34. PORE-WATER CHEMISTRY AND CARBONATE DIAGENESIS IN SEDIMENTS FROM LEG 115: INDIAN OCEAN¹

Peter K. Swart² and Stephen J. Burns^{2,3}

ABSTRACT

Analyses of the Sr²⁺ concentrations of interstitial fluids obtained from sediments squeezed during Leg 115 were used to estimate the rates and total amount of recrystallization of biogenic carbonates. The total amount of recrystallization calculated using this method varies from less than 1% in sediments at Site 706 to more than 40% at Site 709 in sediments of 47 Ma. Five of the sites drilled during Leg 115 (Sites 707 through 711) were drilled in a depth transect within a restricted geographic area so that theoretically they received similar amounts of sediment input. Of these, the maximum rate of recrystallization occurred in the upper 50 m of Site 710 (3812 m). The amount of recrystallization decreased with increasing water depth at Sites 708 (4096 m) and 711 (4428 m), presumably as a result of the fact that most of the reactive calcium carbonate was dissolved before burial. We also observed significant alkalinity deficits at many of these sites, a condition which most likely resulted from the precipitation of calcium carbonate either in the sedimentary column, or during retrieval of the core. Precipitation of CaCO3 as a result of pressure changes during core retrieval was confirmed by the comparison of Ca^{2+} and alkalinity from water samples obtained using the *in-situ* sampler and squeezed from the sediments. At Sites 707 and 716, the shallowest sites, no calcium or alkalinity deficits were present. In spite of our estimations of as much as 45% recrystallization at Site 709, all the carbonate sites exhibited what would be previously considered conservative Ca^{2+}/Mg^{2+} profiles, which varied from -1 to -0.5. By virtue of the position of these sites relative to known basaltic basement or through the actual penetration of basalt (i.e., Sites 706, 707 and 712), these sites are all known to be underlain by basalt. Our results suggest, therefore, that more positive Ca^{2+}/Mg^{2+} gradients cannot necessarily be used as indicators of the nature of basement material.

INTRODUCTION

In previous studies, pore-water analyses of fluids squeezed from carbonate sediments have provided abundant information on diagenetic reactions which take place during burial of deep sea sediments (see Gieskes, 1981). Such methods are potentially much more powerful in studying diagenesis than examining sediments using the scanning electron microscope (SEM), X-ray diffraction (XRD), or even by chemical means, as small amounts of reaction between the sediments and pore waters produce large changes in the accompanying interstitial fluids.

As a first approximation, deep-sea carbonates can be separated into two categories based upon the dominant mineralogies of the original sediments. The majority consist of relatively stable low-Mg calcite coccoliths and foraminifers. Diagenetic processes in these sediments have been studied by numerous workers (Schlanger and Douglas, 1974; Lawrence et al., 1975; Matter et al., 1975; Sayles and Manheim, 1975; Gieskes, 1981; Baker et al., 1982; Elderfield et al., 1982; Stout, 1985a,b and others).

The second type of sediment generally found near shallowwater carbonate platforms consists of a mixture of metastable minerals, high-Mg calcite (HMC), and aragonite as well as low-Mg calcite (LMC). This type of sediment has been termed periplatform sediment (Schlager and James, 1978). The metastable minerals originate on carbonate platforms and become admixed with normal pelagic components during deposition. In contrast to the pure pelagic LMC deposits, pore waters from this type of assemblage have been studied in only one previous study (Swart and Guzikowski, 1988). That investigation involved material re-

land.

covered during Leg 101 off Little Bahama Bank and in Exuma Sound, in the Bahamas.

This investigation will examine diagenetic reactions using Ca^{2+} , Mg^{2+} , and Sr^{2+} gradients in both these types of deposits. In particular, the close spacing of the Leg 115 "carbonate" transect sites (Sites 707 through 711) in a range of water depths allows an examination of the influence of initial water depth on the recrystallization of calcite.

ANALYTICAL METHODS

Pore waters were squeezed from 10-cm-long, whole-round samples on board ship immediately after coring. The water depths and depths of penetration are shown in Table 1. Site locations are shown in Figure 1. Methods and equipment for porewater extraction have been described previously by Manheim and Sayles (1974). At Site 709, samples were also retrieved using the Barnes *in-situ* water sampler.

The pore waters were then titrated for Cl^- , Ca^{2+} , and Mg^{2+} by methods similar to those described by Gieskes (1973, 1974). Dissolved SO_4^{2-} was determined using an ion chromatograph. Alkalinity was determined using a potentiometric titration method as developed by Dyrssen and Sillen (1967) and others (See Grasshof, 1976). Samples were titrated with 0.1 HCl made up in a 0.7 M NaCl solution. The initial pH was measured using electrodes calibrated with TRIS-TRISHCl buffers made up using a 0.7 M NaCl solution and reported relative to the free hydrogen scale (Hansson, 1973).

Pore-water Sr^{2+} concentrations were determined by atomic absorption spectrophotometry. These values have been used to correct the initial Ca^{2+} and Mg^{2+} concentrations reported in Backman, Duncan et al. (1988) according to the procedure of Gieskes and Peretsman (1986). For this reason values reported in this paper are slightly lower than in the original report. For the solid samples, coarse and fine fraction were separated using wet sieving through a 63 μ m sieve using buffered sodium borate solution (pH = 8). Samples were then dried at 40°C, dissolved us-

¹ Duncan, R. A., Backman, J., Peterson, L. C., et al., 1990. Proc. ODP, Sci. Results, 115: College Station, TX (Ocean Drilling Program).

² Stable Isotope Laboratory, Marine Geology and Geophysics, Rosenstiel School of Marine and Atmospheric Science, University of Miami, Miami, FL 33149, U.S.A. ³ Present address: Geologisches Institut, Balterstrasse 1, CH-3012 Bern, Switzer-

Table 1. Water depth and
depth of penetration of
sites investigated during
Leg 115.

Hole	Water depth (m)	Penetration (mbsf)
705A	2318	27.5
706A	2504.3	47.5
706B	2507.8	36.7
706C	2519.0	44.3
707A	1552.3	212.3
707B	1552.3	124.1
707C	1552.3	438.7
708A	4096.5	234.7
709A	3038.2	203.1
709B	3038.2	254.8
709C	3038.2	353.7
710A	3812.0	209.7
710B	3810.5	83.4
711A	4428.2	249.6
711B	4429.7	98.3
712A	2904.3	115.3
713A	2915.3	155.1
714A	2038.3	233.0
714B	2038.3	122.6
715A	2266.3	211.3
716A	544.3	257.1



Figure 1. Location map for ODP sites drilled during Leg 115.

ing 10% HNO₃ and diluted to the required concentration using 1500 μ M La, 1% HNO₃ solution. Strontium concentrations were determined with an atomic absorption spectrophotometer.

RESULTS

Pore Waters

With the exception of the Sr^{2+} data, all other pore-water parameters have been reported in Backman, Duncan, et al. (1988). As noted in the "Analytical Methods" in this chapter, the concentration of Ca^{2+} and Mg^{2+} have been adjusted for the concentration of Sr^{2+} and are therefore different from those originally reported.

Calcium and Magnesium

The concentration of Ca^{2+} in interstitial waters generally increased downcore, whereas Mg^{2+} decreased. The magnitude of these changes varied between 0.006 and .059 mM/m for Ca^{2+} , and between 0.009 and 0.089 mM/m for Mg^{2+} (see Table 1). Samples from Site 709 (WS-12, WS-15 and WS-20), retrieved using the Barnes downhole water sampler, contained excess Ca^{2+} when compared to samples squeezed from comparable depths at the same site. Concentrations of Mg^{2+} from the *in-situ* sampler were not significantly different from those squeezed from the sediment (Table 1).

Pore-water Ca²⁺/Mg²⁺ Gradients

With the exception of Sites 705, 714, and 715, all sites show statistically significant negative relationships between Ca^{2+} and Mg^{2+} (Fig. 2). The slope of this relationship varies between -0.5 and -1.5.

Strontium

Concentrations of Sr^{2+} increase downhole, by modest amounts compared to other previously studied Deep Sea Drilling Project (DSDP) and Ocean Drilling Project (ODP) sites (Gieskes, 1981) (Fig. 3). Site 716 exhibits the largest increase in Sr^{2+} to 512.3 μ M at a depth of 195.75 mbsf. This site also exhibits saturation with respect to celestite by 137.8 mbsf (Fig. 4).

Si Concentrations in Pore Waters

Concentrations of Si in pore waters generally exhibit increase with depth downcore (Table 2). However, there are subtle differences between the various sites. In Site 707, concentrations of Si exhibit a gradual rise, reaching a concentration of 735 μ M at a depth of 79.95 mbsf. The concentrations exhibit a slight decrease between 10 and 20 Ma, although the precise extent of the decrease is blurred as a result of sample collection biases. Maximum Si concentrations of approximately 1000 μ M are obtained at 90 mbsf in sediments of 6.7 Ma.

A minimum concentration of 562 μ M is seen at 177.2 mbsf in sediments of the late early Miocene. In older sediments, concentration levels of Si increase to concentrations similar to those observed in the top of the hole. Site 710 exhibits similar patterns of Si distribution to previous sites. The initially squeezed core exhibited a concentration of 631 μ M, rising to 910 μ M at 53.85 mbsf. Below this depth, the concentration of Si decreases to 620 μ M at 112.7 mbsf in sediments of the middle early Miocene. Concentrations of Si at the bottom of the hole are similar to other holes. Site 711 was the deepest drilled during Leg 115, and exhibited the highest concentrations in the initially squeezed core (711 μ M at 5.95 mbsf). Below this depth, concentrations decreased to 370 μ M at a depth of 53.75 mbsf in sediments of 17.5 Ma.

In summary, all sites exhibit a rise in the concentration of Si in the interstitial pore waters downcore to between concentrations of 600 and 800 μ M in sediments of the Pliocene to late



Figure 2. Calcium and magnesium gradients for Leg 115 sites; for clarity data points are only shown for Site 707. All other data are given in Table 2.



Figure 3. Concentrations of Sr^{2+} in interstitial pore fluids from Sites 707, 708, 709, 710, 711, and 716; data for other sites are given in Table 2.

Miocene. This is followed by a decrease in the middle Miocene and a subsequent rise in sediments of the late Eocene. The decrease in Si concentrations in the interstitial pore-water Si concentrations occurs in an interval depleted of siliceous microfossils



Figure 4. Saturation of pore fluids with respect to the mineral celestite at Site 716. Data for activity coefficient and solubility products are taken from Baker and Bloomer (1988). The SI is defined as SI = log (IAP/ K_{Sp} celestite); IAP = ion activity product; K_{Sp} celestite = solubility product for celestite.

(Mikkelsen, this volume) (Fig. 5), but abundant in the diagenetic mineral clinoptilolite (Hempel and Bohrmann, this volume).

Alkalinity, pH, Sulfate, Phosphate, and Ammonia

Concentrations of organic material at all Leg 115 sites were extremely low, usually below detection limits (0.02%; Backman, Duncan, et al., 1988). In addition, no detectable concentrations of hydrocarbon gases were measured at any of the sites with the Table 2. Interstitial pore-water data for Sites 707 through 716. All data have been previously reported by Backman, Duncan, et al. (1988) with the exception of the Sr^{2+} concentrations and % recrystallization. The Ca^{2+} and Mg^{2+} data have been corrected to account for changes in Sr^{2+} .

Core, sample, interval (cm)	Age (Ma)	Depth (mbsf)	Ca ²⁺ (mM)	Mg ²⁺ (mM)	Sr ²⁺ (μM)	C1- (mM)	Alk. (mM)	pH	s	Si (µM)	NH ₄ ⁺ (μM)	SO ₄ ²⁻ (mM)	PO ₄ ^{3 -} (μM)	Cumulative % recrystallization
Surface 1H-3, 145-150 2H-, 145-150	0.0 0.9 2.5	0.00 4.45 12.95	10.40 11.27 11.44	54.15 52.02 51.62		571.88 564.95 565.94	2.22 3.01 3.03	8.4 7.9 7.7	34.6 35.0 35.4	18 272 265	8.30 38.00 38.00	28.86 27.71 29.35	=	NC NC NC
Site 706							01011							
Surface	0.0	0.00	10.34	54.15	86.1	571.88	2.32	8.4	34.2	18	8.30	28.86	_	
2H-5, 145-150	0.3	9.93	10.90	50.74	86.1	569.90	2.38	7.7	35.0	576	28.00	29.51	-	0.00
3H-4, 145-150	0.5	18.15	12.17	48.20	86.1	576.84	2.44	7.7	35.0	551	24.00	26.72	-	0.00
4H-3, 145-150	0.8	26.35	13.15	46.42	90.2	577.83	2.16	7.8	35.0	496	12.00	28.86	-	0.09
5H-4, 145-150	1.1	37.45	13.92	48.58	90.2	571.88	2.10	7.7	34.8	425	179.00	23.60	-	0.09
6H-2, 145-150 7H-1, 0-1	1.3	44.05	10.35	51.53	88.1	572.88	2.48	8.3	35.2 34.0	464	0.00	29.35	-	0.14
Site 707														
Surface	0.0	0.00	10.18	51.77	88.1	542.56	2.43	8.4	34.2	_	0.00	28.06	_	
1H-3, 145-150	0.9	4.45	10.94	52.04	92.2	554.16	2.90	7.6	35.5	266	0.00	28.92		0.58
2H-3, 145-150	1.7	11.15	11.36	51.92	104.5	557.07	2.79	7.6	35.5	329	0.00	29.91		1.58
3H-2, 145-150	1.7	19.15	11.61	52.31	104.5	563.84	2.86	7.6	35.6	346	0.00	29.75		1.58
4H-3, 145-150	3.8	20.25	11.84	52.71	104.5	560.02	2.92	7.6	35.5	441	0.00	29.75		1.58
6H-5, 145-150	4.4	52.55	13.05	49 73	145 5	556 10	3.08	7.5	35.0	665	0.00	28.56		2.62
9H-4, 145-150	6.6	79.95	14.15	48.53	168.0	553.20	3.21	7.6	35.2	735	0.00	28.56	_	3.57
12H-4, 145-150	9.0	108.75	14.34	48.26	163.9	555.13	3.29	7.5	35.2	720	0.00	30.93		3.81
15H-3, 145-150	18.8	136.05	14.91	47.54	157.8	556.10	3.27	7.6	35.2	677	0.00	28.90	-	5.31
20X-3, 145-150	34.5	178.15	16.35	45.40	147.5	556.10	3.21	7.3	35.2	946	0.00	28.49	-	7.90
23X-3, 145-150	36.0	200.95	17.92	44.47	143.4	556.10	3.41	7.4	34.8	979	0.00	28.07	-	8.09
5R-3, 145-150	37.2	207.15	17.45	44.70	143.4	554 16	3.23	7.5	35.0	945	0.00	28.00		8.09
9R-2, 145-150	40.0	254.35	18.49	44.30	122.9	548.36	3.19	7.4	34.0	1027	0.00	28.90	_	9.84
15R-1, 145-150	55.0	310.45	17.63	44.53	118.8	550.30	2.62	7.6	34.0	585	0.00	28.92		10.58
Site 708														
Surface	0.0	0.00	10.25	53.09	88.0	554.05	2.58	8.4	34.4	6	2.56	28.74		
1H-4, 145-150	0.5	5.95	10.37	54.71	149.6	567.90	3.93	7.7	35.0	671	35.00	28.93	3.34	2.04
2H-4, 145-150	0.7	14.95	11.18	53.23	184.4	587.69	3.81	7.6	35.4	805	36.00	27.84	2.81	2.34
3H-4, 145-150	1.1	24.55	11.59	51.80	243.8	583.73	4.10	7.6	35.2	907	53.00	28.43	2.28	4.30
4H-4, 145-150	1.7	34.05	12.45	52.27	297.1	586.70	4.95	7.6	35.2	801	33.00	27.09	1.89	6.95
6H-3 145-150	2.0	43.55	12.24	51.75	295.0	586.70	4.03	7.5	35.0	902	34.00	26.72	1.89	8.09
9X-1, 145-150	5.0	77.45	13.30	51.27	295.1	592.64	4.79	7.4	35.2	860	39.00	26.00	1.75	8.62
12X-4, 120-125	7.5	107.10	12.90	50.29	284.8	588.68	4.45	7.4	35.0	1000	45.00	25.45	2.68	9.31
15X-4, 120-125	15.0	136.00	13.04	49.42	284.8	580.77	4.71	7.3	34.8	847	43.00	24.18	2.28	9.31
18X-3, 120-125	21.6	162.00	13.49	49.29	293.0	565.93	4.60	7.4	34.8	860	31.00	24.91	2.68	10.95
22X-4, 145-150 24X-4, 145-150	28.5	203.45 222.75	13.58	48.98 48.37	262.3 264.3	566.92 581.76	4.56	7.4	34.5	901 1037	23.00	23.64 28.36	2.55	14.98
Site 709														
Surface	0.0	0.00	10.48	54 89	88.0	575.63	2.52	8.4	35.0	0	0.00	28.98	_	
1H-4, 145-150	0.5	5.95	10.69	54.17	114.8	554.38	3.42	7.7	34.5	610	0.00	21.12		1.46
2H-4, 145-150	1.1	16.05	11.52	52.91	161.9	568.24	3.66	7.4	35.0	710	4.28	25.12		3.28
3H-4, 145-150	2.2	25.65	11.56	52.67	196.7	549.76	3.82	7.3	34.9	753	12.15	25.82		5.88
4H-3, 145-150	3.5	33.85	11.67	52.38	227.5	570.09	3.78	7.5	35.2	683	5.82	27.22		9.05
0H-5, 145-150 7H-5, 145-150	4.5	54.05	11.71	52.31	202.3	546.06	3.90	7.5	35.1	784	32 00	20.94		10.59
10H-5, 120-125	6.7	90.00	12.10	51.80	317.6	546.99	4.25	7.5	35.2	822	11.20	27.92		12.36
13H-5, 120-125	11.0	123.40	12.32	51.73	321.7	549.76	4.31	7.4	35.2	574	18.90	25.20	1000	12.70
16H-5, 120-125	16.0	152.40	12.56	50.79	299.2	546.06	4.42	7.5	35.0	402	18.13	26.94		15.23
19H-2, 140-145	19.0	177.20	12.85	50.55	336.1	542.37	4.53	7.5	34.8	562	11.97	29.13		18.13
22X-5, 120-125	26.0	204.00	12.29	50.96	313.5	545.14	4.09	7.6	34.4	687	22.70	29.44		22.96
25X-4, 145-150	29.0	250.65	12.81	50.20	305.3	540.52	4.29	7.5	34.4	835	37.00	28.50	1000	22.55
31X-4, 145-150	38.5	291.75	13.14	49 79	305.3	550.68	4.59	7.6	34.4	942	29.70	27.15	_	32.26
34X-4, 145-150	41.0	320.75	13.29	49.46	340.2	547.91	4.50	7.5	34.8	849	38.10	27.36		34.21
37X-4, 145-150	47.0	349.85	12.98	49.64	291.0	546.99	4.22	7.5	34.9	759	15.80	26.59		40.81
WS12-1		102.20	12.96	51.99	317.0	549.76	4.90	7.8	35.0	680	18.13	28.36		
WS12-2		102.20	12.99	51.80	317.0	549.76	5.02	7.8	35.0	670	26.59	27.28	_	
WS15-1 WS20-1		131.10 179.50	13.17 13.39	51.21 51.06	321.0 336.0	545.14 546.99	4.90	7.7	35.5 34.9	335 596	22.00 45.80	26.61 26.21		
Site 710		1910/1917		1111111111				0.550	2.00	್ರಾಕ್ಟೇಶನ		10001000		
Surface	0.0	0.00	10.39	53 53	86.1	554 33	2.62	8.4	34.8	1	0.00	29.54		
1H-4, 145-150	0.6	5.95	11.12	52.45	110.7	540.34	3.62	7.6	34.5	631	7.36	28.42	_	2.34
2H-4, 145-150	1.5	15.45	11.68	51.78	157.8	537.54	3.84	7.4	34.5	703	8.90	28.26		6.56

Table 2 (continued).

Core, sample,	Age	Depth	Ca ²⁺	Mg ²⁺	Sr ²⁺	Cl-	Alk.		0.75	Si	NH ⁺	so42-	PO4 ³⁻	Cumulative %
interval (cm)	(Ma)	(mbsf)	(mM)	(mM)	(µM)	(mM)	(mM)	pH	S	(μM)	(µM)	(mM)	(µM)	recrystallization
Site 710 (Cont.)														
3H-2, 145-150	2.5	22.15	12.06	50.66	184.4	559.93	3.84	7.4	35.0	807	14.28	28.10		10.32
4H-4, 145-150 6H-4, 145-150	4.4	34.75	12.58	50.60	207.0	557.13	3.94	7.4	35.2	791	15.05	28.10		13.53
9H-5, 145-150	10.2	83.80	13.35	50.30	219.5	554 33	3.99	7.5	35.2	885	35.85	26.03		16.41
12H-5, 120-125	17.3	112.70	14.81	48.02	231.5	580.46	4.15	7.5	35.2	620	32.75	24.28		16.88
15X-3, 115-125	24.4	136.55	15.19	48.04	250.0	534.74	3.68	7.4	35.5	737	7.36	25.24	-	22.07
18X-3, 115-125	28.4	165.55	15.58	48.21	254.1	566.47	3.74	7.5	35.6	857	0.43	24.44		22.60
23X-3, 115-125	34.3	204.25	16.13	47.73	266.4	534.74	3.79	7.5	35.5	976	4.28	23.80		24.37
Site 711														
Surface	0.0	0.00	10.54	54.92	88.0	567.53	2.51	8.5	35.5	4	0.00	29.70		
1H-4, 145–150	0.7	5.95	10.67	51.63	90.2	559.95	3.26	7.8	34.2	711	0.00	27.94	-	0.27
2H-3, 145-150	2.4	12.55	10.86	52.08	94.3	553.32	3.36	7.7	35.2	668	0.00	28.58	100	1.40
AH-5 145-150	7.0	23.03	11 12	51.24	90.2	565 63	3.45	7.7	35.0	688	0.00	28.74		2.55
5H-5, 145-150	11.0	44 35	11.12	51.02	96.3	568 47	4.02	77	35.0	472	0.00	27.70	_	4.29
6H-5, 115-120	17.5	53.75	11.13	51.16	98.4	574.16	3.85	7.6	34.6	370	0.00	27.06		5.81
9H-5, 115-120	25.7	82.75	11.44	50.92	106.6	559.00	3.69	7.6	35.0	520	0.00	26.98		8.30
12X-2, 115-120	29.5	107.15	11.50	50.94	110.7	579.84	3.76	7.5	34.8	661	0.00	26.74	-	8.98
15X-5, 115-120	35.0	140.75	12.19	51.07	106.6	568.47	3.79	7.5	35.0	741	0.00	27.38		9.70
18X-3, 140-145	37.5	167.10	12.48	50.29	110.7	542.89	4.08	7.6	35.2	797	0.00	26.98		10.12
21X-4, 140-145 24X-3, 140-145	45.0 48.0	197.60 225.10	12.60 12.86	50.32 50.37	125.0 127.0	552.37 552.37	4.12	7.6 7.7	35.0 35.2	835 833	0.00	27.38 26.65	_	13.90 14.14
Site 712														
Surface	0.0	0.00		_	_	561.84	2.51	8.5	35.5	_	0.0	29.15		
1R-5, 145-150	0.8	7.45	10.51	53.16	88.1	548.58	2.90	7.8	35.0	449	77.0	28.55		
2R-4, 145-150	1.7	15.48	10.57	52.85	90.2	551.42	3.03	7.7	35.2	594	190.0	28.12		0.13
3R-3, 140-150	2.5	23.4	10.51	53.08	94.3	567.53	3.05	7.7	35.2	655	69.0	28.11		0.38
4R-2, 140–150 6R-2, 140–150	8.2	31.5	10.76	54.28 52.80	98.4 106.6	572.26 557.11	2.98	7.8 7.8	35.8	605 615	71.0 44.0	28.60 28.31	_	3.54
Site 713														
2R-4, 145-150	1.4	7.55	11.10	53.53	106.6	571.32	3.07	7.8	35.0	497	40.0	28.51		
3R-4, 145-150	3.1	17.15	11.47	53.24	112.7	565.63	3.00	7.7	35.5	577	72.0	28.17		0.69
4R-2, 140-150	4.9	26.75	11.46	52.11	114.7	557.11	2.91	7.7	35.0	756	65.0	27.44	1000	0.93
5R-2, 145-150	41.0	33.45	11.80	51.12	118.8	560.89	2.77	7.5	35.0	775	50.0	27.72	100	22.59
6R-2, 145-150	41.5	43.05	12.12	51.21	118.8	570.37	2.63	7.5	35.0	743	43.0	28.24		22.59
12P-1 147-150	45.0	70.55	14.02	40.14	122.9	559.05	1.79	2.1	35.2	534	40.0	27.80		23.31
17R-3, 150-155	48.0	150.22	20.36	39.32	120.9	571.32	1.10	8.1	34.8	279	41.0	26.19	_	23.37
Site 714														
Surface	0.0	0.00	10.59	55.21	90.2	577.00	2.47	8.5	35.4	_	0.0	29.48	1.85	10111114-0
1H-1, 145-150	0.0	1.45	10.58	51.22	92.2	540.05	3.30	7.6	35.2	575	46.5	27.46	6.99	0.04
2H-4, 145-150	0.2	8.75	10.68	52.14	127.0	578.90	3.88	7.5	35.2	621	112.0	26.51	6.22	0.73
3H-4, 143-150 4H-5, 145-150	0.5	18.35	10.04	52.23	131.0	591 74	4.32	7.6	34.8	746	135.0	20.88	4.10	3.28
5H-5, 145-150	9.0	39.15	10.75	52.17	159.8	576.05	4.08	7.6	35.2	568	125.0	27.17	3.78	3.98
6H-4, 145-150	9.5	47.35	10.90	51.90	151.6	565.63	4.23	7.6	35.4	704	114.0	26.51	2.36	4.35
9H-2, 145-150	11.0	73.15	10.87	50.71	163.9	572.26	3.99	7.7	35.0	769	111.0	26.30	2.24	4.77
12H-4, 120-125	14.5	104.80	10.95	49.99	172.1	559.00	4.19	7.6	35.2	783	129.0	26.29	2.49	5.37
15X-3, 120-125	16.0	131.00	11.20	50.05	192.6	552.37	4.00	7.5	35.2	797	112.0	26.64	2.11	6.16
18X-4, 120-125	17.3	161.40	11.01	50.64	176.2	558.05	3.78	7.5	34.8	808	94.0	26.42	2.24	6.60
22X-4, 120-125 25X-1, 145-150	22.0	200.10 224.75	11.38	52.55	161.9	560.89 570.37	3.63	7.6 7.8	35.2	870	69.0 42.0	26.67	1.98	11.58
Site 715														
Surface	0.0	0.00	_	_		577.00	2.47	8.5	35.4	-	3.7	27.80	3.76	
1R-3, 145-150	0.1	4.45	10.28	51.84	86.1	552.48	3.38	7.8	34.4	671	74.0	27.25	13.55	0.05
2R-4, 145-150	0.2	14.05	10.54	52.55	94.3	556.21	3.97	7.7	34.5	662	163.0	26.92	12.07	0.10
3R-4, 145-150	0.3	23.75	10.54	52.95	100.4	545.96	4.20	7.5	34.2	727	174.0	26.37	10.04	0.17
4K-4, 145-150	0.4	33.45	10.63	53.42	110.7	540.37	4.38	7.5	35.0	702	165.0	26.70	10.05	0.28
5R-4, 145-150 6P.4 145 150	12.0	43.05	10.50	52.01	110.7	562.73	4.40	7.3	34.8	783	188.0	26.70	12.63	0.28
9R-4, 145-150	15.0	81.65	10.67	53.28	102.5	564.59	3.45	7.8	35.0	479	108.0	27.48	7.27	0.98
Site 716														
Surface	0.0	0.00	10.43	54.37	90.2	535.31	2.53	8.5	34.5		81.4	27.17	2.47	
1H-3, 145-150	0.3	4.45	10.71	53.11	102.5	538.16	2.90	7.9	34.2	88	75.7	28.58	3.21	0.28
211-4, 145-150	0.5	12.85	10.77	53.62	106.6	550 47	2.95	1.5	35.0	75	93.0	25.73	2.4/	0.32
511-4, 120-125	0.7	22.20	10.70	54.00	110.0	550.47	5.00	1.0	54.0	01	108.0	20.1/	3.39	0.50

Table 2 (continued).

Core, sample, interval (cm)	Age (Ma)	Depth (mbsf)	Ca ²⁺ (mM)	Mg ²⁺ (mM)	Sr ²⁺ (μM)	Cl ⁻ (mM)	Alk. (mM)	pH	s	Si (μM)	NH ₄ ⁺ (μM)	SO4 ² - (mM)	PO ₄ ^{3 -} (μM)	Cumulative % recrystallization
Site 716 (Cont.)														
4H-4, 145-150	0.8	32.05	10.88	54.05	135.2	534.37	3.15	8.0	35.0	96	109.0	28.61	3.39	0.42
5H-4, 145-150	1.0	41.75	10.88	54.46	135.2	531.52	3.00	7.7	35.2	86	110.0	29.00	3.39	0.42
6H-4, 120-125	1.4	51.20	11.19	53.54	182.4	546.68	3.19	7.7	35.5	90	102.0	28.74	5.05	1.02
9H-4, 120-125	2.4	80.00	12.90	53.14	383.2	564.68	4.69	7.6	35.5	0	252.0	28.54	5.79	3.79
12H-4, 120-125	3.6	108.90	14.51	51.14	471.3	541.95	5.11	7.6	35.2	448	275.0	27.86	6.35	7.82
15H-4, 120-125	4.2	137.80	16.05	47.55	487.7	533.42	5.74	7.5	35.2	362	286.0	27.87	8.01	8.94
18H-4, 120-125	4.6	166.65	16.72	46.46	497.9	536.26	5.49	7.4	34.2	534	451.0	26.22	9.67	9.38
21H-4, 115-125	5.4	195.75	17.26	46.65	512.3	536.26	5.92	7.3	35.2	686	334.0	26.99	14.3	11.14
24H-4, 140-150	6.1	225.10	_	$\sim \sim 10^{-1}$	_	531.52	5.80	7.3	34.8	1004	358.0	26.27	17.25	12.49
27H-4, 140-150	6.5	254.00	17.68	46.02	473.3	540.05	6.05	7.3	34.8	774	388.0	26.41	13.55	12.93

Note: Dash (-) indicates that no analyses were performed.



Figure 5. Pore-water Si profiles and distribution of diatoms (D, solid bars), and radiolarians (R, stippled bars) in Sites 707 through 711 (data for Si distribution is from Mikkelsen, this volume). The Si data for Site 707 have been compiled from Holes 707A and 707C, and the data for Site 709, from Holes 709B and 709C. Note the decrease in the pore-water Si concentration between 15 and 20 Ma.

exception of Site 716, where very small increases were noted. As a consequence of the low concentrations of organic matter, changes in the concentration of alkalinity, pH, phosphate, and ammonia were extremely low at all sites. Alkalinity generally increased downcore.

The highest amounts of sulfate reduction occurred at Sites 709 and 716 and are associated with small increases in phosphate, ammonia, and alkalinity. Site 716 also exhibited the highest concentration of organic material and showed evidences of methane (Backman, Duncan, et al., 1988). Changes in the concentration of sulfate associated with increases in ammonia were observed at Sites 708, 709, and 710. Samples retrieved using the Barnes downhole water sampler at Site 709 contained excess alkalinity compared with waters squeezed from sediments from comparable depth intervals.

Solids

The X-ray mineralogy of all samples showed them to consist largely of low- Mg^{2+} calcite. The exception to this was at Site 708, where small quantities of aragonite were detected and at Site 716, which is composed of periplatform sediments (Backman, Duncan, et al., 1988). At Site 716, the concentrations of aragonite decrease from approximately 30% to less than 5% by 50 mbsf (Malone et al., this volume; Droxler et al., this volume).

Strontium

The Sr concentrations of the <63- and >63- μ m fractions, together with their percentages, are shown in Figure 6 and Table 2. There do not appear to be any systematic differences in the Sr



Figure 6. Concentration of Sr^{2+} in fine and coarse fraction, as well as predicted equilibrium concentration using a D_{Sr} of 0.037 (Baker et al., 1982). (A) Site 707, (B) Site 708, (C) Site 709, (D) Site 710, (E) Site 711, and (F) Site 716. In the profile at Site 710, two data points have been omitted from the trend. These correspond to samples with excess amounts of insoluble material and therefore may have given incorrect Sr values.

concentration between the coarse and fine fractions. In several of the "carbonate" sites, high concentrations of Sr suggest the presence of small amounts of aragonite (Site 708 and 711). In all sites other than Site 716, Sr concentrations do not exhibit any systematic trend with increasing sub-bottom depth. There is, however, a large amount of variability in the strontium content of all the solid samples, but it does not show any consistent trend in concentration downhole. The only exception occurs in Hole 709C, in which there is a slight decrease at the bottom of

the hole, and in Site 716, where the initial sediment consists of mixtures of bank-derived, Sr-rich aragonite and high-Mg calcite, as well as low-Mg calcite.

Finally, we note that values for the Sr concentration of the fine fraction measured in the upper portion of Site 709 sediments were significantly lower than data reported for the same sediments by Baker et al. (this volume). In the lower portion of Site 709, data concurs between this study and that of Baker et al. (this volume). Our data for Site 715 also agrees with that of



Figure 6 (continued).

Malone et al. (this volume), the samples of which were prepared similarly to those of Baker et al., and measured in the same laboratory. We have no explanation for this discrepancy at the present time and can only speculate that it represents some systematic difference in preparation method carried out by the respective laboratories.

DISCUSSION

Rates of Recrystallization

Interstitial Strontium Concentrations

All sites examined from Leg 115 showed modest increases in the dissolved Sr^{2+} concentration of the interstitial fluid downcore (Fig. 3). Such increases have been shown at other DSDP and ODP sites to be a result of the recrystallization of biogenic calcite to inorganic calcite and aragonite, with the consequent release of Sr^{2+} to the pore fluids (Baker et al., 1982). At sites where the Sr^{2+} and SO_4^{2-} concentrations are below celestite saturation, the diffusive flux of Sr^{2+} from the sediments can be calculated and an estimate of recrystallization obtained (Baker, 1986; Stout, 1985a, 1985b; Swart and Guzikowski, 1988). Such a technique would only be valid in the absence of advective flow through the sediments (see later discussion). Since all Leg 115 sites, apart from Site 716 (Fig. 4), fulfill this condition, we have estimated recrystallization with the method outlined by Baker (1986) (Table 2 and Fig. 7).

In this method, the Sr flux out or into the sediments, given by Equation 1, is summed over the time interval represented by two successive pore-water samples. If the Sr content decreases, we have assumed there is some sink for Sr in the sediments, and this flux is therefore counted as a loss of Sr^{2+} .

$$Flux = -D_b \partial c / \partial x, \tag{1}$$

where $D_b = \text{diffusion coefficient } (4 \times 10^{-6} \text{ cm}^2/\text{s}), \, \partial c = \text{concentration gradient, and } \partial x = \text{depth interval in question.}$

If it is assumed that the average Sr/Ca molar ratio of the sediment is 2×10^{-3} , a typical value for pelagic calcite (Baker, 1986), then the total amount of Sr in the sediment in each interval can be calculated using the percent insoluble data shown in Table 3. If any carbonate is initially present which contains a higher Sr/Ca ratio, for example, aragonite in Site 716, the calculated rate will be lower; therefore, for this site we have used a Sr/Ca ratio of 4 \times 10⁻³. This reflects a mixture of aragonite with a Sr/Ca ratio of 9 \times 10⁻³ and LMC. The total amount of Sr lost is then compared with the amount of Sr available in the sediment. The percentage of the amount of Sr lost compared to Sr available yields the amount of recrystallization that has occurred over the time interval represented by the sampling interval. Assuming that the present pore-water profile has remained approximately the same over time, the total amount of recrystallization of a particular interval can be obtained by summing all the intervals over which pore-water data are available. These data are shown in Table 2 and Figure 7.

This approach suggests that the maximum rate of recrystallization occurs in the upper 50 m of the core, the rate decreasing with increasing depth sub-bottom. Of the "carbonate" sites, low rates of recrystallization are shown at Sites 707 and 711, the shallowest and deepest sites (1541.4 m and 4428.2 m respectively). At Site 707, the maximum amount of recrystallization is approximately 11% in sediments of 55 Ma. The similar rates of recrystallization at Site 711 compared to the shallowest site, Site 707, result from the fact that Site 711 is situated below the present-day CCD and, therefore, substantial dissolution of the most reactive calcium carbonate has occurred on the sea floor before burial. The highest initially calculated rates of recrystallization occurs in sites at intermediate depths, such as Sites 709

Recrystallization %





and 710. Of these, Site 710 exhibits the highest initial rates of recrystallization, reaching 27% by 204.25 mbsf in sediments of 34.3 Ma. Site 709 has the highest overall percentage of recrystallization, 43% by a depth of 349.85 mbsf. Progressively lower rates of recrystallization occur in the deeper sites (Sites 708 and 711), probably a consequence of the greater amounts of dissolution occurring at the seafloor as in the case of Site 711.

Surprisingly, comparable rates of recrystallization were measured at Site 716, the site that contains periplatform sediments and large concentrations of metastable aragonite. This is similar to results from Leg 101, which were obtained using the Sr flux method for estimating recrystallization (Swart and Guzikowski, 1988). The precise reasons for the low calculated rates of recrystallization are uncertain, as the decrease in the concentration of aragonite between the sediment surface and 50 mbsf (>30% to <5%), noted by Malone et al. (this volume), has been interpreted as being the result of recrystallization. One possible explanation would be that the method used in this paper to calculate the Sr gradient in the zone of celestite saturation underestimates the amount of Sr lost as celestite. The percent recrystallization (%R) shown in Figure 2 and Table 2 for the depths that are above celestite saturation have been extrapolated from the strontium gradient between 51.2 and 80 mbsf (Fig. 4). It is also possible that either the decrease in aragonite noted by Malone et al. (this volume) results from a decrease in the input of aragonite from the bank and is therefore not diagenetic, or that significant amounts of aragonite dissolution are occurring on the seafloor before burial. If either of these last scenarios were applicable, the initial Sr concentration used in the calculations shown in Figure 7 would need to be lowered for Site 716. Consequently, higher rates of recrystallization would be calculated.

Oxidation of Organic Material

A significant factor in determining rates of recrystallization of carbonate sediments is the amount of organic material that is buried with the sediment. Organic material, if present, normally becomes oxidized by an electron acceptor such as oxygen or sulfate, liberating CO2 thereby promoting recrystallization of the biogenic carbonate. Although all sites drilled during Leg 115 (with the exception of Site 716) contained extremely low concentrations of organic material (Backman, Duncan, et al., 1988), it is possible that small differences in the quantities of organic material between the "carbonate" sites could have been responsible for the observed differences in recrystallization between sites. For example, Site 707, which showed no decreases in the concentration of interstitial sulfate, accordingly had the lowest rates of recrystallization. Sites 708, 709, and 710, however, did exhibit decreases in sulfate, the lowest value (21.12 mM) occurring at Site 709 at 5.95 mbsf. These sites accordingly have higher calculated rates of recrystallization.

The method of estimating recrystallization from the Sr^{2+} flux provides only a minimum estimate of recrystallization, since it makes no assumption for the incorporation of Sr^{2+} into calcite. In order to constrain the possible effect of precipitation on the concentration of Sr^{2+} , it is possible to estimate the amount of net precipitation from the increase in alkalinity. Generally, changes in alkalinity are related to either the oxidation of organic material by sulfate reduction, through a reaction similar to the following equation:

$$53SO_4^{2-} + C_{106}H_{263}O_{110}N_{16}P = 106HCO_3^- + 16NH_3 + 53H_2S + H_3PO_4$$
(2)

or through the dissolution of carbonate minerals such as calcite and aragonite. As noted in the "Results" in this chapter, increases in alkalinity were observed in most of the sites investi-

Core, sample, interval (cm)	Depth (mbsf)	Sr	Sr concentration solid (ppm)			Percentage of sediment				
		>62	< 62	Equil.	>62	< 62	Insoluble			
Received of the second second	05.54			Equil		100				
115-705A-1H-3, 145-150	4.45	1168	861	-	37.70	59.64	0.00			
115-705A-2H-3, 145–150	12.95	1070	807	-	30.50	66.32	0.00			
115-706A-2H-5, 145-150	9.95	1123	743	256	2.50	94.65	23.02			
115-706A-3H-4, 145-150	18.15	1121	664	240	1.58	96.45	16.34			
115-706A-4H-3, 145-150	26.35	1087	716	223	2.41	95.42	16.80			
115-706A-6H-2 145-150	44 05	1119	555	203	0.61	*	46.32			
		1016	0(0	074	22.05	64.60	0.00			
115-707A-1H-5, 145-150	4.45	968	1075	274	32.05	04.08	22.00			
115-707A-3H-3, 145-150	19.15	965	935	292	18.89	75.53	18.00			
115-707A-4H-3, 145-150	30.25	948	947	286	28.16	69.90	15.54			
115-707A-5H-4, 145-150	41.45	965	1113	332	20.89	75.32	20.24			
115-707A-6H-5, 145-150	52.55	940	926	361	16.39	80.51	16.34			
115-707A-9H-4, 145-150	79.95	882	820	384	10.52	86.78	14.00			
115-/0/A-12H-4, 145-150	108.75	928	033	369	34.29	91 72	16.40			
115-707A-20X-2, 145-150	178.15	1001	942	292	0.62	94.18	50.78			
115-707C-3R-5, 145-150	200.95	935	522	259	0.83	97.33	10.87			
115-707A-25X-5, 145-150	207.15	1208	569	266	0.57	98.82	63.64			
115-707C-6R-2, 145-150	225.45	1001	567	283	1.03	96.84	19.89			
115-707C-9R-2, 145-150	254.35	907	485	215	12.01	90.61	24.70			
115-/0/C-15K-1, 145-150	310.35	780	622	219	20.69	65.89	31.08			
115-708A-1H-4, 145-150	5.95		1124	467	1.06	94.05	—			
115-708A-2H-4, 145-150	14.95	1737	1554	532	10.79	86.21	87.63			
115-708A-3H-4, 145-150	24.55	1169	1152	676	4.28	91.67	22.49			
115-708A-4H-4, 145-150	34.05	2105	3030	766	2 57	94 32	24 21			
115-708A-6H-3, 145-150	51.65	1079	1023	759	25.31	73.18	17.60			
115-708A-9X-1, 145-150	77.45	630	738	712	62.74	35.97	22.22			
115-708A-12X-4, 120-125	107.10	828	874	708	1.24	97.01	17.48			
115-708A-15X-4, 120-125	136.00	1374	1150	701	0.37	77.70	24.68			
115-708A-18X-3, 120-125	162.00	1765	1357	697	1.10	97.49	38.33			
115-708A-22X-4, 145-150 115-708A-24X-4, 145-150	203.45	1245	1942	603	26.59	71 44	32.00			
115-7007-247-4, 145-150	222.13	405	1105	005	20.55	/1.44	32.00			
115-709A-1H-4, 145-150	5.95	1143	1242	342	6.16	91.73	10.32			
115-709A-2H-4, 145-150	25.65	1126	1546	549	8 71	92 27	33 33			
115-709A-4H-3, 145-150	33.85	1113	1230	627	5.67	92.67	17.13			
115-709A-6H-5, 145-150	54.65	949	1083	719	2.95	95.96	14.34			
115-709A-7H-5, 145-150	64.25	1010	1032	753	3.94	_	8.40			
115-709A-10H-5, 120-125	90.00	1090	1339	840	_		26.80			
115-709A-13H-5, 120-125	123.40	1112	1036	835	3.68	64.12	6.43			
115-709A-10A-3, 120-123	177.20	1025	1114	836	1.00	97.29	11.20			
115-709B-22X-5, 120-125	204.00	1040	1289	816	2.17	93.29	17.60			
115-709B-25X-4, 145-150	231.75	1390	1500	763	1.67	94.06	22.40			
115-709C-28X-2, 145-150	259.65	1038	1124	879	1.25	95.52	14.00			
115-709C-31X-4, 145-150	291.75	863	943	745	2.83	95.91	16.34			
115-709C-34X-4, 145-150	320.75	904	586	819	1.66	96.39	23.20			
115-709C-37X-4, 145-150	349.85	155	/90	/19	0.82	91.28	31.20			
115-710A-1H-4, 145-150	5.95	1254	1344	323	11.09	80.52	18.65			
115-710A-2H-4, 145-150	15.45	1278	1265	437	6.62	90.90	23.60			
115-710A-3H-4, 145-150	22.15	1133	1450	530	0.66	95.13	24.40			
115-710A-6H-4, 145-150	53.85	1167	1472	530	0.60	99.05	87.00			
115-710A-9H-5, 120-125	83.80	2303	2524	547	23.09	71.00	63.60			
115-710A-12H-5, 120-125	112.70	2040	2430	504	0.22	96.53				
115-710A-15X-3, 115-125	136.55	1142	1611	530	0.84	97.23	35.00			
115-710A-18X-3, 115-125	165.55	1729	1602	525	1.03	97.54	26.40			
115-/10A-22X-3, 115-125	204.25	1636	1463	532	0.36	97.98	37.62			
115-711A-1H-4, 145-150	5.95	1368	684	274	1.56	94.98	73.31			
115-711A-2H-3, 145-150	12.55	3663	628	282	7.03	87.72	63.20			
115-711A-3H-4, 145-150	23.65	297	123	269	0.30	95.19	-			
115-711A-4H-5, 145-150	34.75 44 35	1/40	1005	273	0.79	91 52	_			
115-711A-6H-5, 115-120	53.75	-	200	287	0.12	97.90				
115-711A-9H-5, 115-120	82.75	1596	1359	302	0.61	97.70	4.44			
115-711A-12X-2, 115-120	107.15	2451	1437	312	0.51	75.05	86.15			
115-711A-15X-5, 115-120	140.75	1498	1492	284	0.33	97.72	52.22			
115-711A-18X-3, 140-150	167.10	1413	1369	288	0.56	98.42	57.27			

Table 3. The concentration of Sr in the coarse and fine fractions from the sediment from which waters were squeezed in Leg 115.

Table 3 (continued).

Core, sample, interval (cm)	Depth (mbsf)	Sr o	concentr olid (pp	ation m)	Percentage of sediment			
		>62	< 62	Equil.	>62	< 62	Insoluble	
115-711A-21X-4, 140-150	197.60	1507	938	321	1.48	97.15	29.20	
115-711A-24X-3, 140-150	225.10	1297	980	320	31.06	64.61	35.60	
115-712A-1R-5, 145-150	7.45	877	988	264	8.84	89.34	17.60	
115-712A-2R-2, 15-150	15.48	932	1019	274	9.61	87.23	10.84	
115-712A-3R-2, 140-150	23.40	871	1118	288	10.19	85.78	16.73	
115-712A-4R-2, 140-150	31.50	1047	818	304	7.30	88.55	11.20	
115-712A-6R-2, 140-150	50.80	755	697		23.19	74.23	0.00	
115-713A-2R-4, 145-150	7.55	1031	1046	295	12.95	84.73	25.79	
115-713A-3R-4, 145-150	17.15	962	1065	302	10.40	85.71	19.20	
115-713A-4R-4, 145-150	26.75	1075	1077	307	11.20	83.02	15.94	
115-713A-5R-2, 145-150	33.45	826	545	309	7.55	90.01	36.40	
115-713A-6R-2, 145-150	43.05	1089	670	301	1.35	95.60	60.59	
115-713A-9R-1, 145-150	70.55	974	597	280	3.00	96.03	25.90	
115-713A-12R-1, 147-150	99.57	1133	396	269	6.78	88.23	27.60	
115-713A-17R-3, 150-155	150.22		78	182	47.37	48.07		
115-714A-1H-1, 145-150	1.45	1564	1417	283	20.73	77.85	32.00	
115-714A-2H-4, 145-150	8.75	2000	2484	385	12.24	85.41	25.00	
115-714A-3H-4, 145-150	18.35	1211	1328	461	23.63	89.47	15.14	
115-714A-4H-5, 145-150	28.08	1074	1677	442	17.04	81.02	43.20	
115-714A-5H-5, 145-150	35.15	971	1087	480	16.84	80.09	20.72	
115-714A-6H-4, 145-150	47.35	1412	1548	450	19.53	61.90	36.65	
115-714A-9H-2, 145-150	73.15	1228	1307	487	20.90	19.71	23.60	
115-714A-12H-4, 120-125	104.58	1176	1042	507	11.25	90.52	15.54	
115-714A-15X-4, 120-125	131.07	1194	1002	555	14.53	80.29	18.25	
115-714A-18X-4, 120-125	161.40	979	843	517	15.06	81.12	16.27	
115-714A-22X-4, 120-125	200.10	1291	1086	460	21.24	73.75	13.94	
115-714A-25X-1, 145-150	224.75	1266	916	388	31.62	63.24	9.16	
115-715A-1R-3, 145-150	4.45	1622	2404	268	17.98	81.40	62.30	
115-715A-2R-4, 145-150	14.05	987	2144	291	7.03	92.52	34.92	
115-715A-3R-4, 145-150	23.75	1871	2622	310	10.69	87.58	65.34	
115-715A-4R-4, 145-150	33.45	1522	2177	338	8.22	87.76	46.80	
115-715A-5R-4, 145-150	43.05	1730	2839	343	11.77	83.83	71.71	
115-715A-6R-4, 145-150	52.75	1087	_	337	21.84	76.53	35.46	
115-715A-9R-4, 145-150	81.65	1263	922	314	13.50	81.27	25.60	
115-716A-1H-3, 145-150	4.45	2611	4056	273	24.25	57.21	52.78	
115-716A-2H-4, 145-150	12.85	2892	4643	309	30.69	66.79	59.60	
115-716A-3H-4, 120-125	22.20	2316	2551	323	23.74	74.37	9.92	
115-716A-4H-4, 145-150	32.05	2762	2439	353	50.09	48.22	21.12	
115-716A-5H-4, 145-150	41.75	2081	4362	402	18.77	79.09	35.06	
115-716A-6H-4, 120-125	51.20	1975	3637	390	28.13	68.91	41.04	
115-716A-9H-4, 120-125	80.00	2793	2115	451	26.86	91.49	49.80	
115-716A-12H-4, 120-125	108.90	1018	1198	840	29.94	68.34	0.00	
115-716A-15H-4, 120-125	137.80	2020	1861	935	28.37	69.64	29.37	
115-/16A-18H-4, 115-125	166.65	1087	1487	929	31.46	00.99	39.29	
115-/16A-21H-4, 115-125	195.75	2427	1191	919	10.42	86.99	10.04	
115-/10A-24H-4, 140-150	225.10	1039	2034	928	17.73	/8.12	10.00	
115-/10A-2/H-4, 140-150	254.00	2540	1429	822	4.81	93.46	18.80	

Note: The equilibrium refers to the calculated concentration of Sr in calcite precipitated in equilibrium with the present-day pore fluids. Dash (—) indicates that no analyses were performed; asterisk (*) denotes that recovery was greater than 100%.

gated. When normalized to surface seawater chloride ratios using the following equation, the absolute changes in excess alkalinity (A) can be established. Similar calculations can be made for SO_4^{2-} . The results of these calculation are shown in Figures 8A and 8B.

Excess (A) =
$$[A(sample)/Cl (sample)]$$

- $[A(seawater)/(Cl(seawater))]$
· $Cl(sample).$ (3)

Using the reaction in Equation 2, it can be calculated that for every mole of SO_4^{2-} used during the oxidation of organic materials, two moles of carbonate alkalinity are created. Therefore, in the absence of the precipitation or dissolution of calcium carbonate, the alkalinity should increase at twice the rate at which sulfate is removed. Similar calculations can be carried out using phosphate and ammonia at those sites for which data are reported. The use of such a strict stoichiometry has been suggested to be not completely valid, as the differential diffusion coefficients of O_2 , HCO₃, and SO₄²⁻ act to change concentrations of these species with time (Emerson et al., 1982).

As an example of the magnitude of change that might be expected from the diffusion of sulfate and alkalinity, let us consider a difference in sulfate concentration of 8 mM, corresponding to a change of alkalinity of 16 mM. Using a standard diffusion equation and the diffusion coefficients for HCO₃ and SO₄²⁻ given by Li and Gregory (1974) (11.8 vs. 10.7×10^{-6} cm/sec at 25°C), the magnitude of the changes in the concentration of these species as a result of diffusion and the resultant alkalinity anomaly can be estimated for different periods of time. These calculations are shown in Figure 9.

As may be observed, within 1 m.y. the original sulfate and alkalinity gradients have almost disappeared. As most of the sediments are older than 1 m.y., and the sulfate and alkalinity



Figure 8. Excess alkalinity (A) and excess SO_4^{2-} (B) for the "carbonate" sites and Site 716.



Figure 9. Results of the changes in the concentration (c) of sulfate and alkalinity (A) as a result of diffusion $(\partial c/\partial t = D_b \partial^2 c/\partial x^2)$ for different times of diffusion (t) and depths (x). The diffusion coefficient D_b for sulfate and alkalinity is taken from Li and Gregory (1974). Calculations assume an initial section of sediment 50 m thick with a concentration of 20 mM SO₄²⁻ and 16 mM alkalinity. Further reactions involving these components is then stopped, and diffusion along the concentration gradients takes place. The alkalinity anomaly produced as a result of diffusion is shown in (**B**).

gradients are considerably less than those used in this example, we feel that diffusion along concentration gradients cannot be responsible for the deficit of alkalinity observed at the Leg 115 sites. In fact, as the diffusion coefficient of O_2 is approximately 2 times that of HCO₃, there should be an excess of alkalinity production relative to sulfate reduction, particularly in the upper portion of the profile, whereas there is less alkalinity than expected. Other reactions involving either sulfate or alkalinity such as methanogenesis or precipitation of celestite can be ruled out as there is no evidence of any methane production in these sediments (Backman, Duncan, et al., 1988), and, with the exception of Site 716, all sediments are undersaturated with respect to celestite.

The calculations using Equation 3 for sulfate suggest that some sites, notably those with the highest calculated rates of recrystallization, show SO_4^{2-} reduction in excess of what is visible in the alkalinity measured in these pore waters. For example, at Site 709 there is a reduction of approximately 7 mM of SO_4^{2-} at 5.95 mbsf. The alkalinity, however, increases only by approximately 1 mM. In order to account for this loss in alkalinity, calcium carbonate must be precipitated and Ca^{2+} lost from solution. Such precipitation is not visible in the calcium concentration, which actually increases over the same interval. Apparently, either substantial amounts of Ca^{2+} have been diffused or advected into the sediment and have been removed as calcium carbonate, or sulfate is involved in the precipitation of some other mineral phase and the decrease observed is not totally a result of the oxidation of organic material. However, if the sulfate decreases represent the true increase in alkalinity, alkalinity must be lost from the pore waters in the form of the precipitation of calcium carbonate. The problem with this notion is that, in order to account for 14 mM of alkalinity, the Ca^{2+} concentration must decrease by 50% of this amount, or 7 mM.

Such a loss of alkalinity and calcium could occur in two places, either within the sediments themselves or during the retrieval and degassing of the cores. Some evidence for this later hypothesis is provided by comparison of samples taken with the Barnes in-situ water sampler and waters squeezed from similar intervals (Table 2). The in-situ samples, which were retrieved and analyzed with only minimal pressure loss compared to the normal squeezed samples, contained approximately 1 mM more Ca2+ and alkalinity than water from the squeezed intervals at comparable depths. Whereas this change is still insufficient to make up for the apparent depletion in sulfate, it is possible that significantly greater amounts of calcite could have precipitated in the time taken to retrieve the sample from the chamber of the Barnes water sampler and perform the analyses. If the loss in the calcium and alkalinity takes place during retrieval, the interstitial calcium concentrations can be corrected for the calcium lost during this precipitation.

The results of these calculations are shown in Figure 10. Note that this calculation assumes that for every mole of Ca^{2+} precipitated, two moles of alkalinity are lost. From these data it can be seen that in the two shallowest Sites 707 and 716, the excess Ca^{2+} and corrected Ca^{2+} profiles are in good agreement with measured concentrations, considering the errors and assumptions involved in the calculations. Hence the loss of Ca^{2+} and alkalinity during retrieval from shallow-water depths is not

as severe as from the deeper sites and may therefore support the notion that the loss in alkalinity and calcium is a depth-related effect, the largest discrepancies occurring at samples retrieved from the deepest water depths.

In Sites 708, 710, and 711, the Ca^{2+} profile is changed from a profile which is seemingly diffusively controlled to one in which there appears to be water movement out of the sediments (Fig. 10). That is to say the gradient is the steepest nearest the surface. At Site 709, the corrected Ca^{2+} profile does not show any consistent trend with depth, and in fact rises very sharply near the sediment-water interface, decreasing rapidly with increasing depth sub-bottom. While we do not have any definitive explanation for this trend, the observed gradients at Site 709 could be consistent with horizontal convection of fluid through the sediments.

Other anomalies have been reported in the sediments from Site 709. For example in a study of the magnetic properties of the sediments from Leg 115, Robinson (this volume) noted that the magnetic signal had been largely removed between 20 and 120 mbsf. This, he concluded, was a result of conversion of magnetite to pyrite under suboxic conditions in the presence of abundant organic material. While the pore-water and bulk-sediment geochemistry do not support this idea, we cannot help but notice the apparent similarity in the distribution of the anomalous magnetic susceptibility (Robinson, this volume; Fig. 23) with the unusual Ca^{2+} concentrations. Perhaps horizontal advection of normal seawater would enhance the removal of magnetic minerals and eliminate the Ca^{2+} gradients.

Finally, it may be important that the same phenomenon of excess sulfate depletion is evident in data collected from DSDP



Figure 10. Measured Ca^{2+} and "corrected" Ca^{2+} profiles for Sites 707 (A), 708 (B), 709 (C), 710 (D), 711 (E); and 716 (F). Note the change in the shape of the profile in Sites 708, 710, and 711, the absence of significant changes in Sites 707 and 716, and the irregular pattern in Site 709.

and ODP sites. For example, in the studies of Baker (1986) in which the profiles of trace elements were largely considered to be diffusively controlled, significant Ca^{2+} deficiencies also exist. Whether such discrepancies are sampling artifacts or are in fact real, the flux and Ca^{2+} gradients in oceanic carbonate sediments need to be reexamined.

Some support for the notion that the observed sulfate changes are artifacts is provided by comparison of the change in the concentrations of ammonia at Site 709. Increase in ammonia is considerably lower than that suggested by Redfield stoichiometry. They are, however, much more in agreement with increases in alkalinity. It is possible, based on the evidence, that depletion in SO_4^{2-} is not entirely a result of oxidation of organic material, but may be a consequence of the participation of SO_4^{2-} in some other system, or perhaps is a result of its adsorption by clay minerals.

Solids

A further method used to estimate recrystallization involves the comparison of Sr content of the sediment with the equilibrium Sr concentration predicted from the pore-water chemistry (Baker et al., 1982). The depth at which the predicted equilibrium values coincide with the actual values theoretically is the depth of 100% recrystallization. This calculation is shown graphically for Sites 707-711 and Site 716 in Figures 6A to 6F, and can be expressed by the following equation:

$$\% \text{ recrystallization} = \frac{(Sr^{2+}/Ca^{2+})_{\text{initial}} - (Sr^{2+}/Ca^{2+})_{\text{observed}}}{(Sr^{2+}/Ca^{2+})_{\text{initial}} - (Sr^{2+}/Ca^{2+})_{\text{equilibrium}}}.$$
 (4)

This method has not proven useful for estimating recrystallization in Leg 115 carbonates for several reasons. First, Baker et al. (1982) stated that the equation was useful only if the $Sr^{2+}/$ Ca²⁺ ratio of the fluids did not vary through time. Such is obviously not the case for our samples. Second, the calculation assumes that the initial Sr²⁺/Ca²⁺ ratio of the solids has been constant through time and is necessarily very sensitive to the value chosen. At many Leg 115 sites, the Sr²⁺/Ca²⁺ ratio has apparently varied through time and in some instances actually increases with depth (i.e., Site 708). Third, small amounts of true recrystallization can result in apparently large %R values using this method because of its sensitivity to the Sr²⁺/Ca²⁺ ratio of the pore fluid. For example, if it is assumed that 2% of a sediment with an initial Sr2+ content of 1500 ppm becomes recrystallized with a content of 750 ppm Sr, and all the excess Sr2+ goes into the pore fluids, then the Sr²⁺/Ca²⁺ of carbonates precipitated in equilibrium should change by a factor of 5. According to the equation proposed by Baker et al. (1982), the calculated recrystallization is 60%. In essence, the formula assumes that the pore fluid Sr^{2+}/Ca^{2+} ratio controls the same ratio in the solid, when in fact the Sr^{2+}/Ca^{2+} ratio of the fluids is controlled by the small amount of carbonate which is recrystallized at any one time.

Although much better estimates of recrystallization can be obtained by examining the total loss of Sr^{2+} from the system, the graphical presentation provides a qualitative estimate of visualizing recrystallization. For example, at Site 707 (Figure 6A), the site with the lowest estimated rate of recrystallization, the calculated equilibrium Sr concentration remains below that of the measured concentrations of the fine and coarse fractions throughout the core, showing no convergence. In contrast, at Site 709 (Figure 6C), the sediment and the equilibrium concentration are in approximate agreement in the sediments at the bottom of the hole, where we estimate recrystallization to be as much as 50%.

Calcium and Magnesium

A significant finding of previous work on pore waters obtained from DSDP sites is that positive Ca^{2+} and negative Mg^{2+} gradients with increasing depth sub-bottom in the interstitial pore fluids can be related to the alteration of underlying crustal rocks (Lawrence et al., 1975). Such fluxes can be compared using a diffusion-sedimentation-compaction model as given by the following equation:

$$\partial C(z,T)/\partial T = D_b \partial^2 C/\partial Z^2 + \nu \partial C/\partial Z + \Sigma J.$$
(5)

In this equation, C = the concentration of either the species under consideration as a function of depth (z) and time (T); ΣJ = sum of production or consumption terms involving the relevant elements; ν = the sedimentation rate; and D_b = solute diffusion coefficient.

If Ca^{2+} and Mg^{2+} are controlled principally by this equation, and there are no chemical reactions involving these elements occurring in the sediments, then J = 0 and the behavior of Ca^{2+} and Mg^{2+} can be considered to be conservative and their concentrations linearly correlated. Based on such an assumption, McDuff (1981) classified data from DSDP Legs 1 through 53 into sites (1) without gradients; (2) with gradients but no linear correlations; and (3) with gradients and linear correlations. Although conservative behavior for Ca^{2+} and Mg^{2+} is implied if there is a linear correlation between these elements, McDuff (1981) provided no criteria to assess whether a correlation actually exists. It is assumed in this paper that a conservative relationship exists if there is a statistically significant correlation between Ca^{2+} and Mg^{2+} .

The magnitude of the Ca^{2+}/Mg^{2+} gradient has been suggested to be a result of nature of the underlying basement rocks. For example, Baker (1986) proposed that more positive Ca^{2+}/Mg^{2+} gradients (> -0.6) were representative of felsic basement rocks. In support of this contention, he noted that Ca^{2+}/Mg^{2+} gradients from three groups of sites (Sites 346 and 349 on the Jan-Mayen ridge; Site 116 of the Rockall bank; and Site 237 on the Mascarene Ridge) all possessed Ca^{2+}/Mg^{2+} gradients between -0.6 and -0.4 and were all presumed to be underlain by felsic basement. On the basis of this comparison, Baker concluded that Sites 588, 590, 591, and 592 on the Lord Howe Rise were also resting on felsic basement. However, in none of these sites were felsic materials actually drilled.

In addition, as discussed previously, alkalinities at the Lord Howe Rise sites were not as high as might be expected from sulfate reduction, suggesting that calcium and alkalinity concentrations of the pore waters have been significantly altered during retrieval or through carbonate reactions in the sediments. Loss of Ca^{2+} by this process would substantially reduce the measured Ca/Mg ratio. For example, Table 4 shows the gradients for the Leg 115 sites calculated before and after making a correction for Ca^{2+} loss. At all sites other than 709, the Ca/Mg ratio becomes substantially more negative and closer to values proposed as a result of basaltic alteration.

Of particular relevance to the Leg 115 studies are the observations on pore water from Site 237, drilled close to Site 707 on the northern Mascarene Plateau (Fig. 1). Although both Sites 237 and 707 penetrated similar types of sediments, were drilled in similar water depths (Site 237 was drilled in 1623 m water depth), and were geographically very close, their Ca/Mg gradients were significantly different (Site 707 = -0.82; Site 237 = -0.57; Sandstrom and Gieskes, 1974). Other "carbonate" sites such as Sites 708 and 709 have Ca/Mg gradients similar to Site 237, but are situated farther away from the Seychelles bank. Site

Table 4. The Ca/Mg gradients measured from the "carbonate" sites before and after correction for Ca^{2+} loss as discussed in the text.

	Ca/Mg				
Site	1	r	2	r	n
707	-0.82 (0.03)	0.94	-0.87 (0.06)	0.98	15
708	-0.54 (0.07)	0.82	-1.29(0.18)	0.85	11
709	-0.55 (0.02)	0.97	+0.66(0.32)	0.23	16
710	-1.01 (0.09)	0.93	-2.00 (0.24)	0.90	10
711	-0.82 (0.17)	0.68	-0.38(0.44)	0.50	12
716	-0.83 (0.05)	0.95	-0.81(0.05)	0.96	13
236	-1.70				
237	-0.57				
239	-1.85				
245	-1.00				

Note: Ca/Mg gradients are given for Sites 236, 237, 239, and 245 (see Fig. 1 for locations; data from Sandstrom and Gieskes, 1974; Gieskes, 1974).

710, situated close to Site 709 on the Madingley Rise, has a gradient similar to Site 711. Site 237, as noted previously, has been used by various authors (McDuff, 1981; Baker, 1986) as an example of a site which might be underlain by felsic basement; however, by virtue of the positions of Site 707 and the other "carbonate" sites relative to Site 237 and the Seychelles bank (Fig. 1), where granitic rocks are found exposed on the surface, the Ca/Mg gradient at Site 237 cannot be used to support a granitic basement at Site 237.

Based the apparent random distribution of the Ca/Mg gradients of the Leg 115 sites and the sites drilled during DSDP Legs 24 and 25, we conclude that previous assessments regarding the magnitude of the Ca/Mg gradient in relation to the nature of the basement rocks, at least in the Indian Ocean, are probably incorrect. For example, the wide range of Ca/Mg gradients measured in this study (-0.54 to -1.01) and from nearby Sites 236, 237, 238, 239, and 245 (-0.57 to -1.85) (Table 4) would lead to the conclusion that a wide variety of basement rock types were present in this area, whereas in fact all the basement rocks are probably basalts.

The precise reasons for the wide variation in Ca/Mg gradients are probably at least partially related to the observation of Ca^{2+} loss during the retrieval of the core and the presence of significant carbonate reactions in the sediment which do not alter the apparent conservative relationship between Ca^{2+} and Mg^{2+} . Additional constraints may be placed by the actual Ca/ Mg ratio of the basalts and the rate of hydrolysis of the aluminosilicates. As proposed by McDuff (1981), at low rates of hydrolysis, Mg^{2+} uptake exceeds Ca^{2+} release, the proportion being controlled by the ratio of alkalinity supplied by the dissolution of calcic aluminosilicates to that supplied by sodic aluminosilicates. Hence, low rates of basalt alteration would produce Ca/Mg gradients close to unity when compared to basalts altered at higher rates.

Interpretation of Pore-water Si Profiles

Concentrations of Si are typically extremely low in the surface oceans as a result of the incorporation of Si in skeletons of siliceous microorganisms living in the photic zone. In fact, in this study, concentrations of Si were below detection levels (1 μ M), lower than the 2 μ M values reported by Weiss et al. (1983) for surface Indian Ocean waters. As radiolarians and diatoms die and sink to the bottom, their siliceous valves dissolve, resulting in an increase in Si concentration in the deeper water. Typical bottom-water Si concentrations at 1522 m are approximately 100 μ M, increasing to 127 μ M at 4487 m water depth (data from Station 424 of the GEOSECS expedition; Weiss et al., 1983).

In contrast to these bottom-water concentrations, pore water from the first squeezed section of each core showed a large increase in the concentrations of Si, ranging from 711 μ M at Site 711 to 449 μ M at Site 712, reflecting the dissolution of siliceous tests in a semi-closed system. An exception to this occurs at Site 707, where Si concentrations in the pore fluids are initially as low as 266 μ M. This low concentration corresponds to an absence of radiolarians and diatoms in the sediments and is a consequence of the location of this site at the southern limit of the present equatorial belt of silica production.

Increases in the pore fluid concentration of Si at Site 707 and other sites during the Pliocene and late Miocene result from the continued dissolution of siliceous fossils and is limited by the saturation of authigenic silica minerals opal-CT and quartz (Kastner, 1979); Site 707 was located in the silica-producing belt during this period (Mikkelsen, this volume). During the early and middle Miocene, the absence of siliceous components in the sedimentary record correlates with a decrease in the interstitial pore-water Si concentrations at all sites. The extent of this depletion cannot be fully appreciated as a result of the small numbers of samples taken in this time interval.

To constrain the extent of diagenetic reactions involving Si that occur in the sediments, the Si profiles that might be produced as a result of diffusion only can be calculated using a simple diagenetic equation previously described (Equation 5).

If Site 707 is used as an example and it is assumed that the Si concentration of the interstitial waters was approximately 700 μ M for a period of 20 m.y. (corresponding to an interval of 150 m), and then became 100 µM (approximate modern bottom-water Si concentrations) for an interval of 30 m.y. up to the present day with no further reactions involving either the dissolution or precipitation of silica (J = 0), then the results of this equation predict that the original Si concentration gradient should not be visible at the present time. In fact, there should be only a minimal difference in the Si concentrations between sediments older than 20 Ma and those younger, less than that currently observed. Slight changes in the bulk diffusion coefficient will not appreciably change this calculation. Therefore, to maintain the lower Si concentrations in the portions of the core that do not contain siliceous microfossils, there must be consumption of Si in these areas. Similarly, there must be continued dissolution of siliceous microfossils in other siliceous-rich areas.

Other studies of Leg 115 materials (Hempel and Bohrmann, this volume) have indeed documented the presence of clinoptilolite, a diagenetic silicate mineral, forming mainly in the sediments devoid of siliceous microfossils. It is unclear, however, why this mineral should form in these areas and not in sediments rich in siliceous microfossils. One possible explanation is that as clinoptilolite is a K-rich silicate; its formation needs the addition of Al(OH)⁻ and K⁺. Such species would be present in higher concentrations in sediments that contain a greater concentration of insoluble minerals. In fact, the interval between 10 and 20 Ma corresponds to a period of relatively low carbonate accumulation and high concentrations of acid-insoluble minerals (Peterson and Backman, this volume).

We propose, therefore, that the low Si concentrations of present-day power waters in sediments between 10 and 20 Ma are primarily a consequence of the formation of clinoptilolite in this interval. The formation of this mineral would not be possible without the presence of K^+ and $Al(OH)^-$, and thus, the lower Si concentrations are a response to the presence of these elements. However, if abundant siliceous microfossils were originally present in these sediments, their dissolution would have provided a local source for Si and there would have been no present-day Si minimum unless all the available microfossils had already been dissolved. Although it is also possible that most of the siliceous fossils dissolved before burial during this time interval as a consequence of the lower rates of sedimentation, the disappearance of siliceous fossils, the shoaling of the CCD, a pronounced carbon isotopic shift at Site 709, and numerous other geochemical changes (Baker et al., this volume) are surely more than coincidence.

CONCLUSIONS

The total amounts of carbonate recrystallization based on the Sr^{2+} flux from the sediments range from <0.2% at Site 705 to >50% at Site 709. Of the so-called "carbonate" sites, the total amount of recrystallization was the highest at Site 709, and decreased with increasing water depths at Sites 708 and 711. Low rates of recrystallization were also observed at Site 707, the shallowest site. At all sites the highest rates of recrystallization occurred in the upper 50 mbsf in sediments of less than 5 Ma.

The rate of carbonate recrystallization calculated at Site 716 using the Sr^{2+} flux method was similar to rates at Sites 709 and 710. This result was similar to that obtained from previous sites drilled in metastable carbonate assemblages containing high amounts of aragonite and HMC.

In the deeper water sites (Sites 708, 709, 701, and 711), concentrations of sulfate in the interstitial pore fluids decreased in excess of what might be expected from the rise in alkalinity, suggesting loss of Ca^{2+} and alkalinity during the precipitation of calcium carbonate. Such precipitation could have occurred either in the sediments or during retrieval of the core. Evidence for this latter hypothesis is provided by a comparison of chemical analyses on fluids obtained using the Barnes *in-situ* water sampler and waters squeezed from the sediments. Recalculation of the apparent Ca^{2+} concentration gives, in some instances, a profile with a concave upward slope, suggesting convection of fluid through the sediments (Sites 708, 709, 710, and 711).

Although the gradients of Ca^{2+} and Mg^{2+} in the Leg 115 sites would normally be considered to be conservative, they are influenced by recrystallization and loss of Ca^{2+} during core retrieval. These processes produce differences in correlation between these two elements. For these reasons, measured Ca/Mg gradients are not truly reflective of those actually produced as a result of basement alteration and subsequent diffusion, and therefore cannot be used to indicate either the felsic or mafic nature of basement rocks.

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