13. INTERSTITIAL WATER STUDIES, LEG 15 – DISSOLVED CARBON DIOXIDE CONCENTRATIONS¹

Taro Takahashi², Linda A. Prince, and Lawrence J. Felice, Queens College, City University of New York, Flushing, New York and Lamont-Doherty Geological Observatory, Columbia University, Palisades, New York

ABSTRACT

The concentrations of total carbon dioxide dissolved in 100 interstitial water samples collected during the Legs 6, 7, 8, 10, 11, 12, and 15, Deep Sea Drilling Project, were determined by means of the vacuum extraction of CO₂ from the samples followed by the determination of CO₂ using an infrared gas analyzer. In the samples collected in the Pacific and Atlantic Oceans (Legs 6, 7, 8, 10, 11, and 12), the observed CO₂ concentrations generally range between 2 millimoles/kg and 5 millimoles/kg. Unusually high values, up to 33 millimoles/kg, were observed in the cores from the Blake-Bahama Outer Ridge (Leg 11). The CO2 concentrations in the samples from the Caribbean Sea (Leg 15) range between 2.9 millimoles/kg and 15.4 millimoles/kg and appear to show maxima at or above 70 meters below the water-sediment interface. Comparison between the CO2 concentrations and the alkalinity values determined in these Caribbean samples by Gieskes (this volume) indicates that the change in CO2 concentration is directly proportional to the change in alkalinity. Assuming that no CO₂ was lost from the interstitial water samples during sampling and that no reaction took place between the interstitial water and the sediments during the storage and squeezing, the degree of saturation of calcite and dolomite in the Leg 15 interstitial water was calculated from the pCO₂ and total carbon dioxide data using the Garrels-Thompson seawater model modified by Simpson and Takahashi (this volume). The interstitial waters above the sediment depth of 150 meters appear to be supersaturated with respect to calcite by as much as a factor of seven, whereas the water appears to be undersaturated below the sediment depth of 150 meters. The water is, in turn, supersaturated with respect to dolomite. This suggests that calcite is being dissolved as dolomite is being precipitated, and that a favorable condition for dolomitization exists below a sediment depth of about 150 meters.

INTRODUCTION

The solubility of calcium carbonate in aqueous solutions depends upon various physicochemical factors such as the calcium ion concentrations, pH, total carbon dioxide dissolved in solution, temperature, pressure, and the concentrations of other ions such as Mg^{++} and $SO_4^{=}$. Since a large proportion of the recent deep-sea sediments consists mainly of the skeletal calcareous shells, a study of these parameters in the sediment interstitial water is important for the understanding of the nature of the chemical alterations taking place between the calcerous shells and the interstitial waters of sediments. Some of the chemical

parameters, such as alkalinity and major cation and anion concentrations, in the interstitial water samples collected from the DSDP cores have been measured by a number of investigators (Manheim and Sayles, 1971a, 1971b; Sayles and Manheim, 1971; Presley and Kaplan, 1971a, 1971b; Gieskes, this volume); however, direct measurements of the total dissolved CO₂ concentration in interstitial water samples have been scarcely reported. Furthermore, due to the small quantity of samples available for pH measurements, some of the pH values reported in literature appear to be unreliable. In this study, we determined the concentrations of the total CO2 dissolved in interstitial water samples by means of an infrared absorption method in order to achieve an improved precision and accuracy of measurements. In addition, the partial pressure of CO₂ gas exerted by each interstitial water sample was determined using the infrared absorption method. Using these two sets of measurements and the chemical model for saline solutions described in this volume by Simpson and

¹Lamont-Doherty Geological Observatory Contribution Number 1921.

²Also a member of the University Institute of Oceanography, City University of New York, New York, N. Y.

Takahashi, we computed various chemical parameters necessary to characterize the calcium carbonate-interstitial water system in sedimentary columns.

SAMPLING AND ANALYTICAL PROCEDURES

Approximately 10 ml of interstitial water were squeezed out of a sediment sample about 20 cm long through a Millipore filter according to the DSDP manual (Waterman, 1970) at room temperature, and were injected into a special sample container made of Pyrex glass. The sample container (Figure 1) is equipped with two stopcocks and is filled with a reference gas (1000 ppm CO_2 and remainder N_2) at one atmosphere pressure prior to sampling. When the sample water is being introduced into the middle section of the container (section C), stopcock A is closed so that no water can enter into section D. After section C is fully or partially filled with the sample water, stopcock B is closed and the container is placed in the upright position (section D pointing upward). Stopcock A is then opened so that the gas contained in section D is now exposed to the sample water placed in section D and can be equilibrated with the sample water via gaseous exchange through stopcock A. Laboratory experiments show that, when a 4-millimeterbore stopcock is used, the gas contained in section D reached to 90% of the equilibrium value 1 hour after stopcock A was opened. For shipboard operation, stopcock A was left open for 1 to 2 hours at the room temperature condition. After the equilibration period, stopcock A is closed so that the equilibrated gas contained in section D is completely isolated from the sample water in section C. The temperature and the duration of equilibration is recorded for each container, and a drop of the saturated mercuric chloride solution is then added to the sample water through stopcock B for the purpose of poisoning biological activities. The equilibrated and poisoned samples were then shipped to the shore-based laboratory for the measurement of the total dissolved CO2 concentration (ΣCO_2) and the CO₂ partial pressure (pCO₂).

In the shore-based laboratory, the ΣCO_2 and pCO_2 values were determined by means of the infrared gas absorption method similar to the one described by Broecker and Takahashi (1966). The sample water was first weighed and then placed in an evacuated extraction chamber acidified by concentrated phosphoric acid. The CO_2 gas released from the sample water was swept by N₂ carrier gas into a calibrated reservoir (2000 ml) in which the extracted CO_2 and the carrier gas were homogenized before the gas mixture was introduced into the infrared gas analyzer. The precision and accuracy of the ΣCO_2 measurements reported here have been estimated to be ± 0.7 and ± 1 percent respectively. The ΣCO_2 values thus obtained are listed in Tables 1-7.

The pCO₂ samples were first diluted quantitatively with a reference gas of a known CO₂ concentration and then introduced into the infrared gas analyzer. Due to the small number of moles of CO₂ present in the sample, a precision of ± 5 percent was attained in the measurements. Furthermore, an additional uncertainty of 5 to 10 percent is estimated for the incomplete equilibration between the sample water and the gas in the sampler. Therefore, the



Figure 1. Pyrex glass sampler for pCO_2 and ΣCO_2 determinations.

over-all accuracy of the pCO_2 measurements has been estimated to be about 10 percent.

CALCULATION OF THE CARBONATE CHEMISTRY PARAMETERS

A chemical model of seawater (Simpson and Takahashi, this volume) revised from the Garrels-Thompson model (1962) was used to calculate various carbonate chemistry parameters using the total CO₂ concentration (Σ CO₂) and the CO₂ partial pressure (pCO₂) values. The apparent dissociation constants for ion complexes used for the present computations are listed below, and are assumed to be independent of temperature and pressure.

- K'_3 = (Na⁺)(CO₃⁼)/(NaCO₃⁻) = 1.35, Simpson and Takahashi (this volume);
- $K'_4 = (Ca^{++})(CO_3^{-})/(CaCO_3^{\circ}) = 0.0127$, Garrels and Thompson (1962);
- $K'_5 = (Mg^{++})(CO_3^{=})/(MgCO_3^{\circ}) = 0.00918$, Simpson and Takahashi (this volume);
- $K_6' = (Na^+)(HCO_3^-)/(NaHCO_3^\circ) = 3.89$, Garrels and Thompson (1962);
- K'_7 = (Ca⁺⁺)(HCO₃⁻)/(CaHCO₃⁺) = 0.239, Simpson and Takahashi (this volume);
- K'_8 = (Mg⁺⁺)(HCO₃⁻)/(MgHCO₃⁺) = 0.239, Simpson and Takahashi (this volume);

- $K'_{9} = (Na^{+})(SO_{4}^{-})/(NaSO_{4}^{-}) = 0.495$, Kester and Pytkowicz (1968, 1969);
- $K'_{10} = (CA^{++})(SO_4^{-})/(CaSO_4^{\circ}) = 0.0926$, Kester and Pytkowicz (1968, 1969);
- $K'_{11} = (Mg^{++})(SO_4^{-})/(MgSO_4^{\circ}) = 0.0980$, Kester and Pytkowicz (1968, 1969).

The quantities in parentheses represent molalities and the apparent dissociation constant is related to the thermodynamic constant, K, multiplied by the respective activity coefficients, γ . Thus,

$$K_4' = (Ca^{++})(CO_3^{-})/(CaCO_3^{\circ}) = \frac{\gamma_{CaCO_3^{\circ}}}{\gamma_{Ca^{++}}\gamma_{CO_3^{-}}} = K.$$

The first and second dissociation constants for carbonic acid obtained respectively by Harned and Davis (1943) and Harned and Scholes (1941) were used along with those dissociation constants for ion complexes and the activity coefficients in the formulation described by Simpson and Takahashi in this volume. For the solubility of carbon dioxide in pure water and seawater, the recent data obtained by Li and Tsui (1971) as a function of temperature and chlorinity were adopted. Among the dissociation constants used, those of carbonic acid were changed as a function of temperature and those for complex ions were assumed to be independent of temperature.

In the process of computing carbonate chemistry parameters in the interstitial water samples, the carbonate alkalinity and pH values at the equilibration temperature were calculated from the ΣCO_2 , pCO₂, and major ion concentration data. Once the carbonate alkalinity value was obtained, then the pH and (CO3⁼)T values at the in situ temperature were computed using the ΣCO_2 value and the computed carbonate alkalinity value. Table 7 gives the ion activity product and ion concentration product values computed for 1 atm total pressure and the in situ temperature. The saturation factors were calculated using the solubility product (K_{sp}) data of McIntyre (1965) at one atmosphere total pressure for calcite and the effect of pressure on the solubility product for calcite obtained by Pytkowicz and Fowler (1967). The effect of temperature on the effect of pressure was assumed to be negligibly small. The K_{sp} and the effect of pressure on K_{sp} were expressed by:

$$K_{sp} = (0.69 - 0.0063 T^{\circ}C) \times 10^{-6} \times (Cl^{\circ}_{\circ}/19) \text{ moles}^{2}/\text{liter}^{2}$$

$$\log (K_{sp} \text{ at } P)/(K_{sp} \text{ at } P = 1) = 5.20 (P - 1) \times 10^{-4}$$

where P is pressure in bars (Li, Takahashi and Broecker, 1969). The pressure to which the interstitial water was subjected was calculated from:

$P(\text{bars}) = [(\text{water depth, m})/10] + [(\text{sediment thickness, m}) \times 0.15]$

TABLE 1 Interstitial Water ΣCO_2 , Leg 6

Sample	Location	Water Depth (km)	Sediment Depth (m)	ΣCO ₂ (mM/kg)
6-45.1-1-1	24° 16'N 178° 31'W	5.51	2	2.54
6-47.0-1-3	32°27'N 157°43'E	2.69	4	3.05
6-47.2-2-3	32°27'N 157°43'E	2.69	23	0.89
6-47.2-4-3	32°27'N 157°43'E	2.69	42	1.66
6-47.2-7-1	32°27'N 157°43'E	2.69	64	2.99
6-47.2-10-2	32°27'N 157°43'E	2.69	95	3.83
6-48.2-1-2	32°24'N	2.62	54	1.99
6-48.2-2-2	32°24'N 158°01'E	2.62	63	2.69
6-49.0-1-2	32°24'N	4.28	3	2.98
6-49.1-1-3	32°24'N	4.28	9	2.73
6-50.1-1-4	32°24'N	4.49	10	2.50
6-50.1-3-5	32°24'N	4.49	29	2.77
6-52.0-1-4	27°46'N 147°08'E	5.74	6.	2.12
6-52.0-3-2	27°46'N	5.74	23	2.05
6-53.1-1-4	18°02'N	4.64	5.5	1.57
6-53.0-3-1	18°02'N 141°12'F	4.64	137	0.18
6-53.0-6-2	18°02'N 141°12'E	4.64	197	0.67

The in situ temperature was calculated from the water temperature and the geothermal gradient data obtained by Langseth and Grim (1964), using the equations

> $T(^{\circ}C) = 16.9 + 0.055$ (sediment thickness, m), for Site 147B (Cariaco Basin), and

 $T(^{\circ}C) = 4.2 + 0.055$ (sediment thickness, m), for Site 148 (Aves Ridge).

The major ion concentration data used for the present calculations are those of Sayles and Manheim, this volume.

DISCUSSION

Distribution of Total Dissolved CO₂ Concentrations

Leg 15

A systematic trend in the distribution of the total dissolved CO_2 concentrations in the interstitial water samples was observed in the sedimentary columns sampled during Leg 15. In particular, the ΣCO_2 value for Site 148

T. TAKAHASHI, L. A. PRINCE, L. J. FELICE

TABLE 2 Interstitial Water ΣCO₂, Leg 7

Sample	Location	Water Depth (km)	Sediment Depth (m)	ΣCO ₂ (mM/kg)
7-62.0-1-2	1° 52'N	2.59	91	3.20
7-62.0-3-2	1°52'N 141°56'E	2.59	320	2.11
7-62.0-4-4	1° 52'N 141° 56'E	2.59	400	1.56
7-62.1-2-4	1°52'N 141°56'E	2.59	21	2.12
7-63.0-1-5	0° 50' N 147° 53' E	4.47	8	3.09
7-63.0-2-3	0° 50'N 147° 53'E	4.47	65	3.15
7-63.0-4-2	0° 50' N 147° 53' E	4.47	231	3.29
7-64.0-1-3	1°45'N 158°37'E	2.05	5	3.02
7-64.0-2-2	1° 45'N 158° 37'E	2.05	103	3.79
7-64.0-4-5	1°45'N 158°37'E	2.05	311	4.44
7-65.0-3-4	4°21'N 176°59'E	6.13	19	3.44
7-65.0-7-6	4°21'N 176°59'E	6.13	55	3.30
7-65.0-9-6	4°21'N 176°59'E	6.13	73	3.52
7-65.0-11-5	4°21'N 176°59'E	6.13	92	3.68
7-65.0-16-5	4°21'N 176°59'E	6.13	133	3.62
7-65.1-4-5	4° 21'N 176° 59'E	6.13	160	3.40
7-66.0-2-2	2°24'N 166°07'W	5.29	80	3.11
7-66.0-7-3	2°24'N 166°07'W	5.29	178	2.77
7-66.0-9-3	2° 24'N 166° 07'W	5.29	191	2.60

(Aves Ridge) increases from about 3 mM/kg to 7.7 mM/kg at a sediment depth of 70 meters (Figure 6). It then decreases to 3 mM/kg at a depth of 150 meters and remains unchanged at depths below 150 meters down to 210 meters. In the sedimentary column at Site 148, down to 70 meters, the observed ΣCO_2 increase of 2.2 times (3 to 7.7 mM/kg) is accompanied by a decrease of SO₄⁼ by 2.5 times from 26 mM/kg to 10 mM/kg (Sayles and Manheim, this volume). This suggests that, in this depth range, CO₂ is generated by reactions between organic debris and SO₄⁼.

The observed decrease in ΣCO_2 below 70 meters indicates that CO_2 is being consumed at sediment depths below 100 meters. The interstitial water in this depth range exhibits a much lower degree of saturation with respect to calcite than in the sedimentary column above 100 meters (Figure 9). Furthermore, the carbonate alkalinity value decreases nearly proportional to the ΣCO_2 decrease (Figure 8). However, if the removal of CO_2 from a solution is entirely due to the precipitation of carbonate crystals, the observed change in alkalinity should be twice the change in ΣCO_2 . This is not the case in this sedimentary column. These observations indicate that precipitation of calcite

8-69-3-3 8-69-5-3	6°00'N 152°52'W	1.00		(mwi/kg)
8-69-5-3	152° 52'W	4.98	27	3.04
8-69-5-3	A			
	6°00'N	4.98	120	2.83
	152°52'W			
8-69-6-4	6°00'N	4.98	192	3.00
	152°52'W			
8-69A-8-6	6°00'N	4.98	143	3.37
	152°52'W			
8-70-3-1	6°20'N	5.06	18	3.05
	140°22'W			
8-70A-7-4	6°20'N	5.06	176	2.48
	140°22'W			
8-70A-15-2	6°20'N	5.06	244	1.44
	140°22'W			
8-71-2-3	4°28'N	4.42	14	2.88
	140°19'W			
8-71-14-3	4°28'N	4.42	119	2.86
	140° 19'W			
8-71-28-2	4°28'N	4.42	246	2.95
	140°19'W			
8-71-48-2	4°28'N	4.42	434	1.82
071 102	140° 19'W	1000		
8-72-4-4	0°26'N	4 3 3	155	3.70
	138°52'W	00754T		
8-72-5-6	0°26'N	4.33	219	3.90
01200	138°52'W	1100		0.00
8-72-7-4	0°26'N	4 3 3	317	3.33
01211	137° 52' N	1100	211	0.00
8-724-2-3	0°26'	4 33	21	3 26
0-12112-5	137°52'W	1.55		0.00
8-73-2-3	1°55'S	4 39	8	3 24
0-15-2-5	137°28'W	4.57	0	0.21
8-73-12-3	1°55'S	4 30	143	3 31
0-75-12-5	137°28'W	T.57	145	5.51
8-73-16-3	1°55'S	4 39	264	3 22
5-75-10-5	137° 28' W	4.59	204	3.44
8-73-20-5	1°55'9	4 30	200	3 28
0-15-20-5	137° 28'W	4.37	277	5.20

TADLE 2

TABLE 4 Interstitial Water 2CO₂, Leg 10

Sample	Location	Water Depth (km)	Sediment Depth (m)	ΣCO ₂ (mM/kg)
10-89-1-3	20° 53' N	3.07	4	4.16
10-95-2-3	95° 71'W 24° 09'N 86° 24'W	1.63	87	3.12
10-95-3-5	24° 09' N 86° 24' W	1.63	129	3.05
10-95-5-4	24° 09' N 86° 24' W	1.63	202	2.51

and/or dolomite should be only partially responsible for the decrease in ΣCO_2 in the interstitial water.

The samples from Site 147B (Cariaco Basin) exhibit more irregular distribution of ΣCO_2 in the interstitial water (Figure 7); however, the general trend is similar to that observed at Site 148 in that it increases rapidly with depth

TABLE 5 Interstitial Water ΣCO₂, Leg 11

Sample	Location	Water Depth (km)	Sediment Depth (m)	ΣCO ₂ (mM/kg)	
11-99A-1-4	23°41'N N 73°51'W	4.91 9		1.40	
11-101-1-5	1-1-5 25°12'N 4.87 49 74°26'W 1-2-3 25°12'N 4.87 80 74°26'W		49	9.07	
11-101-2-3			12.15		
11-101A-2-5	25° 12' N 74° 26' N	4.87	172	11.34	
11-102-2-5	30° 44' W 74° 29 N	3.43	34	26.24	
11-102-5-5	30°44'W 74° 29'N	3.43	149	13.93	
11-102-11-2	30°44'N 74°29'W	'N 3.43 364 'W		4.90	
11-104-2-5	30 [°] 50'N 74 [°] 20'W	3.81	52	22.91	
11-104-4-5	30 [°] 50'N 74 [°] 20'W	3.81	149	33.05	
11-104-6-5	30 [°] 50'N 74 [°] 20'W	3.81	235	33.21	
11-106-1- 2	36 [°] 26'N 69 [°] 28'W	4.49	20	4.95	

TABLE 6 Interstitial Water 2CO₂, Leg 12

Sample	Location	Water Depth (km)	Sediment Depth (m)	ΣCO ₂ (mM/kg)		
12-112-3-6 54°01'N 46° 36'W		3.66	158	0.47.		
12-112-4-2	54° 01'N 46° 36'W	3.66	202	1.40		
12-112-5-5	54° 01'N 46° 36' W	3.66	277	2.30		
12-112-9-4	54°01'N 46°36'W	3.66	311	2.47		
12-116-4-6	57° 30'N 15° 56'W	1.15	217	4.57		
12-116-5-6	57° 30'N 15° 56'W	1.15	268	5.79		
12-116-6-4	57° 30'N 15° 56'W	1.15	314	4.62		
12-116-9-2	57° 30'N 15° 56'W	1.15	461	4.12		
12-118-2-6	45°03'N 9°00'W	4.90	208	4.14		
12-118-3-3	45°03'N 9°00'W	4.90	308	3.72		
12-118-4-3	45°03'N 9°00'W	4.90	358	5.82		
12-118-5-3	45° 03'N 9° 00'W	4.90	407	5.94		

down to 10 meters and decreases with depth below 10 meters down to 50 meters. A maximum ΣCO_2 value of 15 mM/kg was observed at a depth of 7 to 8 meters and is nearly six times the ΣCO_2 value in the bottom seawater.

Legs 6, 7, 8, 10, 11, and 12

In contrast to the Site 148 (Leg 15) profile, in which a systematic trend in ΣCO_2 distribution was observed, no obvious trend in ΣCO_2 distribution is observable in the profiles obtained for Legs 6, 7, 8, 10, 11, and 12 (Figures 2-5). The lack of observable trend may be attributed to the small number of samples analyzed for each sampling site. The trend clearly observed in Sites 147B and 148 (Figures 6-8), Leg 15, for the upper 50 meters is that ΣCO_2 in the interstitial water is greater than in the overlying seawater. Hence, CO_2 should be diffusing from the sediments to seawater. On the other hand, some data for Leg 6 (Figure 2) show a decreasing trend of ΣCO_2 with depth and, hence, suggest that CO_2 in seawater is diffusing into the sedimentary column.

One of the most unusual features in ΣCO_2 distribution was observed at Sites 102 and 104, Leg 11, which were located on the Blake-Bahama Outer Ridge at 30°51'N and 74°20'W, approximately midway between Cape Kennedy and Bermuda Island. Extremely high ΣCO_2 values ranging from 22 to 33 mM/kg were observed in this profile (Figure 5). The sediments from which the interstitial water samples were obtained are of middle Miocene age and contain about 10 percent carbonate. No obvious explanation for such extreme CO_2 concentrations can be given on the basis of core descriptions. However, it is speculated that if the Blake-Bahama Outer Ridge is a manifestation of igneous activities, the observed high ΣCO_2 in the interstitial water could be attributed to igneous emanations.

Degree of Saturation of Carbonates in Interstitial Waters

The major ion concentration data cited in this volume by Gieskes, Sayles and Manheim, and Presley and Kaplan for Site 148, Leg 15, indicate that, in sediment depth greater than 100 meters, the Mg/Ca concentration ratio in interstitial water decreases with increasing sediment depth. These observations suggest that dolomitization might be taking place in this depth range. Therefore, the degree of saturation of dolomite in the interstitial water samples was calculated in order to test such a hypothesis for the change in Mg/Ca ratios. However, the results of the calculation depend sensitively on the assumption that no CO₂ loss and no reaction between carbonate sediments and interstitial water took place during the handling of the core and water samples. Since the presence of CO2 loss and the occurrence of chemical reactions between sediments and interstitial water have been suspected by Gieskes (this volume) and by Hammond (this volume), the following discussion should be considered as valid only when such perturbations in the water sample did not take place.

The degree of saturation of calcite in the interstitial water samples decreases almost linearly with depth from 2.0 at 87 meters to 0.4 at 210 meters (Figure 9). At 210 meters (Sample 15-148-23-4), the activities of uncomplexed Ca⁺⁺, Mg⁺⁺, and CO₃⁼ ions were calculated to be 2.83 × 10⁻³, 1.22 × 10⁻², and 1.05 × 10⁻⁶ respectively at the in situ temperature of 12.1°C. The ion activity product for calcite ($a_{Ca}^{++} \times a_{CO_3}^{-}$) is thus 3.0 ×10⁻⁹ and that for dolomite ($a_{Ca}^{++} \times a_{Mg}^{++} \times a_{CO_3}^{-2}$) is 3.8 × 10⁻¹⁷.

		Water	Sadimant				T(°	C)	Carbonata			ICDC	Satura
Sample Location	Depth Depth $\Sigma CO_2 p CO_2^a$ Cal ocation (m) (m) (mM/kg) (mb)	Calculated pH ^a	Equili- bration ^b	Equili- bration ^b In situ (meq/kg)	Alkalinity (meq/kg)	рН ^с	IAP ^c 10 ⁻⁸	$\frac{10^{-6}}{(m/kg)^2}$	tion Factor ^d				
15-147B-1-3	10° 42'N 65° 10'W	0.89	6	15.01	6.05	7.90	25	17.2	15.60	7.96	2.23	2.68	4.1
15-147B-1-4 (15-33)		0.89	7	13.43	-	2	\simeq		-		-		-
15-147B-1-4 (57-95)		0.89	7	14.62	8.53	7.75	25	17.3	14.89	7.80	0.90	1.03	1.6
15-147B-2-2		0.89	13	8.18	2.70	7.95	25	17.6	8.64	8.02	3.43	4.97	7.7
15-147B-2-6		0.89	20	12.50	2.43	8.20	25	18.0	13.62	8.25	4.49	5.08	7.9
15-147B-6-2		0.89	52	9.49	2.26	8.15	25	19.8	10.08	8.18	2.83	2.48	3.9
15-148-1-4A	13° 25' N 63° 43' W	1.23	7	3.18	1.28	7.94	25	8.9	3.78	8.14	1.41	1.99	2.7
15-148-1-4B		1.23	7	3.60	1.51	7.87	25	8.9	3.74	8.07	1.20	1.70	2.3
15-148-2-1		1.23	10	2.91	2.08	7.65	25	8.9	2.94	7.83	0.48	0.65	0.9
15-148-3-3		1.23	22	5.21	2.78	7.78	25	9.1	5.34	7.95	1.14	1.57	2.1
15-148-4-3		1.23	32	4.80	2.51	7.78	25	9.2	4.93	7.96	1.08	1.47	2.0
15-148-7-3A		1.23	59	7.59	3.24	7.88	25	9.6	7.87	8.04	1.77	2.19	3.0
15-148-7-3B		1.23	59	7.54	5.45	7.65	25	9.6	7.60	7.79	1.02	1.26	1.7
15-148-8-3		1.23	68	7.70	4.79	7.72	25	9.7	7.82	7.87	1.15	1.40	1.9
15-148-10-3		1.23	87	6.54	3.33	7.81	25	10.1	6.70	7.95	1.29	1.51	2.0
15-148-12-4		1.23	107	4.71	2.45	7.80	25	10.4	4.82	7.93	1.04	1.10	1.5
15-148-18-2		1.23	159	2.86	2.82	7.53	25	11.3	2.83	7.61	0.61	0.66	0.9
15-148-20-3		1.23	180	3.24	2.98	7.57	25	11.6	3.33	7.37	0.38	0.40	0.5
15-148-23-4		1.23	210	2.88	3.07	7.51	25	12.1	2.94	7.30	0.30	0.32	0.4

 TABLE 7

 Carbonate Chemistry Data: Pore Water Samples, Leg 15

^aAt equilibration temperature.

^bDue to the lack of data, the equilibration temperature was estimated.

^cIon activity product, concentration product, and pH at in situ temperature and 1 atmosphere.

dAt in situ temperature and pressure.



Figure 2. Plot of the total dissolved CO_2 in the interstitial water samples collected during Leg 6 versus the sediment depth. The CO_2 concentrations are given in millimoles of CO_2 dissolved in one kilogram of interstitial water.

These values are compared with the thermodynamic equilibrium values for calcite and dolomite in the table below:

	$(a_{Ca}^{HAP}+aCO_{3}^{=})$	$(a_{Ca^{++}} a_{Mg^{++}} a^2 CO_3^{=})$
Sample solutions 148-23-4 (12.1°C, 1 atm)	3.0 × 10 ⁻⁹	3.8 × 10 ⁻¹⁷
Thermodynamic equilibrium value for calcite (12.1°C and 1 atm)	5.6 × 10 ⁻⁹	5
Thermodynamic equilibrium value for dolomite (12.1°C and 1 atm)	-	4.7 × 10 ⁻²¹

It appears that the interstitial water is undersaturated with respect to calcite but is supersaturated as much as four orders of magnitude with respect to dolomite. This means that dolomite is being formed while calcite is being dissolved.

SUMMARY AND CONCLUSIONS

1. The results of 100 analyses for the total dissolved CO_2 in the interstitial water samples collected during Legs 6, 7, 8, 10, 11, 12 and 15 are reported. The total CO_2 values from the open-ocean cores range mostly between 2 mM/kg and 5mM/kg. However, unusually high values up to 33 mM/kg were observed in the samples from the Blake-Bahama Outer Ridge (Leg 11).

2. The total CO₂ values at Site 148, Leg 15, show a maximum at a depth of about 70 meters (Figure 6). This indicates that CO₂ is migrating in the ocean water through the seawater-sediment interface as well as into the deeper region of sediments. Correlation observed between the total CO₂ concentrations and SO₄⁼ concentrations in this core suggests that CO₂ is formed by a reaction between organic debris and SO₄⁼.

3. Assuming that neither CO_2 loss nor chemical reaction between sediments and interstitial waters took place during handling and sampling, the degree of saturation of calcite and dolomite in the interstitial waters was calculated using the chemical model of saline waters proposed by Simpson and Takahashi (this volume). At Site 148, the interstitial water appears to be supersaturated with respect to calcite above 150 meters, but becomes undersaturated below this



Figure 3. Plot of the total dissolved CO_2 in the interstitial water samples collected during Leg 7 versus the sediment depth.

depth (Figure 9). On the other hand, the interstitial water below 150 meters appears to be supersaturated with respect to dolomite. Hence, a favorable condition for dolomitization appears to exist at sediment depths below 150 meters.

4. The total CO_2 values at Sites 147 and 148, Leg 15, are proportional to the total alkalinity values obtained by Gieskes (this volume). The observed slope of $\Delta A/\Delta \Sigma CO_2$ = 1 suggests that the precipitation and/or solution of carbonates are only partially responsible for the observed changes in the chemical composition of interstitial waters.

ACKNOWLEDGMENTS

We thank Lee Waterman, David Bos, and Richard DuBois for collecting samples on board the R/V *Glomar Challenger* and Ross Horowitz for preparing sample containers. J. Scott Weaver provided valuable assistance in computational procedures.

This work was partially supported by Atomic Energy Commission Grants AT (30-1) 2493 and AT (30-1) 2663 and by the Deep Sea Drilling Project. A portion of the computational equipment used in this work was purchased by a grant from the Research Foundation of the City University of New York, No. 1188.

REFERENCES

- Broecker, W. S. and Takahashi, T., 1966. Calcium carbonate precipitation in the Bahama Banks. J. Geophys. Res. 71, 1575.
- Garrels, R. M. and Thompson, M. E., 1962. A chemical model for seawater at 25°C and one atmosphere total pressure. Am. J. Sci. 260, 57.
- Harned, H. S. and Scholes, S. R., 1941. The ionization constant of HCO₃⁻ from 0 to 50°. J. Am. Chem. Soc. 63, 1706.
- Harned, H. S. and Davis, R., 1943. The ionization constant of carbonic acid in water and the solubility of carbon dioxide in water and aqueous salt solutions from 0°, to 50°C, J. Am Chem. Soc. 65, 2030.
- Kester, D. R. and Pytkowicz, R. M., 1968. Magnesium sulfate association at 25°C in synthetic seawater. J. Lim. Ocean. 13, 670.
- _____, 1969. Sodium, magnesium and calcium sulfate ion-pairs in seawater at 25°C. J. Lim. Ocean. 14, 686.
- Langseth, J. G. and Grim, P. J., 1964. New heat-flow measurements in the Caribbean and western Atlantic. J. Geophys. Res. 69, 4916.
- Li, Y. H., Takahashi, T., and Broecker, W. S., 1969. Degree of saturation of CaCO₃ in the oceans. J. Geophys. Res. 74, 5507.



Figure 4. Plot of the total dissolved CO₂ in the interstitial water samples collected during Legs 10 11, and 12 versus the sediment depth.

- Li, Y. H. and Tsui, F. T., 1971. The solubility of CO₂ in water and seawater. J. Geophys. Res. 76, 4203.
- McIntyre, W. G., 1965. The temperature variation of the solubility product of calcium carbonate in seawater. Fisheries Res. Board, Canada. Manuscript Report Series, No. 200, 153.
- Manheim, F. T. and Sayles, F. L., 1971a. Interstitial water studies on small core samples, Deep Sea Drilling Project, Leg 6. In Fischer, A. G., Heezen, B. C. et al., 1971. Initial Reports of the Deep Sea Drilling Project, Volume VI. Washington (U. S. Government Printing Office). 811.
- , 1971b. Interstitial water studies on small core samples, Deep Sea Drilling Project, Leg 8. In Tracey, J. I., Jr., Sutton, G. H. et al., 1971. Initial Reports of the Deep Sea Drilling Project, Volume VIII. Washington (U. S. Government Printing Office). 857.
- Presley, B. J. and Kaplan, I. R., 1971a. Interstitial water chemistry: Deep Sea Drilling Project, Leg 6. Initial

Reports of the Deep Sea Drilling Project, Volume VI. Washington (U. S. Government Printing Office). 825.

- , 1971b. Interstitial water chemistry: Deep Sea Drilling Project, Leg 8. In Tracey, J. I., Jr., Sutton, G. H. et al., 1971. Initial Reports of the Deep Sea Drilling Project, Volume VIII. Washington (U. S. Government Printing Office). 853.
- Pytkowicz, R. M. and Fowler, G. A., 1967. Solubility of Foraminifera in seawater at high pressures. Geochem. J. 1, 169.
- Sayles, F. L. and Manheim, F. T., 1971. Interstitial water studies on small core samples, Deep Sea Drilling Project, Leg 7. In Winterer, E. L., Riedel, W. R. et al., 1971. Initial Reports of the Deep Sea Drilling Project, Volume VII. Washington (U. S. Government Printing Office). 871.
- Waterman, L., 1972. Manual for extraction of pore water samples. Deep Sea Drilling Project publication.





Figure 5. Plot of the total dissolved CO₂ in the interstitial water samples collected during Legs 10, 11, and 12 versus the sediment depth.

Figure 6. Plot of the total dissolved CO_2 in the interstitial water samples collected at Site 148, Leg 15 (Aves Ridge) versus the sediment depth. The data point at the 0 meters sediment depth indicates the ΣCO_2 value for the bottom seawater.



Figure 7. Plot of the total dissolved CO₂ in the interstitial water samples collected at Site 147, Leg 15 (Cariaco Basin) versus the sediment depth.



Figure 8. Plot of ΣCO_2 versus the total alkalinity measured by Gieskes (this volume) for the samples collected at Sites 147 and 148, Leg 15.



