## 19. PORE-WATER CHEMISTRY, SITES 506-509, DEEP SEA DRILLING PROJECT<sup>1</sup>

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#### ABSTRACT

Geological and geophysical data collected during Deep Sea Drilling Project (DSDP) Leg 70 indicate that hydrothermal solutions are upwelling through the sediments of the mounds hydrothermal field (Sites 506, 507, and 509) and downwelling in the low heat-flow zone to the south (Site 508). Pore-water data are compatible with these conclusions. Pore waters at mounds sites are enriched in Ca and depleted in Mg relative to both seawater and Site 508 pore waters. These anomalies are believed to reflect prior reaction of the interstitial waters with basement rocks. The mounds solutions are also enriched in iron, which is probably hydrothermal and *en route* to forming nontronite. Concentrations of Si and NH<sub>3</sub> in mounds pore water increase upcore as a result of the addition of dissolving biogenic debris to ascending hydrothermal solutions.

Some low heat-flow pore-water samples (Site 508) are enriched in Ca and depleted in Mg. These anomalies likely reflect the presence of pockets of hydrothermal solutions in areas otherwise dominated by downwelling bottom water.

### INTRODUCTION

As discussed at length elsewhere in this volume, the mounds hydrothermal field is thought to be a site where hydrothermal solutions are upwelling through and out of the sediments, supplying Mn2+ and Fe2+ to form metalliferous deposits. Geological studies (Corliss et al., 1979; Williams et al., 1979), deep-tow studies (Klitgord and Mudie, 1974; Lonsdale, 1977), heat-flow work (Green, 1980; Green and Von Herzen, 1980; and others), and geochemical and mineralogical investigations (Corliss et al., 1978, 1979) all point strongly to this conclusion. Pore-water studies by Maris et al. (1979) confirmed that pore waters depleted in Mg by 2 to 3 mM ( $\sim 5\%$ ) and enriched in Ca by 1 to 1.5 mM ( $\sim 10\%$ ) were upwelling at a rate of ~1 cm/y. through the pelagic sediments surrounding the mounds. Pore-water studies were carried out on DSDP Leg 70 in order to gain a more comprehensive understanding of the pattern of upwelling in the mounds field, the end-member chemistry of the hydrothermal solutions, and the processes leading to formation of metalliferous sediments. Our specific objectives were as follows: (1) to determine whether the composition of hydrothermal solutions in pore waters change with depth, (2) to determine whether the composition of solutions in mounds differs from that in the surrounding pelagic sediment, (3) to search for a flux of hydrothermal iron and manganese, and (4) to study porewater chemistry at a nearby low heat-flow site and to contrast these results with mounds field data. Locations of holes drilled by Leg 70 on the southern flank of the Galapagos Spreading Center are shown in Figure 1.

# EXPERIMENTAL PROCEDURES AND RESULTS

#### Methods for Taking Pore-Water Samples

Pore waters were separated from subcores by refrigerated centrifugation at temperatures close to *in situ* values. Ten- to eleven-centimeter whole-core sections were cut and stored at 7°C or 22°C for esti-



Figure 1. Locations of Leg 70 holes.

mated *in situ* temperatures less or greater than  $12^{\circ}$ C, respectively. Within 1 to 24 hours (generally about six hours) the samples were subcored and extruded into 150 cm<sup>3</sup> centrifuge tubes, after 1 cm<sup>3</sup> slices had been cut from the top and bottom of the core sections and discarded. To slow oxidation, N<sub>2</sub> was blown into the volume between the sediment and the top of the centrifuge tube; the samples, in groups of four, were then packed into plastic bags filled with N<sub>2</sub> and sealed.

It is well documented that sampling temperature affects the chemistry of pore-water samples. In these studies we were searching for small chemical anomalies in samples whose *in situ* temperatures varied

<sup>&</sup>lt;sup>1</sup> Honnorez, J., Von Herzen, R. P., et al., *Init. Repts. DSDP*, 70: Washington (U.S. Govt. Printing Office).

from ~2 to 20°C as a result of the high geothermal gradient. Consequently, we took great care to sample at temperatures as close as possible to the in situ values, in order to avoid reversible temperature-dependent concentration changes. The bags described above, each containing four samples, were placed in water-filled Tupperware containers, thermostated at the desired "sampling temperature" to ±2°C by periodically adding ice. The intended sampling temperature was chosen as the estimated average in situ temperature of the four sediment samples. The temperature estimates were generally made from previously collected heat-flow data; when compared with Glomar Challenger temperature data subsequently collected with the Barnes-Uyeda probe, our estimates were found to deviate from interpolated in situ temperatures by  $\pm 2^{\circ}C$  (1 $\sigma$ ) (Fig. 2). The samples were equilibrated in the baths for about two hours, then centrifuged at 8500 rpm for 10 minutes in a Sorvall RC5B refrigerated superspeed centrifuge. The centrifuging temperature was kept 3°C below the "sampling temperature" to compensate for frictional heating. Water samples were drawn from the centrifuge tubes into Plastipak syringes and filtered through 25mm, 0.4 µm acid-washed Nuclepore filters into various glass and plastic bottles.

Figure 2 establishes that our *a priori* estimated temperatures were within  $\pm 2^{\circ}$ C of actual downhole temperatures measured with the Barnes-Uyeda probe. Our thermostating method succeeded in giving temperatures of pore-water equilibration and separation close to the intended sampling temperatures. Centrifuge cake temperatures of 10 samples, measured immediately after the pore waters were drawn off, were  $\pm 1^{\circ}$ C (1 $\sigma$ ) different from the intended "sampling temperatures is about  $\pm 3^{\circ}$ C; of this error, about 1° results from imperfect sample equilibration and 2° results from erroneous *a priori* estimates of downhole temperature variations. Under these circumstances, reversible temperatures of squeezing artifacts are minimal.

Sediment samples were encapsulated in Cu tubes for subsequent noble gas analysis. For these samples, subcores were taken adjacent to the core liner. A copper tube was then pushed through the sediment adjacent to the subcore; before insertion the tube was partly filled with deionized water to prevent inclusion of air in the sample. There was always 1 cm of sediment between the site where the Cu tube was pushed in and the core liner (this space serves to minimize diffusive exchange of gases between pore waters and the sampled sediment). After sampling, the tube was clamped to seal off a volume of sediment.

Squeeze pore-water samples were also collected at room temperature for noble gas analysis. Inside an N<sub>2</sub>-filled glove bag, 5-cm core sections were extruded into Reeburg squeezers. Pore waters were expressed through Tygon tubes into 1 cm<sup>3</sup> volume aluminum tubes. After an Al tube was flushed with several tube volumes of sample, it was sealed and stored. Samples of the squeezed waters were also collected for Si and trace metal analyses. Note that, since samples were squeezed at room temperatures, measured Si concentrations are upper limits to the *in situ* values. Si data are reported here, but noble gas analyses have not yet been run.

In situ pore-water samples were collected with the Barnes-Uyeda probe. In this apparatus, pore waters are sucked under hydrostatic pressure through a stainless steel filter into a stainless steel tube.

All pore waters were filtered through 0.4  $\mu$ m Nuclepore filters immediately after collection.

#### **Analytical Techniques**

Ca and Mg were measured by colorimetric titration using standard DSDP methods (Tsunogai et al., 1968; Gieskes, 1973). Si and NH<sub>3</sub> were measured within 7 and 1 days, respectively, of sample collection, using standard colorimetric techniques (Strickland and Parsons, 1968; Solorzano, 1969). Mn and Fe were measured in acidified samples by direct injection, flameless atomic absorption spectrophotometry. Precision is about  $\pm 0.5\%$  for Ca and Mg,  $\pm 2\%$  for Si,  $\pm 5\%$  for NH<sub>3</sub>, and  $\pm 8\%$  for Mn and Fe. The NH<sub>3</sub> detection limit is taken as  $4 \mu M/l$ , and that of Fe as  $0.4 \mu M/l$ . The high detection limit for NH<sub>3</sub> reflects the small amounts of sample analyzed and variable contamination from the deionized water.

#### Results

The pore-water work done at Sites 506 to 509 is summarized in Tables 1–12. Results for shipboard-sampled pore waters are summarized in Tables 1–11; those for *in situ* samples are given in Table 12.



Figure 2. Comparison of *in situ* and estimated squeezing temperatures.

Table 1. Pore-water chemistry of samples from Hole 506.

			10				
IW No. <sup>a</sup>	Depth (m)	SiO <sub>2</sub> (μM/l)	NH3 (μM/l)	Ca (mM/l)	Mg (mM/l)	Mn (µM/l)	Fe (µM/l)
1	0.75	450	5			33	< 0.3
2	2.64	560	16	10.30	53.37	101	0.9
3	8.35	410	5	11.72	51.94	33	23
4	13.25	370	7			37	24
5	14.05	380	5	11.56	51.70		
6	20.3	350		11.14	48.50	36	16.8
7	24.9	460				37	16.6
8	26.45	440		11.14	51.48	39	14.7
9	27.79	450		10.51	51.76	38	14.8

<sup>a</sup> IW refers to Leg 70 interstitial water sample number.

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Table 2. Pore-water chemistry of samples from Hole 506B.

IW No. <sup>a</sup>	Depth (m)	SiO2 (µM/l)	NH3 (μM/l)	CA (mM/l)	Mg (mM/l)	Mn (µM/l)	Fe (µM/l)
10	1.24	600	45	11.49		47	5.4
11	2.95	540	22			38	13.9
12	4.45	510	20	11.64	50.45		
13	5.95	400		11.26	50.12	31	7.4
14	7.35	440	15			36	8.0
19	8.85	470		11.18	51.79	41	16.5
15	10.24	400	11			32	6.5
16	11.75	410				38	19.2
20	13.25	390				42	27
21	14.62	390	6	11.58		43	22
22	15.85	390				36	9.2
23	17.65	420	16	11.47	51.61	36	12

<sup>a</sup> IW refers to Leg 70 interstitial water sample number.

Table 3. Pore-water chemistry of samples from Hole 506C.

IW No. <sup>a</sup>	Depth (m)	SiO <sub>2</sub> (μM/l)	NH3 (µM/l)	Ca (mM/l)	Mg (mM/l)	Mn (μM/l)	Fe (μM/1
24	1.45	570		10.55		126	0.7
25	2.95	540		10.95	51.43	129	0.5
26	9.35						
27	10.85	230		10.95	53.24	28	2.2
28	12.08	93		11.58		24	0.6
29	13.75	97		11.83			
30	15.25						
31	15.72	210		12.29	51.14	25	1.3
32	18.15	530		11.32		35	2.9
33	19.65	540		11.37	51.60	33	6.3
34	21.04	520				42	6.5
35	22.55	520		11.41	51.91	36	7.2
36	24.05	530				36	8.4
37	25.37	490		11.49	51.47	38	6.0

<sup>a</sup> IW refers to Leg 70 interstitial water sample number.

Table 4. Pore-water chemistry of samples from Hole 506D.

IW No. <sup>a</sup>	Depth (m)	SiO <sub>2</sub> (μM/l)	NH3 (μM/l)	Ca (mM/l)	Mg (mM/l)	Mn (µM/l)	Fe (µM/l)
38	1.45	600		10.55	52.88		
39	5.00	490		11.85	51.82	73	12.8
40	6.87	215		11.37		25	
41	8.35	610		11.64		52	0.5
42	9.85	560					4.3
43	10.99	540		11.58	51.45	49	4.9
44	12.75	500				43	13.5
45	14.25	480		11.51	52.27	43	9.1
46	15.67	410		11.15		34	7.6
47	17.15	460				47	10.1
48	18.65	520		11.45	50.93	45	10.3
49	19.82	480				52	10.3
50	24.41	510		11.32	51.81	44	6.1
51	27.94	500		11.26	51.00	46	2.6

<sup>a</sup> IW refers to Leg 70 interstitial water sample number.

### Sample Integrity

It is crucial to examine sample integrity, since pore-water chemistry differs little from that of bottom water. One line of evidence involves comparing data for *in situ* and centrifuged samples. The raw data are compared in Table 13 and Figure 3, and the differences summarized in Table 14. When all results are considered, there are large differences between centrifuged and *in situ* data: the standard deviation from the mean is  $\pm 0.3$  mM for Ca,  $\pm 0.5$  mM for Mg, and  $\pm 70$ mM for Si. These differences far exceed analytical error. If we restrict the comparison by eliminating the samples showing severe disagreement in Mg (Hole 508) and Si (Hole 509) on the grounds that they may record local variability (and in the case of Hole 509, surface water

Table 5. Pore-water chemistry of samples from Hole 507D.

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IW No. <sup>a</sup>	Depth (m)	SiO2 (µM/l)	NH3 (μM/l)	Ca (mM/l)	Mg (mM/l)	Mn (µM/l)	Fe (µM/l)
63	6.84	160	<4	10.40	51.74	2.1	2.8
64	9.24	270	<4			14.8	4.8
65	11.24	350	<4	11.56	51.93	23	5.6
67	13.84	250		11.70		14.7	6.0
68	15.65			11.41		15.2	1.9
69	18.44	350	<4	10.66	51.61	20	13.1
70	22.99	260	9	10.82	51.85	18.1	11.1
71	24.45	410		10.82		23	17.9
72	28.84	310				20	3.8
73	31.62	400	<4	10.61	51.48	23	7.4
74	33.25	450				21	12.2
75	35.85	370	<4	10.68	51.76	20	4.2
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<sup>a</sup> IW refers to Leg 70 interstitial water sample number.

Table 6. Si concentrations of Hole 507D pore waters squeezed at room temperature (21-22°C)

Depth	Si
(m)	(µM/l)
3.51	150
7.63	340
16.87	490
25.97	460
30.37	460
34.76	480

Table 7. Pore-water chemistry of samples from Hole 507F.

IW No. <sup>a</sup>	Depth (m)	SiO2 μM/1	NH3 μM/1	Ca mM/l	Mg mM/l	Mn μM/l	Fe µM/l
76	1.45	570	24	10.11	51.92	95.0	0.4
77	3.85	340	11	10.18		48.0	0.4
78	5.35	410		11.32	52.57	45.0	< 0.4
79	6.84	390				30.0	< 0.4
80	10.96	510	7	11.22	51.8	18.3	6.5
81	12.64	490				19.0	9.5
82	15.24	410		10.86	51.92	17.1	5.9
83	17.04	420	0			20.0	8.0
85	19.9	450				22.0	11.2
86	21.44	430	0	11.01	51.95		8.1
87	25.84	440	0			22.0	16.4
88	28.62	410		10.86	51.92	20.0	19.5

<sup>a</sup> IW refers to Leg 70 interstitial water sample number.

Table 8. Pore-water chemistry of samples from Hole 508.

IW No. <sup>a</sup>	Depth M	SiO2 μM/1	NH3 μM/1	Ca mM/l	Mg mM/l	Mn μM/l	Fe µM/l
90	1.44	550				78	< 0.4
91	1.94			10.23	53.06	64	< 0.4
92	3.75	560	13	10.38	52.55	61	< 0.4
95	8.33	610	54	10.3	52.7	58	< 0.4
96	12.58	610		10.34	52.83	56	< 0.4
99	14.24	640				53	< 0.4
101	17.21	650	32	10.29	53.19	50	< 0.4
102	18.64	660				38	< 0.4
105	23.00	660		10.17	52.52	25	< 0.4
109	27.44	650		10.24	52.96	13.2	0.5
111	30.23	520	8			15.2	0.9
112	31.84	460		10.25		27	6.0
113	33.05	400		10.59	52.76	27	8.3
114	34.62	440	9	10.89	52.17	31	2.0

<sup>a</sup> IW refers to Leg 70 interstitial water sample number.

Table 9. Si concentrations of Hole 508 pore waters squeezed at room temperature (21-22°C)

Ľ	epth (m)	Si (µM/l)
	6.94	804
1	1.34	860
1	5.74	920
1	9.84	910
2	4.54	840
2	8.94	830

Table 10. Pore-water chemistry of samples from Hole 509.

	Depth	SiO <sub>2</sub>	NH3	NH3 Ca		Mn	Fe
IW No.ª	(m)	(µM/l)	(µM/l)	(mM/l)	(mM/l)	(µM/l)	(µM/l)
122	2.45	640	35	12.29	51.54	32	< 0.4
124	5.44	590	27	12.25	51.71	33	< 0.4
125	0.071429	630	27			43	< 0.4
126	8.34	660	22			44	< 0.4
127	9.77	620	22	12.06	51.47	37	< 0.4
129	12.74	510	11			31	5.7
130	14.02	530	10	12.12	50.93	36	9.6
132	17.24	550	10			37	9.6
133	18.43	520	9	12.10	51.55	35	7.9
134	20.04	550	10			35	6.5
135	21.54	540	9	11.41	52.18	32	5.4
137	25.94	510	6			42	6.1
138	27.3	510	9	11.33	51.37	35	8.7
139	28.84	470	5			44	5.0
140	30.04	470	5	11.22	51.48	37	0.7
141	31.56	310	14			31	

<sup>a</sup> IW refers to Leg 70 interstitial water sample number.

Table 11. Pore-water chemistry of samples from Hole 509B.

IW No. <sup>a</sup>	Depth (m)	SiO <sub>2</sub> (μM/l)	NH3 (μM/l)	Ca (mM/l)	Mg (mM/l)	Mn (µM/l)	Fe (µM/l)
Centrifuge	e Samples						
141.5	4.44	390	8			75	< 0.4
142	5.94	390	7	12.27	51.31	78	< 0.4
143	7.44	350				69	< 0.4
144	10.34	330	4	12.08	51.52	74	< 0.4
145	15.85	260		12.27	51.16	53	< 0.4
146	17.64	390	6	11.81	51.39	75	< 0.4
147	19.14	300	6			40	4.8
148	20.10	120					
149	22.04	470		11.79	51.17	50	6.6
150	23.54	470	4			73	15.6
151	24.94	450		11.52	51.56	41	7.5
152	26.44	470	4			38	9.6
154	29.13	420	7	11.18	51.20	34	5.7
155	33.29	450		11.39	50.87	40	11.9
Runoff Sa	mples						
118	1.5	410		12.29	50.67	67	< 0.4
119	8.9	390		12.35	51.31	77	10.000000000
120	10.4	350		12.19	51.36	81	< 0.4
121	13.3	410		12.44	51.58	69	< 0.4

<sup>a</sup> IW refers to Leg 70 interstitial water sample number.

contamination), we end up with a systematic Ca difference of 0.4 mM/l (centrifuge value < in situ value) and no systematic differences and small variability in Mg and Si data. The situation improves slightly when we restrict the comparison to Site 510 samples (those least likely to be affected by local variability). The conclusions are (1) that centrifuge Ca data are systematically low by about 0.4 mM/l, (2) that

Table 12. Pore-water data for *in situ* samples, Holes 506-509.

IW No. <sup>a</sup>	Cast	Hole	Depth (m)	Si (µM/l)	Ca (mM/l)	Mg (mM/l)
53	3	506F	15	540	12.22	51.38
89	7	5071	25	540	11.60	51.44
106	8	508A	26	720	10.98	51.64
115	10	508E	19	660	10.97	51.76
156	12	509C	24	380	11.53	52.22
157	13	509D	18	230	11.07	52.12

a IW refers to Le	g 70 interstitial water	sample number.
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Table 13. Comparison of the pore-water chemistry of centrifuge samples (obtained by interpolation) with that of *in situ* pore-water samples from a nearby hole.

Centrifuge Sample: Depth Hole (m)	Depth	In situ Sample: Hole	Ca (mM/l)		Mg (mM/l)		Si (µM/l)	
	(m)		Centrif.	In situ	Centrif.	In situ	Centrif.	In situ
506B	15	506F	11.6	12.2	51.7	51.4	390	540
508	16	508A	10.3	11.0	52.8	51.8	640	660
508	25	508E	10.2	11.0	53.0	51.6	660	720
509	18	509D	11.9	11.1	51.6	52.1	530	230
509B	24	509C	11.6	11.5	51.4	52.2	460	380
510	39	510	10.9	11.3	53.6	53.8	840	730
510	67	510	11.3	11.8	53.2	53.0	950	1050
510	96	510	11.2	11.9	51.6	51.6	1120	1090

<sup>a</sup> For Site 510 data, see paper on Site 510 pore waters, this volume.

centrifuge Mg data are satisfactory, and (3) that centrifuge Si data show no systematic offset but are slightly compromised by an inherent sampling artifact of  $\pm 10\%$ .

The origin of the Si artifact is not understood. The Ca artifact is probably tied in with the total alkalinity artifact observed by Emerson (personal communication) in Pacific carbonate ooze sediments, in which shipboard-squeezed pore waters have total alkalinity (TA) and total carbon dioxide concentrations up to 0.6  $\mu$ eq/l and 0.6  $\mu$ M/l, respectively, less than those of *in situ* samples. Both the Ca<sup>2+</sup> and TA artifacts can be explained by a pressure-dependent ion-exchange reaction such as:

 $Ca^{2+} + 2HCO_3 + Ca^{2+} - exchange \rightarrow 2CaCO_3 + H_2^+ - exchange$ 

The good agreement between centrifuge and *in situ* Mg concentrations suggests that Mg is not involved in such a reaction.

#### DISCUSSION OF RESULTS

The chemistry of centrifuged pore-water samples is summarized in Figures 4 to 7. The most important feature of the data is that mounds field pore waters are enriched in Ca and depleted in Mg relative to bottom water, and this anomaly results from the fact that they have previously reacted with basement and are now flowing up through the sediments.

## Ca and Mg

The Ca, Mg, NH<sub>3</sub>, and Fe profiles clearly differ between mounds field pore waters and low heat-flow (Hole 508) pore waters. The mounds pore waters are characterized by Ca enrichments of up to 2 mM/l and Mg depletions of 1.5 to 3 mM/l, while low heat-flow pore waters are characterized by small Ca and Mg depletions (~0.1 mM/l and 0.5 mM/l, respectively).

Low heat-flow pore-water Ca concentrations corrected for the 0.4 mM/l sampling artifact (see preceding discussion) are  $\sim 0.3$  mM higher than bottom water;



Figure 3. Comparison of pore-water data for in situ and centrifuged samples.

Table 14. Differences in Ca, Mg, and Si concentrations of *in situ* and centrifuge samples collected at nearby depths and locations (calculated from results in Table 13).

	Ca (mM)		Mg (mM)		Si (µM)	
	Centrif. – In situ	Std. Dev.	Centrif In situ	Std. Dev.	Centrif In situ	Std. Dev
All samples (n = 8)	-0.4	±0.3	+0.2	±0.3	- 50	$\pm 70$
All samples except those from Holes 508 and 509 (n = 5)	-0.4	$\pm 0.2$	-0.1	$\pm 0.2$	-10 (0%)	±50 (±9%)
Hole 510 samples only	-0.5	±0.1	0	$\pm 0.1$	10 (1%)	±50 (±5%)

this difference results from  $CaCO_3$  dissolution driven by metabolic  $CO_2$  input, according to the reaction:

$$CH_2O + O_2 + CaCO_3 \rightarrow Ca^{2+} + 2HCO_3^{-1}$$

The increase of  $\sim 0.3$  mM roughly corresponds to the value predicted from the bottom water O<sub>2</sub>, which limits TA and Ca buildup in the pore waters (Emerson et al., 1980). A slight Ca buildup is a widespread feature of

pore-water chemistry and is well understood (Sayles, 1979). The cause of the Mg anomaly, on the other hand, is unknown. However, the Mg anomaly observed in pore waters at Hole 508 and in samples from gravity and piston cores taken in the low heat-flow band north of the mounds field (Maris et al., 1980) is never as large as it is in the mounds field cores.

The Ca enrichment in the mounds field cores is too great to be explained by  $CaCO_3$  dissolution, and both the Mg and Ca anomalies in the mounds field are far larger than observed in extensive studies of pelagic sediment pore waters (Sayles, 1979; Bischoff and Ku, 1970; Bischoff and Sayles, 1972). We believe the anomalies reflect removal of Mg and release of Ca by basalt during previous basement reactions. Pore waters of the mounds field, then, are hydrothermal solutions upwelling through the sediments.

This important conclusion of our work merits discussion in more detail. Maris et al., (1979), Maris et al., (1980), and Maris (unpublished) analyzed Ca and Mg concentrations in cores taken from the mounds field and the low heat-flow area to the north, by piston and



Figure 4. Chemistry of centrifuged pore-water samples, Site 506. Holes 506 and 506C penetrated mounds; Holes 506B and 506D were off-mounds holes.

gravity coring from R/V Gillis in 1979 and by gravity coring from DSRV Alvin. All mounds field pore waters sampled below 1 meter depth were found to have Ca and Mg anomalies similar to those reported here. Ca concentrations rose from the seawater value toward the asymptotic values. By fitting the Ca-depth profiles to the diffusion-advection model, advection rates of 0.7-20 cm y.<sup>-1</sup> were calculated. Thus, there is considerable evidence that Ca-rich, Mg-poor hydrothermal solutions are upwelling throughout the sediments of the mounds field.

One puzzling question is why, if the Ca anomalies reflect basement reaction, Ca concentrations increase going uphole at Site 509 and, to a lesser extent, at Site 507. We believe that this increase results from input to the sediment column of hydrothermal solutions of varying composition. As we will show later, the Si profiles record the existence of complex plumbing systems within the mounds. The uniform upwelling model appears satisfactory within the top meter of the sediment, but, at depth, gravel lenses provide paths for input of different solutions to different parts of the mounds.

The alternative explanation for Ca increasing upcolumn (CaCO<sub>3</sub> dissolution superimposed on uniformly upwelling solutions) can be dismissed because there is no source of acid to drive the reaction. Upwelling solutions at the base of the sediment column would be saturated with respect to CaCO<sub>3</sub>, since the entire sediment column contains biogenic carbonate. During ascent 0.04 µM/l of CaCO<sub>3</sub> would dissolve as a result of the solubility increase associated with cooling from 20° to 2°C; this change is a negligible fraction of the observed increase. Nontronite precipitation generates acid which dissolves CaCO<sub>3</sub>, but again the amount of dissolution is negligible when  $Fe^{2+}$  is ~0.02 mM/l. Precipitation of other authigenic silicates would dissolve CaCO<sub>3</sub>, but neither pore-water nor sedimentology data give any indication that such a phase is precipitated.

## Silica

The Si profile above 30 meters at Hole 508 is typical of profiles for pelagic sediments underneath highly productive surface waters. Within the top 2 meters, (Si) rises to an asymptotic value of  $600 \pm 50 \ \mu\text{M}$ . The Si in-



Figure 5. Chemistry of centrifuged pore-water samples, Site 507.

crease results from biogenic Si dissolution. There is actually a slight increase in concentrations going downcore. The Si profiles of the mounds field holes contrast markedly with that of Hole 508. Mounds field concentrations are lower and far more erratic. Loder et al., (1978) have shown that during the squeezing of pore waters, precipitation may accompany  $Fe^{2+}$  oxidation, thereby causing artificially low [Si] values. Our Si results cannot, however, be explained by such an effect. First, samples squeezed entirely in an N<sub>2</sub> atmosphere at room temperature had low Si concentrations (see Hole 507D data: Table 6). Second, the dissolved  $Fe^{2+}$  concentrations are far too low to account for Si removal. Third, there is no relation between pore-water Si and  $Fe^{2+}$  concentrations.

In Hole 509, Si systematically increases upcore. This increase probably results from input of dissolving biogenic Si as the water ascends. The same process appears to be occurring in Hole 506B and perhaps in Hole 506D.

In Figures 4, 5, and 7, the depths above which thick hydrothermal deposits first appear are marked with dotted lines. Below these depths, in the pelagic sections of mounds holes, the Si concentrations are relatively consistent and in good agreement with Si concentrations in the comparable depths of the respective nearby offmounds holes. Above the transition, within the thick nontronite beds, Si concentrations are highly erratic and sometimes fall to very low values—90  $\mu$ M/l in Hole 506C for example. Since the erratic Si values cannot be explained easily in terms of any known artifact, and since the Si profiles of off-mounds and low heat-flow areas are smooth, we believe that the low and erratic Si concentrations are real features. They cannot be quantitatively explained in terms of in situ removal reactions. Dissolved Si removal would accompany precipitation of nontronite (Fe<sub>4</sub> Si<sub>8</sub> O<sub>20</sub> (OH)<sub>4</sub>) or a magnesium silicate. However, the dissolved Fe2+ is far too low to account for precipitation of a significant amount of Si. Mg<sup>2+</sup> is present in great excess, relative to Si, of course, but studies of mounds sedimentology and composition have given no evidence for significant Mg-silicate formation.

The low Si concentrations in the nontronite layers are thus believed to be primary features of the ascending hydrothermal solutions. The variability in Si indicates that there is a complex plumbing system in which hydrothermal solutions of variable composition flow through dif-



Figure 6. Chemistry of centrifuged pore-water samples, Site 508.

ferent nontronite gravel layers separated by relatively impermeable biogenic ooze or nontronite muds. Since the hydraulic impedance of the ooze and muds is so much greater than that of the gravels, it is easy to imagine that this scenario is realized. One final implication of this discussion is that the mounds may have "roots" by which they tap the basement aquifer. If we are correct in concluding that the upcore decrease in mounds Si concentration does not reflect Si precipitation, then within mounds the simple, vertical, one-dimensional flow model must not obtain. We must postulate that hydrothermal solutions get to the nontronite gravels by flowing through unsampled channels in the basal pelagic sediments rather than by uniform upward advection through the basal layer.

# NH<sub>3</sub>, Mn<sup>2+</sup>, and Fe<sup>2+</sup>

The profiles of  $NH_3$ , Mn, and Fe must be considered in terms of the zonation of organic matter degradation reactions in pelagic sediments, a topic which has received considerable attention (Froelich et al., 1979; Emerson et al., 1980) and will be summarized briefly here. Organic matter in sediments is oxidized by the available oxidant yielding the greatest amount of free energy. As one oxidant is consumed, the reaction proceeds using the next most efficient oxidant;  $O_2$ , MnO<sub>2</sub> and NO<sub>3</sub><sup>-</sup>, Fe<sub>2</sub>O<sub>3</sub>, and SO<sub>4</sub><sup>2-</sup> thus serve sequentially to oxidize organic matter in sediments. The reactions are as follows (with organic matter represented as CH<sub>2</sub>O):

$$CH_2O + O_2 \rightarrow CO_2 + H_2O \tag{1}$$

$$3CO_2 + H_2O + CH_2O + 2MnO_2 \rightarrow 2Mn^{2+} + 4HCO_3^{-}$$
 (2)

$$5CH_2O + 4NO_3 \rightarrow 2N_2 + CO_2 + 4HCO_3 + 3H_2O$$
 (3)

$$7CO_2 + 3H_2O + CH_2O + 2Fe_2O_3 \rightarrow 4Fe^{2+} + 8HCO_3^{-}$$
 (4)

$$2CH_2O + SO_4^{2-} \rightarrow H_2S + 2HCO_3^{-}$$
 (5)

The first reaction is accompanied by an increase in the pore-water  $NO_3^-$  concentration as a result of oxidation of organic nitrogen. The next two reactions are accompanied by an increase in pore water  $[Mn^{2+}]$  and a decrease in  $[NO_3^-]$ . The fourth reaction is accompanied by an increase in  $[Fe^{2+}]$ , and the last (5) results in  $NH_3$ 



Figure 7. Chemistry of centrifuged pore-water samples, Site 509.

production. (Of course, all reactions result in other changes; those listed are the ones most easily detected.)

In the pelagic sediments of the study region, the organic matter content is very high as a result of high productivity and shallow water depth. Consequently, the sequential reactions occur close to the surface. Studies of numerous gravity and piston cores from the mounds field area show that  $NO_3^-$  goes to zero by 15 cm depth,  $[Mn^{2+}]$  increases between 10 and 15 cm, and  $NH_3$  increases within the top few tens of centimeters (Maris, Froelich, and Bender, unpublished results). In other words, the entire sequence of the first four reactions is completed within the top 50 cm or so, and the finial reaction has commenced at this depth.  $Fe^{2+}$  is undetectable in the top few meters; this observation is likely the result of rapid incorporation of  $Fe^{2+}$  into solid phases and not to the absence of  $Fe_2O_3$  reduction.

Ammonia concentrations in Hole 508 pore waters rise to  $60 \ \mu M$  at ~ 10 meters depth and then fall. The increase results from NH<sub>3</sub> production during sulfate reduction (final reaction). The full equation is:

$$(CH_2O)_{106}(NH_3)_{16}(H_3PO_4) + 53SO_2^2 - - 106HCO_3^- + 16NH_3 + 53H_2S$$
 (6)

The decrease below 10 meters depth probably results from  $NH_4$  incorporation into the solid phase.

NH<sub>3</sub> concentration profiles in mounds field pore waters differ sharply from that of Hole 508; mounds profiles reflect addition of metabolic NH<sub>3</sub> to upwelling solutions. In the mounds cores themselves (Holes 506, 506C, 507D, 509B), NH<sub>3</sub> concentrations are low, reaching a maximum of 8  $\mu$ M/l in one deep Hole 507D sample and two Hole 509B samples. NH<sub>3</sub> concentrations are higher in the off-mounds holes (506B, 507F, 509) and clearly increase going toward the surface. The upcore increase in off-mounds holes reflects input to the ascending solutions of NH<sub>3</sub> produced by SO<sub>4</sub><sup>2-</sup> reduction.

 $NH_3$  concentrations are lower in mounds holes than in off-mounds holes for two reasons. First, the organic C and N contents of mounds sediments are very low (Table 15), resulting in low rates of  $SO_4^{2-}$  reduction and  $NH_3$  input to the pore waters. Second, the solutions up-

Table 15. Organic C, organic N, and CaCO<sub>3</sub> concentrations of sediments from Sites 506-509.<sup>a</sup>

Hole 506 $0.84$ 1.14         0.15         78 $3.04$ 0.71         0.090         70 $7.68$ 0.65         0.080         2 $12.35$ 0.12         <0.005         2           Hole 506B         2.13         1.00         0.12         58 $7.46$ 0.53         0.060         62 $12.18$ 0.72         0.072         76 $16.99$ 0.21         0.025         86           Hole 506C         23.45         0.81         0.073         79 $26.70$ 0.21         0.029         71         0.37         60 $9.24$ 0.67         0.084         60         14.01         66 $26.12$ 1.05         0.10         73         30.32         0.27         0.029         78           Hole 507D         2.94         0.39         0.070         0         5.64         0.77         0.30         0 $2.94$ 0.39         0.070         0         5.64         0.77         0.30         0 $2.94$ 0.39         0.070         <	Depth (m)	Corg (%)	Norg (%)	CaCO3 (%)
$\begin{array}{c cccccc} 0.84 & 1.14 & 0.15 & 78 \\ 3.04 & 0.71 & 0.090 & 70 \\ 7.68 & 0.65 & 0.080 & 2 \\ 12.35 & 0.12 & < 0.005 & 2 \\ \hline \end{array}$ Hole 506B $\begin{array}{c ccccccccccccccccccccccccccccccccccc$	Hole 506			
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	0.84	1.14	0.15	78
7.68       0.65       0.080       2         12.35       0.12       <0.005	3.04	0.71	0.090	70
Hole 506B           2.13         1.00         0.12         58           7.46         0.53         0.060         62           12.18         0.72         0.072         76           16.99         0.21         0.025         86           Hole 506C         23.45         0.81         0.073         79           26.70         0.21         0.029         71           0.37         0.94         0.13         68           4.85         0.52         0.072         60           9.24         0.67         0.084         60           14.01         0.78         0.085         63           18.41         0.67         0.060         73           30.32         0.27         0.029         78           Hole 507D         2.94         0.39         0.070         0           5.64         0.77         0.030         0         143           22.53         0.49         0.051         43           24.83         0.62         0.30         72           31.18         0.33         0.404         66           Hole 507F         3.62         3.45         0.35         1	7.68	0.65	0.080	2 2
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	Hole 506B			
1.40       0.33       0.000       76         12.18       0.72       0.025       86         Hole 506C       23.45       0.81       0.073       79         26.70       0.21       0.029       71         0.37       0.94       0.13       68         4.85       0.52       0.072       60         9.24       0.67       0.084       60         14.01       0.78       0.085       63         18.41       0.67       0.060       76         22.04       0.32       0.041       66         26.12       1.05       0.10       73         30.32       0.27       0.029       78         Hole 507D       2.94       0.39       0.070       0         5.64       0.77       0.030       0         9.89       0.19       <0.005	2.13	1.00	0.12	58
16.99         0.21         0.025         86           Hole 506C         23.45         0.81         0.073         79           26.70         0.21         0.029         71           0.37         0.94         0.13         68           4.85         0.52         0.072         60           9.24         0.67         0.084         60           14.01         0.78         0.085         63           18.41         0.67         0.060         76           22.04         0.32         0.041         73           30.32         0.27         0.029         78           Hole 507D         2.94         0.39         0.070         0           5.64         0.77         0.030         0           9.89         0.19         <0.005	12.18	0.53	0.060	76
Hole 506C           23.45         0.81         0.073         79           26.70         0.21         0.029         71           0.37         0.94         0.13         68           4.85         0.52         0.072         60           9.24         0.67         0.084         60           14.01         0.78         0.085         63           18.41         0.67         0.060         76           22.04         0.32         0.041         66           26.12         1.05         0.10         73           30.32         0.27         0.029         78           Hole 507D         2.94         0.39         0.070         0           5.64         0.77         0.030         0           9.89         0.19<<<0.005	16.99	0.21	0.025	86
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	Hole 506C			
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	23.45	0.81	0.073	79 71
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	0.37	0.94	0.13	68
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	4.85	0.52	0.072	60
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	9.24	0.67	0.084	60
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	18.41	0.67	0.060	76
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	22.04	0.32	0.041	66
Hole 507D         2.94         0.39         0.070         0 $2.94$ 0.39         0.070         0 $5.64$ 0.77         0.030         0 $9.89$ 0.19         <0.005	26.12 30.32	1.05	0.10	73 78
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	Hole 507D			1000
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	2.94	0.39	0.070	0
3.63         0.19         0.003         34           17.38         0.65         0.073         34           22.53         0.49         0.051         43           24.83         0.62         0.030         72           31.18         0.33         0.44         66           Hole 507F	5.64	0.77	0.030	0
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	17.38	0.65	0.073	34
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	22.53	0.49	0.051	43
31.18         0.33         0.040         78           35.33         0.38         0.044         66           Hole 507F         3.62         3.45         0.35         1           3.62         3.45         0.35         1         6.26           0.15         0.020         0         76         21.91         0.30         0.041         76           26.22         0.37         0.059         72         30.16         0.066         0.009         83           Hole 507H         2.08         0.82         0.10         63         5.62         0.54         0.066         56           9.81         0.67         0.087         69         18.60         0.36         0.040         75           23.10         0.36         0.035         73         Hole 508         73           Hole 508         1.83         1.40         0.19         62         5.91         0.72         0.086         52           10.69         0.72         0.086         0.040         78         32.75         0.32         0.037         63           32.70         0.52         0.044         70         23.45         0.30         0.040         78	24.83	0.62	0.030	72
Hole 507F $3.62$ $3.45$ $0.35$ 1 $6.26$ $0.15$ $0.020$ 0 $17.69$ $0.36$ $0.050$ 76 $21.91$ $0.30$ $0.041$ 76 $26.22$ $0.37$ $0.059$ 83           Hole 507H	31.18 35.33	0.33	0.040	78 66
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	Hole 507F			
6.26         0.15         0.020         0           17.69         0.36         0.050         76           21.91         0.30         0.041         76           26.22         0.37         0.059         72           30.16         0.066         0.009         83           Hole 507H         2         2         0.10         63           5.62         0.54         0.066         56           9.81         0.67         0.087         54           16.06         0.87         0.090         69           18.60         0.36         0.040         75           23.10         0.36         0.035         73           Hole 508         1.83         1.40         0.19         62           5.91         0.72         0.086         52         10.69         0.72           10.69         0.72         0.11         44         14.94         0.83         0.12         57           18.91         0.86         0.084         70         23.45         0.30         0.040         78           32.70         0.52         0.044         63         32.70         0.52         0.044         63 </td <td>3.62</td> <td>3.45</td> <td>0.35</td> <td>1</td>	3.62	3.45	0.35	1
1.05         0.30         0.031         76           21.91         0.30         0.041         76           26.22         0.37         0.059         72           30.16         0.066         0.009         83           Hole 507H         200         63         5.62         0.54         0.066         56           9.81         0.67         0.087         54         0.066         56           9.81         0.67         0.087         54         0.066         56           9.81         0.67         0.087         54         0.066         52           16.06         0.87         0.090         69         18.60         0.36         0.040         75           23.10         0.36         0.035         73         Hole 508         22         10.69         0.72         0.086         52         10.69         0.72         0.11         44           14.94         0.83         0.12         57         18.91         0.86         0.084         70           23.45         0.30         0.040         78         32.70         0.52         0.044         63           Hole 509         2.94         1.25	6.26	0.15	0.020	76
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	21.91	0.30	0.041	76
30.16         0.000         0.009         83           Hole 507H         2.08         0.82         0.10         63           5.62         0.54         0.0666         56           9.81         0.67         0.087         54           16.06         0.87         0.090         69           18.60         0.36         0.040         75           23.10         0.36         0.035         73           Hole 508         1.83         1.40         0.19         62           5.91         0.72         0.086         52         10.69         70           23.45         0.30         0.040         78         32.75         18.91         0.86         0.084         70           23.45         0.32         0.037         63         32.70         0.52         0.040         78           32.780         0.52         0.040         78         32.70         0.52         0.044         63           Hole 509         2.94         1.25         0.18         49         20.93         0.33         0.050         69           26.11         0.24         0.038         81         10.18         10.18         10.18 </td <td>26.22</td> <td>0.37</td> <td>0.059</td> <td>72</td>	26.22	0.37	0.059	72
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	Hole 507H	0.000	0.009	63
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	2.08	0.82	0.10	63
9.81 0.67 0.087 54 16.06 0.87 0.090 69 18.60 0.36 0.040 75 23.10 0.36 0.035 73 Hole 508 1.83 1.40 0.19 62 5.91 0.72 0.086 52 10.69 0.72 0.11 44 14.94 0.83 0.12 57 18.91 0.86 0.084 70 23.45 0.30 0.040 78 27.85 0.32 0.037 63 32.70 0.52 0.044 63 Hole 509 2.94 1.25 0.18 49 20.93 0.33 0.050 69 26.11 0.24 0.038 81	5.62	0.54	0.066	56
16.06         0.87         0.090         69           18.60         0.36         0.040         75           23.10         0.36         0.035         73           Hole 508           1.83         1.40         0.19         62           5.91         0.72         0.11         44           14.94         0.83         0.12         57           18.91         0.86         0.084         70           23.45         0.30         0.040         78           32.70         0.52         0.044         63           Hole 509         2.94         1.25         0.18         49           20.93         0.33         0.050         69           26.11         0.24         0.038         81	9.81	0.67	0.087	54
1.800         0.300         0.040         73           Hole 508         1.83         1.40         0.19         62           5.91         0.72         0.11         44           14.94         0.83         0.12         57           18.91         0.86         0.084         70           23.45         0.30         0.040         78           27.85         0.32         0.037         63           32.70         0.52         0.044         63           Hole 509         2.94         1.25         0.18         49           20.93         0.33         0.050         69           26.11         0.24         0.038         81	16.06	0.87	0.090	69
Hole 508 1.83 1.40 0.19 62 5.91 0.72 0.086 52 10.69 0.72 0.11 44 14.94 0.83 0.12 57 18.91 0.86 0.084 70 23.45 0.30 0.040 78 27.85 0.32 0.037 63 32.70 0.52 0.044 63 Hole 509 2.94 1.25 0.18 49 20.93 0.33 0.050 69 26.11 0.24 0.038 81	23.10	0.36	0.035	73
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	Hole 508			
3.91         0.72         0.066         32           10.69         0.72         0.11         44           14.94         0.83         0.12         57           18.91         0.86         0.084         70           23.45         0.30         0.040         78           27.85         0.32         0.037         63           32.70         0.52         0.044         63           Hole 509         2.94         1.25         0.18         49           20.93         0.33         0.050         69           26.11         0.24         0.038         81	1.83	1.40	0.19	62
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	10.69	0.72	0.086	44
18.91         0.86         0.084         70           23.45         0.30         0.040         78           27.85         0.32         0.037         63           32.70         0.52         0.044         63           Hole 509           2.94         1.25         0.18         49           20.93         0.33         0.050         69           26.11         0.24         0.038         81	14.94	0.83	0.12	57
23.45 0.30 0.040 78 27.85 0.32 0.037 63 32.70 0.52 0.044 63 Hole 509 2.94 1.25 0.18 49 20.93 0.33 0.050 69 26.11 0.24 0.038 81	18.91	0.86	0.084	70
20.93 0.32 0.044 63 Hole 509 20.94 1.25 0.18 49 20.93 0.33 0.050 69 26.11 0.24 0.038 81	23.45	0.30	0.040	78
Hole 509 2.94 1.25 0.18 49 20.93 0.33 0.050 69 26.11 0.24 0.038 81	32.70	0.52	0.044	63
2.94         1.25         0.18         49           20.93         0.33         0.050         69           26.11         0.24         0.038         81	Hole 509			
26.11 0.24 0.038 81	2.94	1.25	0.18	49
	26.11	0.24	0.038	81
29.70 0.27 0.033 67	29.70	0.27	0.033	67
Hole 509B	Hole 509B			
6.79 1.64 0.21 9 8.97 0.13 < 0.005 0	6.79	1.64	0.21	9
13.65 0.10 <0.005 0	13.65	0.10	< 0.005	o
18.32 0.36 <0.033 78	18.32	0.36	< 0.033	78
22.22 0.34 0.051 70	22.22	0.34	0.051	70
32.69 0.24 0.023 71	32.69	0.18	0.018	71

<sup>a</sup> Corg and Norg determined on acid leached samples aboard ship with Hewlett-Packard CHN analyzer; CaCO<sub>3</sub> determined gasometrically using carbonate bomb. well through mounds so rapidly that any metabolic  $NH_3$ input must be diluted with a relatively large volume of water. According to Maris et al., (1980), upwelling rates are over an order of magnitude faster in mounds than in adjacent pelagic sediments. Thus even if  $NH_3$  input were everywhere equal, mounds pore-water concentrations would only be one-tenth of the off-mounds values.

Near the top of Hole 508,  $[Mn^{2+}]$  rises to 76  $\mu$ M/l; this manganese is derived from reaction 2 (MnO2 reduction), and the concentration is typical for rapidly accumulating pelagic sediments. Mn<sup>2+</sup> decreases with depth; assuming the pore waters are downwelling, the decrease must reflect Mn removal, perhaps as a Ca-Mn-carbonate (Elderfield et al., 1981). In the mounds field holes, the picture is more complicted. For each site, the Mn concentration is constant within the basal pelagic layer (roughly the bottom 10 m). At Holes 506 and 509 [Mn<sup>2+</sup>] is ~40  $\mu$ M/l, and at Hole 507 [Mn<sup>2+</sup>] is about 20  $\mu$ M/l. In most off-mounds holes and in some mounds holes, [Mn<sup>2+</sup>] is either constant going upcore (Holes 506, 506B, 507D, 509) or increases as a result of metabolic  $Mn^{2+}$  input (Hole 507F). The exception is Hole 506D, where [Mn<sup>2+</sup>] scatters considerably. Above the pelagic layer (i.e., within the hydrothermal gravels) in other mounds holes, Mn values are erratic. In Hole 506C, for example,  $[Mn^{2+}]$  drops from 40 to 24  $\mu$ M/l; in Hole 509B,  $[Mn^{2+}]$  varies between 40 and 75  $\mu$ M/l.

It is impossible to determine the source(s) of this dissolved manganese from pore-water data alone. There are three possibilities: (1) the manganese may be hydrothermal; (2) it may be *in situ* diagenetic, deriving from the local sediments; or (3) the manganese may be remembered-diagenetic, deriving from sediments through which the water downwelled before it first entered the basement aquifer. There is a local hydrothermal manganese anomaly above the mounds (Corliss et al., 1978; Klinkhammer et al., 1977; Klinkhammer, 1980), and thus it is clear that the mounds field is a hydrothermal manganese source. From the pore-water data alone, however, it is impossible to separate the diagenetic and hydrothermal manganese components.

There is probably hydrothermal iron in mounds field holes. Fe is present from the base of the sediment column up to depths of 1 to 10 meters. As in the case of manganese, this  $Fe^{2+}$  may be hydrothermal, *in situ* diagenetic, or remembered diagenetic. However, the contrast between the mounds field and low heat-flow holes points strongly to a hydrothermal origin.

An interesting feature of the  $Fe^{2+}$  profiles is that dissolved iron is present to shallower depths in the offmounds holes than in the mounds holes (compare Holes 506B and 506D with 506 and 506C, and Hole 509 with 509B). This difference may reflect mixing of small amounts of seawater into the hydrothermal gravel, and iron precipitation by the reaction:

$$4Fe^{2+} + O_2 + 4H_2O \rightarrow 2Fe_2O_3 + 8H^+$$
(7)

Taking the pore-water  $Fe^{2+}$  concentration as 10  $\mu$ M/l and bottom water O<sub>2</sub> as 150  $\mu$ M/l, seawater would have to mix with pore water at a ratio of 1/60 to cause com-

plete  $Fe^{2+}$  precipitation. The presence of 2% seawater in the pore waters would not noticeably alter any other chemical properties. If such mixing is occurring, then the presence of  $Fe^{2+}$  in shallower depths in off-mounds holes results from the fact that the high impedance of the pelagic sediments prevents the mixing of seawater and pore water.

### **Composition of Pore Waters at the Bottom of Hole 508**

In low heat-flow Hole 508, pore-water compositions change abruptly at 30 meters depth. Above this depth, [Ca2+] and [Mg2+] are close to seawater values (Mg actually is depleted by about 0.5 mM/l), [Si] is typical for equatorial pelagic sediments, Fe2+ is undetectable, and Mn has fallen to ~13  $\mu$ M/l. Below 30 meters, the solutions show the hydrothermal characteristics of mounds field pore waters. Ca rises, Mg appears to fall slightly, Si falls sharply, and Mn<sup>2+</sup> and Fe<sup>2+</sup> both rise. This change probably reflects the diffusion or mixing upward of hydrothermal Ca, Mg, Mn, and Fe against downwelling through the sediments. However, there are some problems with this explanation. First, fits to a one-dimensional diffusion-advection model would give a downwelling rate of about 0.4 cm y.-1. Rates calculated from heat-flow data (this volume) are about an order of magnitude higher. Second, the explanation requires that, at the top of the basement aquifer, solutions are well mixed between the mounds field and the low heatflow area. While such extensive mixing seems unlikely, its existence is supported by two in situ samples collected at Site 508 which had small positive Ca anomalies and negative Mg anomalies (Table 12).

### SUMMARY AND CONCLUSIONS

Pore waters from the mounds hydrothermal field are enriched in Ca and depleted in Mg; they are hydrothermal solutions which have reacted with basalt and are now upwelling through the sediment column.  $NH_3$  concentrations in the mounds field increase upward as a result of diagenetic input superimposed on upwelling. Hydrothermal iron is present in mounds and off-mounds pore waters but is oxidized and precipitated before reaching the sediment-water interface. Si and Fe concentrations are erratic; rapid flow and a complex plumbing system in the mounds allow nearby solutions to have widely varying compositions.

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