12. INTERSTITIAL WATER STUDIES, LEG 15 – STUDY OF CO₂ RELEASED FROM STORED DEEP SEA SEDIMENTS¹

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ABSTRACT

Thirty-five samples of deep sea sediments were collected on DSDP Leg 15 and stored in sealed kettles for over a year. The PCO₂ of these kettles was monitored as a function of time and temperature. When CO₂ is removed for analysis, the decrease observed in kettle PCO₂ is consistent with the assumption that equilibration of water and calcite controls the alkalinity and pH of the interstitial water. An empirical relation between Σ CO₂ and PCO₂ is selected which allows correction for CO₂ removal and comparison of PCO₂ to other carbonate parameters (i.e., pH) measured on Leg 15. The resolution of the data is limited, but pH and PCO₂ appear to be consistent within 0.1 pH units.

Calculation of the degree of calcite saturation is used to suggest that pressure may significantly influence ionic equilibria between clay and pore waters, causing samples from Site 149 to appear understaurated with calcite.

Sediment samples from regions with strong $[SO_4^{=}]$ gradients show increases in PCO₂ with time, indicating active sulfate reduction continuing in the kettles. Comparison of the CO₂ generation rate in the laboratory with that in situ at Sites 147 and 148 suggests that the process may be limited by the availability of suitable organic substrates, which is a function of temperature.

INTRODUCTION

The carbonate chemistry of the interstitial fluids of deep sea sediments presents a challenging problem to geochemists. The system, defined here as including alkalinity, total CO₂, pH, the partial pressure of CO₂ (PCO₂), Ca⁺⁺ (titrated Ca), total HCO₃⁻⁻, and total CO₃⁼, may be completely defined by a knowledge of any two parameters, the equilibrium constants of the reactions which relate them, and the degree of calcite saturation.

A number of processes may affect the system:

1) Bacterial oxidation of organic matter to produce CO_2 .

2) Solution and precipitation of carbonate minerals.

3) Cation and hydroxyl exchange between clay minerals and interstitial water which may be very important in buffering pH.

4) Solution of conjugate bases such as NH_3 , $PO_4^=$, FeO, and reduction of weak bases to stronger bases (such as $SO_4^=$ to $S^=$).

In an attempt to study these processes, and also to evaluate the pH measurements made on shipboard, 35 samples of sediment were collected in sealed kettles on DSDP Leg 15 and returned to Lamont-Doherty Geological Observatory where the PCO₂ was monitored as a function of time and temperature. Thirteen of these samples are from the Cariaco Trench (Site 147), twelve from the Aves Rise (Site 148), and ten from the Venezuelan Basin (Site 149). One core-storage kettle was broken in transportation.

These three sites are interesting to geochemists, because they cover a wide range of sedimentary and chemical environments. The Cariaco Trench is a structural depression on the continental shelf surrounded by water less than 200 meters deep. Because it is separated from the deep water of the Caribbean Sea and receives a large amount of organic material, its bottom water has become anoxic and has an unusually high temperature (17°C). Site 147 (882 m below sea level) is a rather uniform calcareous clay with authigenic dolomite, calcite, and pyrite. A high sedimentation rate (50 $cm/10^{3}y$) prevails, the material is rich in organic material (dry weight carbon $\approx 2\%$), and is consequently an anaerobic environment. The Venezuelan Basin is a deep (Site 149 is 3472 m below sea level), open basin with low organic content (~0.1%), and low sedimentation rate (Av. $0.8 \text{ cm}/10^3 \text{y}$). Sulfate changes very little with depth in the core, indicating limited biological activity. The sediment changes from a calcareous clay above 250 meters to a diatom ooze below. The Aves Rise site (1223 m deep) is also a calcareous clay with an average sedimentation rate of $3 \text{ cm}/10^3 \text{y}$. Sulfate is reduced in the upper 100 meters of the sediment.

COLLECTION AND ANALYTICAL PROCEDURE

The shipboard handling of samples is described in Horowitz et al. (this volume). Briefly, a 10 to 15 cm section was cut from the core and moved to a dry box flushed with

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argon. In an effort to avoid oxidation, the sediment surface was scraped away and the remainder sealed in kettles for storage. The kettles were approximately half filled with sediment. CO_2 loss from the sediment during this process and during coring is difficult to estimate, but should be small except for samples from the Cariaco Trench where the gas content was so high it caused difficulties in drilling. The gas pressure was sometimes sufficient to blow the sediment out from the pipe on the ship. The kettles were refrigerated ($T = \sim 4^{\circ}C$) from the time of collection until the first set of measurements was carried out, about 5 months later. While still refrigerated, an aliquot of gas (about 1/6 of the total) was taken from each kettle for infrared (IR) analysis and the kettle refilled with nitrogen to about 1 atmosphere total pressure. To determine the CO² content, each gas sample was diluted 10 to 50 times with N² and compared with laboratory standards. Results are listed in Table 1.

TABLE 1 Partial Pressure of CO₂ at 4°C and 22°C

÷	Depth (m)	DSDP No.	Sample Interval (cm)	4°C		22° C				
Kettle				PCO2 ^a (mb)	Np _{CO2} ^c (mmol/1)	p _{CO2} ^a (mb)	Np _{CO2} ^d (mmol/1)	p _{CO2} ^b (mb)	^p CH4 ^b (mb)	p _{CO2} ^a (mb)
Number										
15-147 C	ariaco Tr	ench (10°42.6	5'N, 65°10).46'W) D	epth below s	ea surface:	882 m.			
1	4.2	147B-1-3	93-110	9.92	1.3	20.4	2.4	18.7	n.d.	19.7
2	2	147A-1-2	60-96	(0.284)	12	_	_			-
3	5.2	147B-1-4	95-110	6.45	0.87	13.2	1.6	13.5	n.d.	13.7
4	14	147B-2-2	38-53	4.47	0.45	7.64	1.6	(4.30)	n.d.	1.1.1.1.1.1.1.1.1.1.1.1.1.1.1.1.1.1.1.1.
5	20	147B-2-6	38-53	11.1	1.2	20.7	2.2	19.3	8.46	-
6	4.5	147B-1-4	2-15	7.95	0.77	16.4	1.4	16.5	n.d.	17.7
7	56	147B-6-2	96-140	933	14	13.0	3.1	12.9	0.924	_
8	64	147B-7-4	77-97	127	1.6	25.9	4 5	16.6	1.70	
0	84	1478.0.4	111.126	21.1	2.8	50.7	73	46.2	6.70	24
10	104	1470-9-4	60.94	16.2	2.0	22.6	6.4	20.4	1.20	
10	104	1470-2-2	09-04	10.5	2.5	22.0	5.2	19.0	0.2	100
11	120	1470-2-2	0-41	12.5	1.0	21.0	5.2	10.9	0.5	11.0
12	148	14/C-4-4	0-34	12.2	1.7	16.0	4.5	11.9	~0.1	11.0
13	177	147C-7-4	119-129	7.65	0.92	15.3	5.7	12.5	0.838	-
15-148 A	ves Rise	(13°24'N, 63°	°45'W) De	pth below	sea surface:	1223 m.				
14	6	148-1-4	135-150	2.04	0.23	5.84	0.67	5.87	n.d.	5.80
15	10	148-2-1	135-150	1.93	0.36	4.88	1.1	4.59	_	5.15
16	26	148-3-3	70-85	2.78	0.37	7.71	1.3	7.97	n.d.	7.78
17	35	148-4-3	120-135	2.47	0.29	6.81	1.0	5.98	n.d.	7.13
18	63	148-7-3	135-150	4.37	0.28	10.9	1.1	(15.0)		10.1
19	70	148-8-3	45-60	6.27	0.50	10.7	14	11.0	n.d.	_
20	90	148-10-3	45 00	2.85	0.19	8.09	19	8 64	n d	-
21	00	148-10-3		2.05	0.17	9.05	0.82	9.22	n d	947
21	107	148-10-5	75.00	2 99	0.21	6.66	1.1	6 38	1.17	6.70
22	107	140-12-4	00 105	2.00	0.21	6.75	1.1	7.00	0.59	0.70
23	161	140-12-4	90-105	2.74	0.19	5.19	0.60	1.53	3 36	
24	101	140-10-2	90-105	2.00	0.14	5.10	0.00	4.55	4.00	_
25	210	148-23-4	120-135	2.16	0.12	5.80	0.50	0.30	4.99	
15-149 \	enezuela	n Basin (15°0	6.25'N, 69	°21.95'W)	Depth below	w sea surfa	ce: 3472 m.			
26	73	149-9-5	135-150	1.06	0.073	3.33	0.32	2.94	n.d.	3.31
27	101	149-12-5	105-120	0.478	0.031	1.52	0.13	1.38	n.d.	1.52
28	136	149-16-4	0-15	1.95	0.15	2.45	0.28	2.14	n.d.	2.26
29	157	149-18-3	105-120	2.00	0.16	1.51	0.56	0.858	n.d.	0.943
30	3	149-2-2	135-150	1.27	0.12	1.80	0.19	1.37	n.d.	
31	23	149-4-3	135-150	1.18	0.11	2.91	0.31	2.49	n.d.	÷
32	230	149-26-2	105-120	5.65	0.49	8 32	1.01	7.25	n.d.	-
33	315	149-35-4	105-120	113	0.087	5.68	0.47	5.09	n d.	—
34	360	140.41.5	105-120	2.28	0.007	1.50	0.17	0.731	n d	_
54	309	147-41-2	105-120	2.20	0.20	1.59	0.17	0.751	n.u.	

^aGas chromatograph data.

^bInfrared data.

^cTotal CO₂ lost from 1 liter of pore water to gas phase in bottles before the first measurement at 4°C. (Calculated from estimated volume of the sample sediments and measured water content of nearby sediments. DSDP data).

^dTotal CO₂ lost from 1 liter of pore water before the first measurement at 22°C.

n.d.Not detectable.

When this set of measurements was completed, the kettles were removed from cold storage and allowed to sit at room temperature (T = $23^{\circ} \pm 1.5^{\circ}$ C). The extreme sensitivity of PCO2 to temperature (see Table 1 where PCO_2 at 22°C is a factor of 2 greater than PCO_2 at 4°C) indicated that a better control of temperature was needed. The kettles were moved to a thermostated laboratory and placed in styrofoam boxes where the temperature was nearly constant (22°±0.5°C) for 100 days. A set of PCO₂ measurements was then made (Table 1). One hundred days later, a second set of PCO2 measurements was made at 22°C. Some of this second set of measurements were made using IR analysis and all using a gas chromatograph (GC) which required only 0.5 cc of gas (about 1% of the gas in each kettle). At this time, the partial pressure of methane (PCH_4) was also determined in each kettle. All these results are listed in Table 1.

The radius of the core sediments is about 4 cm. If we take 2×10^{-5} cm²/sec as the diffusion constant for CO₂, a mean transportation distance for CO2 in the sediments in 100 days is calculated to be 14 cm. Tortuosity and porosity are not taken into account. However, cracks on the sediments are sufficient to cover their effects. Therefore the PCO_2 we measured is considered to be the PCO_2 of the carbonate system of pore waters. To establish the reliability of PCO₂, another comparison of pH measurements is made. Several kettles were opened and punch-in pH (PIpH) was determined with an Orion pH meter (model 801 digital pH/mV meter) and two electrodes (a Beckman No. 40471 glass electrode and an Orion 90-02 double junction reference electrode). They are listed in Table 2 along with two sets of pH calculated from the most recent PCO₂ measurements: one set was derived from PCO2 and Gieskes' (this volume) titration alkalinity, and one from PCO2 and calcium (see Gieskes; Presley et al.; Sayles et al.; Hammond, this volume), assuming calcite saturation.

 TABLE 2

 Comparison of Laboratory pH and pCO2

Kettle No.	p _{CO2} ^a (mb)	ALK ^b (meq/1)	Ca ^c (mmol/1)	pHd	рН ^е	pH ^f
9	46.2	29.14	5.61	7.35	6.99	7.11
19	11.0	8.08	5.12	7.38	7.31	7.25
20	8.64	6.90	5.02	7.42	7.36	7.30
21	9.47	6.90	5.02	7.38	7.34	7.39
22	6.70	5.62	5.59	7.45	7.39	7.50
23	7.00	5.62	5.59	7.43	7.38	7.41
28	2.14	2.32	21.99	7.52	7.35	7.35
30	1.37	2.44	10.03	7.73	7.62	7.53

^aMeasured at 22°C.

^bGieskes, this volume.

^cSee Hammond, this volume.

^dCalculated from alkalinity + pCO₂.

^eCalculated from calcium + p_{CO_2} (assume calcite saturation). ^fMeasured at 22°C (lab punch-in *p*H).

Average deviation: $(d-f) = \pm 0.12;$ $(e-f) = \pm 0.06.$ A third of the discrepancy between measured and calculated pH can be attributed to pH measurement error (±0.04 pH unit). The remainder is probably due to changes in Ca⁺⁺ and alkalinity which have occurred during storage (a discrepancy of 0.08 pH units could be explained by a 20% change during storage in ALK, [Ca⁺⁺], or a 20% error in the calcite saturation assumption). The reasonable agreement between measured pH and that calculated from PCO₂ and alkalinity indicates that the observed PCO₂ is close to being in equilibrium with the interstitial water after 100 days. The even closer agreement between measured pH (±0.06 pH unit, Table 2) and that calculated from PCO₂ and [Ca⁺⁺] is strong evidence that the water is in equilibrium with calcite and that [Ca⁺⁺] is less susceptible to change during storage than is alkalinity.

Derivation of the equilibrium constants used for this calculation is discussed in the following section.

EQUILIBRIUM CONSTANTS

The chemical equilibria of carbonate system in sea water can be shown as follows (Li, 1967):

For convenience, all aqueous terms are expressed as total concentration (free ion plus complexed species), and the equilibrium constants relating them are named apparent constants. $[H_2CO_3]$ represents the total of hydrated and molecular CO₂. Because the major ion concentrations in the pore water are different than in sea water, use of sea water apparent equilibrium constants in pore water is misleading. We applied the same modification as Hammond (this volume) by using Garrels and Thompson's (1962) model of major ion complexing in sea water:

$$K_1^* = \frac{f_{HCO_3}^-}{f_{HCO_3}^*} K_1^L$$
 (1)

$$K_2^* = \frac{f_{HCO_3}^*}{f_{HCO_3}^*} \cdot \frac{f_{CO_3}^*}{f_{CO_3}^*} K_2^L$$
(2)

$$K_{B}^{*} = \frac{f_{HCO_{3}}}{f_{HCO_{2}}^{*}} K_{B}^{L}$$
(3)

$$K_{sp}^{*} = \frac{f_{Ca^{++}}}{f_{Ca^{++}}^{*}} \frac{f_{CO_{3}}}{f_{CO_{3}}^{*}} K_{sp}$$
(4)

where

- f : fraction of free ions in total concentration.
- * : denote pore water quantities (others are sea water quantities).
- L : Lyman's apparent constants for sea water (Lyman, 1957).
- K_{sp}: apparent solubility product of calcite (MacIntyre, 1965).
- α : solubility of CO₂ in sea water (Li and Tsui, 1971).

Thus, using the major element data determined on squeezed water, equilibrium constants can be computed for each sample.

EFFECT OF TIME AND CO₂REMOVAL ON PCO₂

After 100 days, the gas and water should be in equilibrium. When the system is perturbed by removing CO_2 from the gas phase for analysis, a new equilibrium PCO_2 will be attained. This PCO_2 offers a clue about the interactions occurring between the water and the solid phases over this 100-day time span. Several mechanisms may operate when CO_2 is removed for analysis:

1) Solid phases and water do not exchange:

 ΣCO_2 = initial – gas removed

ALK = initial

2) Solid carbonate (calcite) equilibrates with the ΣCO_2 dissolved in the water:

 ΣCO_2 = initial – gas removed – calcite ppt.

ALK = initial $-2 \times$ calcite ppt.

 $[Ca^{++}] = initial - calcite ppt.$

 $[CO_3^{=}] = K_{sp}^* / [Ca^{++}]$

3) Clay minerals exchange ions with the solution keeping the pH constant:

 ΣCO_2 = initial – gas removed

pH = initial

4) Clay minerals fix pH and water equilibrates with calcite:

 ΣCO_2 = initial - gas removed + calcite dissolved [Ca⁺⁺] = initial + calcite dissolved [CO₃⁼] = K^{*}_{sp}/[Ca⁺⁺]

pH = initialFigure 1, the percent

In Figure 1, the percentage of PCO₂ change from the first set of 22°C measurements to the second set is plotted against the percentage of CO₂ removed (NPCO₂/ALK × 100, assuming titration alkalinity $\approx \Sigma CO_2$). Also plotted are curves representing cases 1, 2, 3, and 4. Cases 1 to 4 are quite similar for samples with low alkalinity and high

calcium, or those with high alkalinity and low calcium. If there were no CO_2 released from sediments to the gas phase in the kettle, after an aliquot of gas was removed for IR, analysis PCO₂ would be reduced by 15 to 22% (see A, B in Figure 1). However, almost all the points distribute along a line traversing cases 1, 2, 3, and 4. The deviation of all the points are caused by the following factors:

1) Molecular diffusion of CO_2 .

- 2) Reactions between sediments and pore water.
- 3) Bacterial activities.

If diffusion controls the PCO_2 , all the points should lie on the line representing case 1. However, almost all of them traverse it toward reactions lines (cases 2, 3, 4) and even cross case 4 to the region where PCO_2 increases.

The group of samples (solid symbols) showing an increase in PCO_2 may be attributed to CO_2 production by sulfate-reducing bacteria and will be discussed later. Many of the remainder (open symbols) fall between cases 1 and 2, indicating that some exchange takes place between solid and aqueous phases. Although it is possible that the silicate phases may contribute to this exchange, the change in PCO_2 can be explained by assuming that calcite precipitation is the mechanism controlling pH and alkalinity in the system over this time span.

Magnesium-rich coatings (Weyl, 1967) and organic coatings (Chave, 1965; Suess, 1970) have been shown to inhibit equilibration between calcite and sea water, and Cooke (1971) has shown that the composition of the fluid may control the chemistry of the surface rather than vice versa. Apparently some of these processes prevent the attainment of complete equilibration.

Although suggesting short-term pH and alkalinity control by carbonate minerals, these observations do not eliminate the possibility that clay minerals exert strong influences, i.e., ion exchange and pH buffering, over the longer time span available for diagenesis.

CONSISTENCY OF LABORATORY PCO₂ AND SHIPBOARD *p*H MEASUREMENTS ON INTERSTITIAL WATER

One purpose of this study was to test the consistency of pH and PCO_2 measurements. To do this, a relation must be found between PCO_2 and the CO_2 removed for analysis. Since stochiometric reactions (such as calcite equilibration) cannot be written, the best approach is to extrapolate the dashed line on Figure 1 to the amount of CO_2 removed before the first analysis. This should be comparable to the conditions under which warm squeezed (WS) samples were collected. The slope of the line is -5, i.e., for every percent of initial ΣCO_2 removed, there is 5 percent decrease in PCO_2 . The same correction can be made for PCO_2 measurements at 4°C, enabling them to be compared with cold squeezed (CS) samples. These extrapolations are plotted in Figure 5.

Figure 2 schematically illustrates the calculation models used to compute pH. In one series (model A), the extrapolated PCO_2 , the titration alkalinity, and the calcium data were used to compute ΣCO_2 and the degree of calcite saturation at the storage temperature (T_S) (saturation results are discussed in the following section). This ΣCO_2



Figure 1. PCO_2 change between two successive measurements at $22^{\circ}C(\Delta PCO_2/PCO_2)$ vs. the ratio of CO_2 removed for analysis to total alkalinity ($NPCO_2/ALK$). (Solid symbols are in or near regions of strong sulfate gradients; dashed line is chosen to relate PCO_2 and ΣCO_2 ; see text for explanations of model curves.)



Figure 2. Flowchart of calculation for comparing extrapolated PCO₂ data with other pore water data ($T_s = 4^\circ$ or 22°C: temperature of squeeze and storage; $T_m =$ temperature of which pore water pH was measured; dashed boxes are calculations done only on 4°C PCO₂).

and the alkalinity were then used to calculate pH at the pH measurement temperature (T_M , model A'). To estimate the effect on pH which could be caused by calcite precipitation between water collection and pH measurement, model A* was used, which assumes that calcite precipitates until it reaches saturation. Models A'' and A** were used to calculate PCO₂ at 22°C on the basis of the 4°C PCO₂ measurements. They have the same constraints as A' and A* and the results are compared to the 22° extrapolated PCO₂ in Figures 5a-c.

The second approach (model B) was to take $[Ca^{++}]$ and PCO₂ and, assuming calcite saturation, calculate ΣCO_2 , and alkalinity. These two quantities were used, as in model A, to obtain model B' (*p*H calculated from ΣCO_2 and ALK at T_M) and model B* (*p*H of calcite-equilibrated solution). Models B'' and B** were used for calculation of PCO₂ at 22°C from the 4°C measurements (Figures 5a-c).

The results of models A', A*, B', B*, and the pH measurements are plotted in Figures 3a-c for 4°C samples and in Figures 4a-c for 22°C samples. In Site 148 and the upper 50 meters of Site 147, model pH is consistently 0.2 pH units lower than the observed values. This may be attributed to CO_2 production in $SO_4^{=}$ reducing regions and will be discussed later. The remaining regions show general agreement (about 0.1 pH units) between the cluster of four model pH values and the observed value. Unfortunately, there is insufficient resolution to choose one of the four models as superior, and all that can be established is a rather crude agreement of about 0.1 pH units between calculated pH and measured pH. The models are interesting in illustrating the effect calcite precipitation between collection and pH measurement can have on pH, usually a decrease of about 0.1 pH unit.

The extrapolated PCO_2 (at $22^{\circ}C$ and $4^{\circ}C$) is plotted in Figure 5a-c for comparison to that predicted from the $4^{\circ}C$ PCO_2 with models A", A**, B", B**. Again, the sulfatereducing regions show higher observed PCO_2 than the models predict, suggesting the continuance of CO_2 production. The other regions show crude agreement (about 25%) between observed and model PCO_2 , but again the data lack sufficient resolution to choose a superior model.

It has been suggested (Hammond, this volume) that an increase in temperature, which causes uptake of divalent cations and release of univalent cations (see Table 3), may also cause release of H^+ ion (or uptake of OH⁻) and solution of carbonate. This effect would make the observed PCO₂ only about 10% greater than the model PCO₂, and cannot be resolved.

DEGREE OF CALCITE SATURATION

The problem of calcite saturation has been discussed extensively in the literature and, as pointed out earlier, calcite and water are rarely in equilibrium. Keeping this in mind, the degree of saturation (DS) of calcite is defined as:

$$DS = [Ca^{++}] [CO_3^{-}] / K_{sp}^{*}$$

DS was calculated using the extrapolated PCO₂, [Ca⁺⁺], and alkalinity (from Gieskes; Presley et al., Sayles et al., and Hammond, this volume). Results are listed in Table 4 and show considerable variation with temperature and from hole to hole. The high values (≈ 1.8) in the Cariaco Trench are probably due to CO2 loss which has not been corrected for during sediment collection, and consequently the extrapolated PCO₂ is too low. The 4°C results on samples from the Aves Rise are reasonable but the 22°C results appear undersaturated. As mentioned earlier, many of these samples appeared to have active sulfate reducers which had been at work longer and at a higher CO₂ production rate (as will be shown later) before the 22°C measurements than before the 4°C measurements. Since the PCO2 was observed to increase with time despite CO2 removal for analysis, the extrapolated PCO2 was probably much too high.

Sediments from the Venezuelan Basin appear to be considerably undersaturated by nearly the same degree calculated by Hammond (this volume) with pH and alkalinity measurements. The cause of this discrepancy is not obvious, but the answer probably lies in the effects of pressure on ionic equilibria between water and silicate phases. The DS calculated by Hammond for Sites 147, 148, and 149 shows smaller values for progressively deeper sites. If a decrease in pressure favors a rapid ion exchange reaction between clays and water, which might be written as

$$Na^{+})_{clay} + Ca^{++} + H_2O \rightarrow Na^{+} + H^{+} + Ca^{++})_{clay} + OH^{-})_{clay}$$

and perhaps be driven by a net increase in volume for the system, the alkalinity of the water would appear smaller and the pH more acid than in situ conditions. If the kinetics of calcite solution are not sufficiently rapid for equilibrium to be re-attained before squeezing takes place, the water will appear undersaturated. It is interesting to note that one sample (149-16-4-WS) was squeezed overnight and had an alkalinity 25 percent greater than the corresponding CS



Figures 3a-c. Comparison of the measured cold squeeze pH with those calculated with different models (see Figure 2).

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Figures 4a-c. Comparison of the measured warm squeeze pH with those calculated with different models (see Figure 2).

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Figures 5a-c. Comparing the extrapolated PCO₂ at 22°C with those calculated from different models using the extrapolated PCO₂ at 4°C. (See dashed boxes in Figure 2.)

		Na ^b				Kb			
	Location	Cold	Warm	Δ(W-C)	(W-C)/C	Cold	Warm	∆(W-C)	(W-C)/C
1.	Cariaco Trench ^e	466.1	470.4	+4.3	+0.93%	7.98	9.41	+1.43	+17.9%
2.	Aves Rise ^e	462.2	467.8	+5.6	+1.2 %	7.57	9.23	+1.66	+21.9%
3.	Venezuelan Basine	464.3	470.4	+6.1	+1.3 %	6.73	7.78	+1.05	+15.6%
4.	San Pedro Basin ^a	-	_			-			+13.3%
			Ca ^c			Mg ^c			
		5.60	5.58	-0.02	-0.4%	39.0	36.7	-2.3	-5.9%
		7.95	7.56	-0.39	-4.9%	46.1	42.9	-3.2	-6.9%
		21.2	19.3	-1.9	-9.1%	44.3	42.8	-1.5	-3.4%
				177	-4.9%		-	-	-2.5%
			Clb			ALK ^c			
		543.1	543.1	±0	±0	20.14	20.44	+0.30	+1.5%
		549.4	555.1	+1.7	+0.3%	4.37	4.50	+0.13	+3.0%
		553.9	555.0	+1.1	+0.2%	2.57d	2.57d	±0.00	±0.0%
		-	-		+1.4%	C			—

TABLE 3 Effects of Squeezing Temperature on Some Major Elements

^aBischoff et al., 1970; $T_C = 5^{\circ}C$; $T_W = 22.5^{\circ}C$.

^bSayles et al., this volume.

^cGieskes, this volume.

^dIn upper 16 samples (0 - 230 m), average warm squeeze datum (2.54) is higher than cold datum (2.49) by 1.9%. In lower 8 samples (259 - 379 m), average warm squeeze datum (2.64) is lower than cold datum (2.74) by 3.2%. For the whole core, the average change is zero.

^eConcentration in mmol/1. $T_C = 4^{\circ}C$; $T_W = 22^{\circ}C$.

sample, which was squeezed for only 30 minutes. Almost all other samples had CS and WS alkalinities within a few percent of each other. The longer time available for calcite equilibration in this WS sample after a rapid clay reaction could be the source of this anomaly. Thus, the DS calculations from PCO₂ portray a picture similar to those from *p*H. Their divergence from the equilibrium value of 1.0 is probably due to the unmeasured amounts of CO₂ lost during sampling and changes in pore water alkalinity during storage.

CO₂GENERATION DURING STORAGE

In Figure 1, one group of samples showed PCO₂ increases with time. Virtually all of these came from, or just below, regions which showed strong gradients in $[SO_4^{=}]$, implying that viable communities of $SO_4^{=}$ reducers (i.e., CO₂ producers) are present in these sediments. The distance of each point from the dashed line in Figure 1 on the NPCO₂/ALK axis should approximate the amount of CO₂ generated over the 100 day period. Plotting this against $[SO_4^{=}]$ (Figure 6) shows little correlation, although an unexplained correlation exists between NPCO2/ALK and $[SO_4^{\approx}]$ (not shown). Apparently, in these sediments, the rate at which CO₂ is produced is independent of $[SO_4^{=}]$ and depth and may, instead, be limited by the rate at which suitable organic substrates are produced. Although the stoichiometry of the reaction is uncertain, it might be postulated as

$$2C(\text{org.}) + SO_4^{=} + 2H_2O \rightarrow 2HCO_3^{-} + H_2S$$
$$H_2S + FeO \rightarrow FeS + H_2O$$
$$Ca^{++} + 2HCO_3^{-} \rightarrow CaCO_3 + H_2O + CO_2$$

so one unit of CO_2 (i.e., NPCO₂) is produced per unit of $SO_4^{=}$ reduced. From Figure 6, the average production rate is 3×10^{-1} mmol/1 per 100 days or 3×10^{-6} mol/1 day. This can be compared with the in situ rate by fitting a steady state model to the observed [SO₄⁼] profile. Choosing

$$D\frac{d^2C}{dz^2} = R$$

and solving

$$C_z = C_0 + C_1 z^2 + C_2 z$$

where

$$C_{z} = [SO_{4}^{=}] \text{ at depth } z$$

$$C_{O} = [SO_{4}^{=}] \text{ at depth } 0$$

$$C_{1} = R/2D$$

$$C_{2} = \frac{d[SO_{4}^{=}]}{dz} \Big|_{z=0}$$

	Depth (m)	Ca ⁺⁺ (r	nmol/l) ^a	ALK (meq/1) ^a	D.S.	
No.		C.S.	W.S.	C.S.	w.s.	4°C	22°C
15-147 C	ariaco Trench						
1	4.2	3.6	3.56	17.7	17.72	1.53	1.53
6	4.5	1.5	1.98	17.6	17.60	0.85	1.23
3	5.2	1.75	1.72	15.2	15.17	1.03	0.93
4	14	9.1	9.25	8.18	7.90	1.70	1.55
5	20	4.2	4.09	13.8	14.22	0.93	1.11
7	56	3.5	3.58	20.0	10.06	0.42	0.61
8	64	5.23	5.23	24.6	24.64	3.45	3.36
9	84	6.15	5.61	27.8	29.14	1.88	2.20
10	104	5.45	5.85	30.0	34.23	3.80	7.82
11	128	6.15	6.00	32.9	32.89	7.15	8.54
12	148	6.40	5.81	31.4	30.80	6.78	10.1
13	177	6.30	6.15	23.7	23.74	6.91	5.46
					Median	1.8	1.8
15-148 A	ves Rise						
14	6	9.22	8.09	4.00	4.16	0.88	0.58
15	10	7.38	7.15	3.50	3.33	0.49	0.27
16	26	7.37	7.10	5.23	5.37	0.84	0.54
17	35	7.58	7.33	5.02	4.76	0.95	0.53
18	63	5.79	5.38	7.61	7.57	1.05	0.77
19	70	5.57	5.12	7.66	8.08	0.63	0.81
20	90	4.72	5.02	6.72	6.90	1.10	0.62
21	90	4.72	5.02	_	6.90		0.80
22	107	6.02	5.59	5.27	5.62	0.83	0.68
23	107	6.02	5.59	5.27	5.62	0.90	0.70
24	161	8.97	7.12	5.72	3.99	0.92	0.65
25	210	10.1	9.72	3.05	3.03	0.64	0.44
					Median	0.90	0.63
15-149 V	enezuelan Bas	sin					
30	3	15.4	10.03	2.29	2.44	0.54	0.96
31	23	17.1	11.64	2.44	2.72	0.77	0.79
26	73	22.8	14.76	1.79	2.06	0.59	0.46
27	101	22.5	16.33	1.29	1.29	0.84	0.54
28	136	10.5	21.99	1.81	2.32	0.41	1.27
29	157	11.95	21.72	2.20	2.29	0.62	1.42
32	230	28.5	27.92	2.90	2.97	0.36	0.49
33	315	30.6	30.66	2.54	2.42	2.33	0.69
34	369	30.95	30.37	2.27	2.22	0.81	2.68
					Median	0.59	0.79

Table 4 DEGREE OF SATURATION (D.S.) CALCULATED FROM Ca⁺⁺, ALK, AND EXTRAPOLATED P_{CO}

^aGieskes; Presley et al.; Sayles et al.; Hammond, this volume.

R = sulfate utilization rate

D = diffusion coefficient of sulfate

Using D = 9.8 ×10⁻⁶ cm²/sec (Y.-H. Li, personal communication) and fitting this equation to the $[SO_4^{-1}]$ profiles in 147 and 148 (Figure 7) yields $R_{147} = 1 \times 10^{-7}$ mol/1 day and $R_{148} = 2 \times 10^{-10}$ mol/1 day. Although the correlation may be coincidental, the increase in R with temperature (in situ $T_{147} \approx 17^{\circ}$ C; $T_{148} \approx 6.7^{\circ}$ C) is striking and may be a crucial factor in controlling sulfate reduction rate.

In Figure 7, PCH₄ in the kettles is also plotted. Methane is absent from regions with significant sulfate, as expected on microbiological grounds (*Desulfovibrio* inhibits *Methanobacterium*, B. Mechalas, personal communication). PCH₄ and $[SO_4^{=}]$ show an inverse correlation in regions of low sulfate, suggesting that the sulfate is probably a contaminant in these samples and has destroyed some methane during storage.

CONCLUSIONS

Monitoring PCO₂ in kettles of stored deep-sea sediment suggests several ideas:

1) pH measurements on interstitial water are probably accurate to 0.1 pH units. Insufficient resolution exists in this PCO_2 study to be any more precise, or to accurately determine the degree of saturation of calcite.

2) The pH and alkalinity of interstitial water are probably controlled by the interaction between bacterial metabolism products such as CO_2 and CH_4 and carbonate minerals (at a constant temperature and pressure) over a time span of months to a few years.



Figure 6. CO₂ generated at 22°C in 110 days vs. interstitial water [SO₄⁼]. (Presley et al.; Sayles et al.)

3) Pressure reduction from in situ to atmospheric may cause clay minerals to exchange cations and hydroxyl ions, significantly decreasing alkalinity and pH, and creating undersaturation for calcite, which cannot dissolve rapidly enough to compensate for this before interstitial water samples are collected. This problem must be investigated further before alkalinity and pH measurements can be relied on to discuss carbonate saturation.

4) The rate of CO_2 production from sulfate reduction appears to increase with temperature. No correlation of rate with depth of $[SO_4^{=}]$ was observed, suggesting that at a constant temperature the process may be limited by the availability of suitable organic substrates.

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Figure 7. $[SO_4^{=}]$ (Presley et al.; Sayles et al.) and partial pressure of CH₄ (in storage kettles) vs. depth. (Solid lines are the equations fitted to the sulfate profile.)

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