. INTERSTITIAL WATER STUDIES, LEGS 47A, B

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INTRODUCTION

During Leg 47, very deep penetrations were attempted at two sites: Site 397 (proximal to Site 369, Leg 41) off northwestern Africa, and Site 398 off Portugal on the Vigo Seamount. Interstitial water samples were collected from the upper 50 per cent of the hole depths at both sites. Notwithstanding this incomplete record, we analyzed the available samples as part of the shipboard work.

A highlight for interstitial water work during Leg 47 was the first successful use of the *in-situ* water sampler, especially built for DSDP operations. One successful sample was obtained and the data look encouraging, as will be shown in this report.

METHODS

Analyses of the samples were made using the methods described by Gieskes (1974), with slight modifications. For dissolved sulfate, we used a polarographic technique (Akiyama, 1977) based on that of Luther and Meyerson (1975).

RESULTS

The data are given in Table 1 and in Figures 1 to 3. The *in-situ* sample was obtained in copper tubing. Work during and subsequent to Leg 47B has shown that this tubing affects the titration data for calcium, magnesium, and alkalinity as a result of reaction between the tubing and the enclosed pore water. This situation since has been rectified by use of teflon-coated, stainless steel tubing, which does not have a deleterious effect on major ion determinations.

DISCUSSION

In-Situ Sampler

Table 2 presents the results obtained with the *in-situ* sampler at 110 meters, and compares these data with those obtained by conventional squeezing techniques at 107.5 meters.

The alkalinity of the *in-situ* sample is 33 per cent higher than the squeezed sample. Subsequent work would suggest that about 6 per cent of this discrepancy was caused by reaction with the copper tube. The remaining 25 per cent difference is in the direction expected if CO_2 loss during recovery and processing of conventional pore water samples leads to calcium carbonate precipitation and loss of alkalinity in these samples.

A most interesting observation was that on opening a small piece of clamped-off tubing after prolonged storage, the sample showed an immediate white precipitate upon leaving the millipore filtering assembly. This precipitate redissolved upon acid addition. We interpret this in terms of rapid CO_2 escape and a subsequent rise in pH, with concomitant calcium carbonate super-saturation. This is no proof for *in-situ* equilibrium with a calcium carbonate phase, but it does show that best estimates for total CO_2 contents of the pore fluids can probably be obtained only by *in-situ* samplers. This problem will receive more attention in the future.

The good agreement for sulfate is expected on the basis of previous comparisons between *in-situ* filtered pore water and conventional squeezed core samples (Sayles et al., 1976).

The measured difference in the calcium is probably caused by reaction of the water with the copper tubing; this reaction leads to an apparent calcium increase of about 10 per cent. When this copper effect is considered, the good agreement of the calcium data gives credence to the low values of calcium obtained by the shipboard extraction methods in many sites where rapid deposition leads to sulfate depletions.

Dissolved potassium is somewhat lower than the shipboard value. This can be expected on the basis of previous evidence of the temperature of squeezing effect (e.g., Manheim and Sayles, 1974).

The agreement between dissolved ammonia data is not very good. Here, two effects may be the cause: (1) ion exchange effects and, more likely, (2) storage effects. Whereas the shipboard samples are stored in an acidified state (sample is titrated for alkalinity), the *in-situ* sample was stored at "normal" pH. Previous work by us has shown that typically lower values of ammonia are observed in samples stored at pH > 7. In addition, some ammonia may have reacted with the copper tubing.

Dissolved strontium shows a 20 per cent discrepancy, but in a direction not expected from traditional temperature of squeezing effects. Therefore, the discrepancy may be due to erroneous data.

Dissolved manganese data are very different and reasons are not readily apparent. However, levels were low in both samples (0.5 and 0.3 ppm) and our error may be appreciable at these concentrations levels.

TABLE 1
Interstitial Water Analyses, Leg 47

DSDP Section	Depth (m)	Na (mm)	K (mm)	Ca (mm)	Mg (mm)	Sr (mm)	Mn (μm)	Cl (mm)	SO$_4$ (mm)	NH$_4$ (μm)	Alk (meq/l)	Si (μm)
Leg 47A												
397-2-3	13.5	476	11.8	8.6	53.1	0.23	3.6	557	23.4	827	7.70	597
397-6-2	50	497	11.1	3.7	39.0	0.17	0	566	5.2	2434	18.2	1360
397-6-2	50	488	11.9	3.9	37.8	0.20	0	566	0	2550	–	1350
397-10-5	92.5	481	10.8	5.3	35.1	0.25	15.7	554	0	2790	19.2	854
397-16-5	149.5	496	10.8	6.1	31.1	0.37	0	566	0	3250	16.2	859
397-21-3	194	500	8.8	7.6	30.1	0.36	0	571	0	2680	13.7	811
397-27-3	251	525	8.9	6.5	27.2	0.40	0	586	4.7	2595	7.3	265
397-32-3	298.5	532	6.7	6.4	28.5	0.54	0	595	4.6	2345	5.6	249
397-39-4	366.5	517	5.9	8.2	29.8	0.62	0	595	0.8	1908	4.7	153
397-44-3	411	518	5.4	9.1	27.9	0.61	1.9	595	1.0	1960	2.4	255
397-52-5	501	528	5.3	11.5	32.9	0.67	0	612	5.1	1768	1.25	92
397-61-3	583	534	4.9	16.6	30.9	0.71	2.4	629	2.6	1729	0.79	56
397-66-3	631	545	5.3	22.4	(14.7)	1.11	3.9	618	4.0	1795	0.58	66
Leg 47B												
398-2-4	14.0	(510)	12.0	7.1	46.7	0.11	19.4	571	25.5	1043	7.75	303
398-4-3	107.5	499	9.9	5.2	49.0	0.14	5.1	566	16.8	1143	8.32	167
in-situ	110.0	–	9.0	5.4	–	0.11	2.7	–	16.3	749	11.10	161
398A-1-4	178.5	486	9.6	6.7	49.0	0.32	2.0	563	19.3	871	6.88	156
398A-2-5	208.5	491	8.9	9.3	47.5	0.40	5.0	571	18.5	758	5.84	395
398B-1-3	234	487	9.5	7.4	49.1	0.38	3.5	571	16.4	1047	6.40	152
398D-2-1	272.5	489	9.0	5.2	49.8	0.16	12.3	568	17.9	886	4.02	184
398D-3-5	326	477	9.4	11.7	48.3	0.62	4.9	568	17.6	827	3.98	126
398D-4-5	375	474	10.1	14.5	47.3	0.71	2.5	565	21.6	786	4.72	167
398D-5-3	398.5	484	9.0	17.1	45.0	0.85	2.5	574	19.7	–	5.53	–
398D-8-4	457.5	493	9.6	19.9	44.3	0.91	3.5	571	(28.3)	568	4.75	711
398D-12-4	514.5	472	7.0	24.9	41.8	0.98	5.85	574	18.1	416	3.83	773
398D-23-2	625	–	6.0	26.3	46.2	0.74	48.1	574	–	444	6.22	884
398D-32-4	714	480	5.5	26.3	44.3	0.60	7.7	574	20.5	613	2.53	653
398D-63-5	1019.5	406	4.4	31.6	36.0	0.66	34.1	534	5.6	781	2.39	372

Excellent agreement is obtained for dissolved silica data. Perhaps this is fortuitous, as silica values are usually strongly dependent on sediment lithology. However, we consider this result encouraging.

SITE 397

Sedimentation rates at this site were large, especially during the Miocene but also during the Quaternary (ca. 5 cm/1000 yr). Therefore, it is not surprising that sulfate reduction is essentially completed within 100 meters from the sediment/water interface. Typically, the sulfate reduction process and its associated bacterial degradation processes are also mirrored in a distinct maximum of ammonia at about 20 meters. Although there is some scatter in the sulfate data, it appears that the sulfate reduction process has been more important in the Quaternary sediments than in the deeper lying Pliocene and Miocene strata. This may well be due to a higher content of degradable carbon in the siliceous sediments of the upper 200 meters at this site (cf. dissolved silica, Figure 1). In addition, of course, the sulfate reduction processes are reflected in an alkalinity maximum at 100 meters.

In many respects, the interstitial water profiles are similar to those of Site 369, which is located near Site 397 (Couture et al., 1977). At the former site, sedimentation rates were much slower than at Site 397. This is typically reflected in a less pronounced maximum in alkalinity and the absence of a calcium minimum at Site 369.

Dissolved calcium and magnesium profiles are complex, and dissolved strontium can be due to both carbonate recrystallization and diffusion from evaporite strata. The latter postulate is based on the distinct increase in chloride concentration, as evidenced in Figure 2. It is unfortunate that no interstitial water samples were obtained in the deeper strata in order to establish whether a continuous increase of Cl occurs throughout the hole or whether a maximum occurs due to advection through the sandstones of the lower units of Site 397. It should be emphasized that the increased chlorinities with depth at Site 397 do not, per se, imply underlying evaporites. This was well demonstrated during Leg 50 at a site near Site 370. Perhaps some discrete samples from deeper strata would reveal data pertinent to this problem.

SITE 398

Except for the *in-situ* sampler, this site yields little information that lends itself to direct geochemical interpretation. The maximum in dissolved strontium occurs (Figure 3) at the base of Unit I, i.e., in the siliceous marly chalks (cf., dissolved silica). Perhaps recrystallization reactions occur at maximum rates in these horizons.
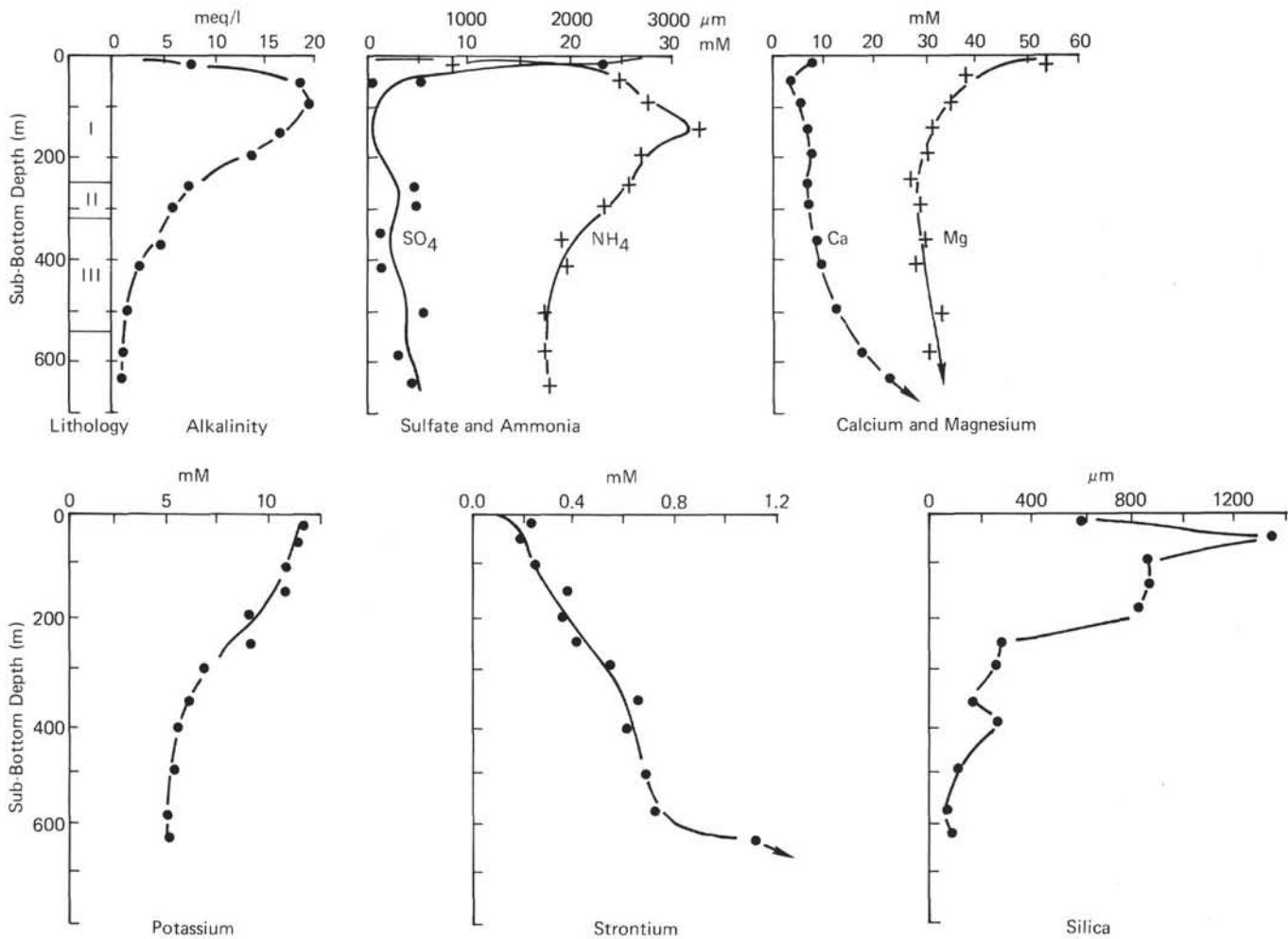
Figure 1. *Interstitial water chemistry at Site 397. Lithology: I = marly nannofossil ooze, siliceous nannofossil ooze; II = marly nannofossil ooze/chalk; III = marly nannofossil chalk.*

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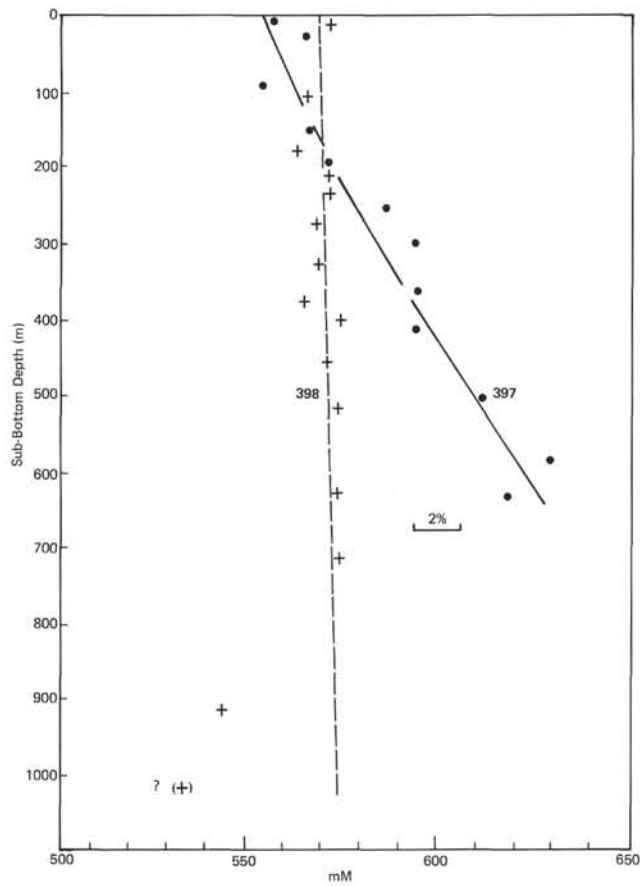
Figure 2. *Interstitial chloride data, Sites 397 and 398. (Note: the bottommost chloride of Site 398 may be suspicious.)*
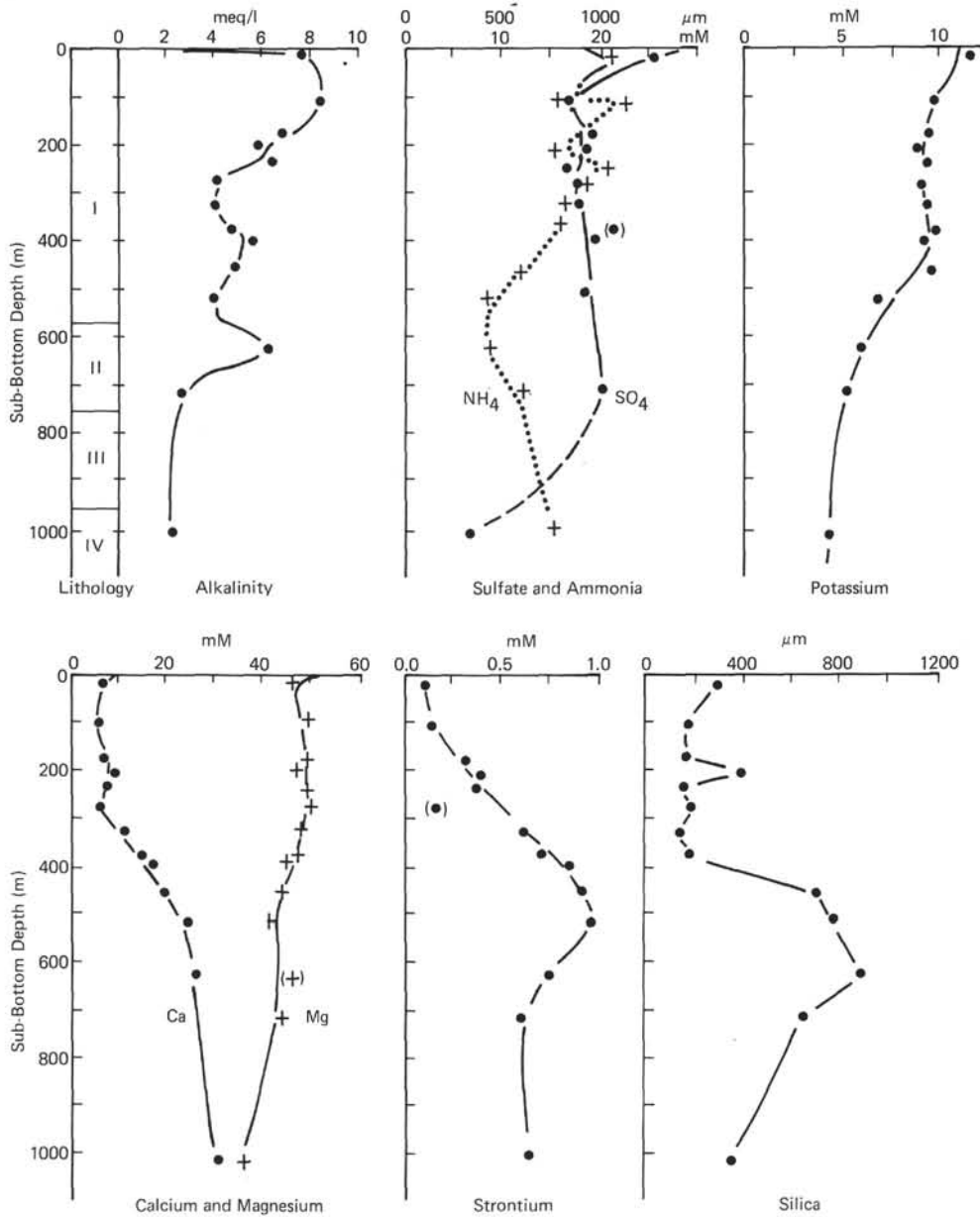
Figure 3. *Interstitial water chemistry at Site 398. Lithology: I = marly nannofossil ooze and chalk, increase in biogenous silica below 440 meters; II = siliceous nannofossil chalk and mudstones; III = marly nannofossil chalk to 832 meters, mudstones below; IV = organic carbon-rich shales.*

TABLE 2
Comparison of *In-situ* Data (110 m) With
Conventional Data (107.5 m)

Property	Shipboard	*In-situ*	Ratio
Alkalinity (meq/l)	8.32	11.10	1.33
Silica (μmoles/l)	167	161	0.96
Ammonia (μmoles/l)	1143	749	0.66
Potassium (mmoles/l)	9.87	9.01	0.91
Calcium (mmoles/l)	5.15	5.38	1.04
Strontium (mmoles/l)	0.14	0.11	0.79
Sulfate (mmoles/l)	16.8	16.3	0.97
Manganese (μmoles/l)	5.1	2.7	0.52