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### ABSTRACT

Interstitial water studies of drill sites off the California Continental Borderland (Sites 467, 468, 469) reveal that fresh water can penetrate through the sediments as far as the San Miguel Gap (Site 467). In the rapidly deposited sediments of Site 467, decreases in magnesium concentrations can be related to the formation of dolomite in the claystone unit of the sediment column. Decreases in magnesium and increases in calcium at Site 469 at the base of the Patton Escarpment are probably the result of alteration of volcanic matter in the sediments and/or the underlying basalts.

Studies of the gradients of calcium, magnesium, potassium, strontium, and lithium at Site 471 indicate that a 150-meter-thick porcellanite-claystone-limestone complex acts as an almost complete barrier to diffusive exchange with the underlying sediments. Uptake reactions involving potassium and magnesium may still occur in the porcellanite complex.

At all sites, with the exception of Site 467, gradients of calcium show concentration increases with depth and simultaneous decreases in dissolved magnesium—a pattern commonly observed in open-ocean environments.

### INTRODUCTION

During Leg 63 of DSDP 11 holes at 7 sites were drilled along the west coast of southern California and Baja California. The locations of the sites are presented in Figure 1.

Interstitial waters were obtained in each hole drilled, and the shipboard analyses included pH, alkalinity, calcium, magnesium, chloride, and salinity. On the basis of concentration depth profiles obtained by these shipboard analyses we decided to carry out more complete studies on samples obtained at Sites 469, 470, 471, 472, and 473. In addition, sulfate analyses were carried out for Sites 467 and 468.

Methods are similar to those used by Gieskes (1974), Gieskes and Lawrence (1976), and Gieskes and Johnson (in press a). Shipboard analyses were carried out by Mr. Richard Myers.

The data are presented in Table 1, as well as in Figures 2 through 6.

## DISCUSSION

#### Site 467

Site 467, drilled at the San Miguel Gap in the outer California Continental Borderland, is characterized by extremely high rates of accumulation during the Quaternary ( $\sim 75 \text{ m/m.y.}$ ) and the Pliocene (100–150 m/m.y.). For these reasons it is not surprising to observe very high values of alkalinity and the complete depletion of dissolved sulfate below a sub-bottom depth of 50 meters (Fig. 2). Typically the high alkalinity values are accompanied by a minimum in dissolved calcium, indicating precipitation of calcium carbonate (Lawrence, 1973; Gieskes, 1975). Shipboard reports indicate the presence of microcrystalline calcite and dolomite rhombs in Unit 2 (367-699.5 m sub-bottom depth), which can explain the rapid decrease in dissolved magnesium to the top of this unit. Note that no increase in dissolved calcium accompanies this sharp decrease in magnesium; also, alkalinity values only start to decrease below 400 meters. Usually decreases in dissolved magnesium have been associated with the alteration of volcanic matter in pelagic sediments (Gieskes and Lawrence, in press; Gieskes, in press). In a continental margin setting, however, where rapid accumulation rates and high organic carbon contents lead to very high alkalinity values, carbonate precipitation and dolomitization may be the causes of the observed magnesium depletions.

The data on dissolved chloride do suggest a trend toward lower chlorides with depth, which can be understood in terms of fresh-water aquifers penetrating into the continental margin sediments (Manheim and Sayles, 1974; Gieskes, in press). Unfortunately no interstitial samples were obtained between 500 and 800 meters, so that a minimum in chloride, as suggested by the data, could not be verified.

Sedimentation rates below 500 meters have been much slower. Thus the elevated value of sulfate at 800 meters may be real—a result of incomplete sulfate reduction.

## Site 468

Site 468 is located on the Patton Escarpment. Accumulation rates during the last 10 m.y. have been low (~5 m/m.y.), and thus diffusive communication with the overlying ocean is easily established. Provided reactions do take place at relatively slow rates, diffusion will annihilate any gradients caused by such reactions (McDuff, 1978). For these reasons no depletion is observed in dissolved sulfate, and only a very slight increase in dissolved calcium and a small decrease in

<sup>&</sup>lt;sup>1</sup> Initial Reports of the Deep Sea Drilling Project, Volume 63.



Figure 1. Map of area drilled by DSDP Leg 63.

dissolved magnesium occur (Fig. 3). The causes of the changes in calcium and magnesium are difficult to establish.

Shipboard observations indicate the presence of dolomitic claystones in Cores 21 to 26, Hole 468 (184-241 m), and in Cores 18 to 37, Hole 468B (235-416 m). Sedimentation rates below about 60 meters sub-bottom depth (i.e., in the sediments older than 13 m.y.) have been relatively rapid, so that much of this dolomitization may have occurred during an early stage of deposition similar to that observed in Site 467. During the last 13 m.y., however, as a result of slow sedimentation rates and the occurrence of hiatuses, the average sedimentation rate has been less than 5 m/m.y., which may have allowed the dissipation of any of the gradients, including that of sulfate. Thus, if in the past, uptake of magnesium from pore waters has been important in the formation of these dolomites, this process must at present have little quantitative significance.

## Site 469

This site is located at the foot of the Patton Escarpment and is characterized by sedimentation rates of about 27 m/m.y. in the upper 90 meters, below which hiatuses occur to a depth of 170 meters (13 m.y.). Below this depth, accumulation rates have been moderately fast—at 60 m/m.y.

The dissolved sulfate profile indicates a rapid decrease in dissolved sulfate to about 20 mM in the first 100 meters (i.e., the recently deposited Quaternary to upper Pliocene section) (Fig. 4). The sulfate reduction process is also reflected in the maxima in alkalinity and in ammonia.

Below 225 meters, low dissolved silica values reflect the increased induration of the sediment and the disappearance of biogenic opal-A. Increases in dissolved calcium and decreases in dissolved magnesium are probably related to reactions taking place in the sediments of Unit 3 as well as in the underlying basalts. These reactions may well be the result of alteration reactions involving volcanic material, much like the reactions identified by Kastner and Gieskes (1976), which were associated with a silicification front in Site 323 (Bellingshausen Abyssal Plain). Additional work on the 18O/16O composition of the interstitial waters as well as that of the strontium isotopic composition of dissolved strontium (Hawkesworth and Elderfield, 1978) will be useful to unravel these processes. Dissolved strontium has a maximum at 190 meters (i.e., in the carbonate section of this site). However, isotopic studies of this dissolved strontium would allow us to distinguish the various contributors to dissolved strontium, that is, carbonate recrystallization versus alteration of volcanic material.

Dissolved potassium does show a decrease with depth, but data quality does not allow an analysis of zones where major sinks may occur. Dissolved lithium has a source in the upper siliceous section, probably related to release by siliceous tests (Gieskes, in press).



Figure 2. Interstitial water chemistry, Site 467. (Lithology: 1-clay; 2-claystone; 3-tuff; and 4-claystone.)



Figure 3. Interstitial water chemistry, Site 468. (Lithology: 1-ooze; 2-claystone. All data are combined; Hole 468B [B] is only indicated for alkalinity.)

## **Site 470**

This site is very close to the first experimental Mohole Site, east of Guadalupe Island. Analyses of calcium and magnesium (Table 1) show minor increases in dissolved calcium and decreases in dissolved magnesium. These observations are in good agreement with data obtained at the Mohole Site (Siever et al., 1965), as is shown in Figure 5.

Most other constituents show little change with depth, and generally the interstitial waters appear little affected by reactions in the sediments.

## Site 471

This site is characterized by a thick 150-meter section of porcellanites, claystones, and dolomites, which yielded very little core recovery. Above the porcellanites, sedimentation rates have been 20 m/m.y. or less, whereas below the porcellanite zone sedimentation rates have been extremely rapid at more than 250 m/m.y.

The most significant observation at this site is the large effect exerted by the porcellanite zone on the various pore-water constituents. Low porosities must



Figure 4. Interstitial water chemistry, Site 469. (Lithology: 1-clay; 2-clay and ooze; 3-claystone; 4-diabase; claystone; basalt.)

have caused low diffusivities, and thus large gradients occur across the porcellanite zone. This is particularly evident for sulfate, magnesium, strontium, and potassium (Fig. 6). Yet the calcium and lithium profiles especially suggest some communication across this fairly efficient diffusion barrier. Similar observations were made at Site 462 of Leg 61 (Gieskes and Johnson, in press b).

Below the porcellanite zone little change occurs in dissolved magnesium, but the gradient in dissolved calcium is large and probably is due to reactions in the underlying basement. Charge balance calculations indicate that the calcium flux implied by the calcium gradient below the porcellanite complex is balanced by a sodium flux into the basalts, a phenomenon previously noticed by McDuff (in press). Similarly, potassium concentrations seem little affected below the porcellanites. Perhaps significant uptake of both potassium and magnesium occur in the porcellanite zone, but data quality does not allow an analysis of this problem similar to the treatment given to the Site 462 data (Gieskes and Johnson, in press b).

Dissolved lithium appears to increase gradually with depth, probably partially as a result of lithium release in the lower sediment column. The source of this lithium is unclear at this stage.

## Site 472

Only three analyses were carried out for this site (Table 1). Dissolved calcium data show a slight increase with depth, whereas dissolved magnesium values decrease. Dissolved potassium concentrations decrease rapidly with depth in this site. These observations are common in open-ocean, pelagic sediments (Gieskes, in press).

# Site 473

This site, on the Rivera plate, south of the Tres Marias Islands, is characterized by rapid Quaternary sedimentation rates (60 m/m.y.) and less rapid Pliocene through late Miocene sedimentation (33 m/m.y.).

As a result of rapid sedimentation rates dissolved sulfate values decrease rapidly with depth, and alkalinity data show a maximum at about 50 meters sub-bottom depth (Fig. 7). Dissolved ammonia values increase to above 1 mM. Organic carbon contents lie between 1.69% at the top to 0.25% at the bottom of the hole. Sulfate is never completely depleted in this hole, and typically no gas production has been observed.

Notwithstanding the high sedimentation rates and the production of alkalinity, no minimum has been observed in dissolved calcium, which increases gradually

Table 1. Interstitial water data, Leg 63.

Sample (interval in cm)	Sub-bottom Depth (m)	pН	Alk (meq/l)	SO4 (mM)	NH4 (µM)	SiO2 (µM)	Ca (mM)	Mg (mM)	Sr (µM)	Mn (µM)	Li (µM)	К (т <i>М</i> )	Cl (‰)	S (‰)	Remarks
Hole 467													1		
2-3, 144-150	15.5	7.23	14.0	16.8			6.36	50.8					19.14	34.4	
7-1, 144-150	63	7.29	33.7	0			4.23	46.5					19.18	34.4	
13-5, 144-150	122	7.05	30.0	1.4			8.54	45.5					19.14	34.4	
18-5, 144-150	158	7.13	50.3	0			8.56	44.5					19.34	34.9	
25-4, 140-150	225	6.99	44.0	0			9.45	36.5					18.98	34.1	
30-2, 140-150	272	6.94	39.8	0.2			8.89	32.0					19.01	34.1	
41.2 140-150	329	7.08	43.3	1.4			8.50	20.0					18.88	33.0	
48-1, 140-150	443	7.03	37.9	1.0			8.62	17.0					18.65	33.0	
54-1, 140-150	500	6.85	33.9	1.0			10.11	15.0					18.28	32.2	
85-1, 130-150	795	7.56	1.1	11.0			22.46	15.0					18.28	25.6	Contamination from rock saw?
Hole 468															
1-1, 144-150	2	7.63	2.48	27.6			10.17	50.5					19.17	35.2	
5-4, 144-150	35	7.73	2.94				10.41	52.3					19.61	36.0	
10-4, 140-150	84	7.44	2.86	28.6			10.49	51.8					19.31	36.8	
A-2-3 144-150	103	7.51	2.08	27.0			12.38	51.5					19.34	30.0	
B-4-1, 144-150	47	6.91	3.08				10.41	52.5					19.38	36.0	
9-3, 144-150	100	6.93	3.73				11.52	52.2					19.34	35.8	
14-4, 129-139	182	7.25	4.21				15.99	48.1					19.24	35.5	H <sub>2</sub> S smell?
21-2, 140-150	260	7.64	1.80	(15.0)			11.88	52.0					19.14	35.5	
25-1, 140-150	300	7.87	1.41	28.0			12.28	53.0					19.48	36.3	
31-1, 140-150	341	7.57	1.75	27.6			14.74	50.2					19.27	35.2	
Hole 409													10.0		
2-1, 144-150	9.0	7.92	4.67	25.0	170	480	9.94	50.7	101	23.0	26	9.8	19.2	35.2	
12-4 144-150	109	7.19	2.00	10.0	462	760	12.64	40.4	180	25 3	45	10.1	19.4	34.9	
20-4, 140-150	185	7.21	2.85	18.9	396	1116	18.93	35.4	220	0	40	7.6	19.3	34.9	
28-1, 54-64	255	8.06	0.72	21.3	363	222	30.2	24.3	170	16.8	47	7.0	18.9	34.4	
36-2, 0-9	332	8.05	-	21.3	319	156	37.9	18.4	144	32.7	45	4.7	18.9	34.4	
43-2, 140-150	390	7.93	0.37	21.9	220	54	41.5	19.3	162	8.2	56	4.5	19.4	34.6	
Hole 470															
2-2, 144-150	12.5	8.06	3.34	28.9	163	337	13.43	48.3	87	75.2	26	12.9	19.27	35.5	
8-2, 144-150	70	7.47	3.32	28.5	117	919	15.35	49.1	81	13.7	28	10.5	19.34	35.8	
12-7, 144-150	113	7.96	2.89	29.4	584	791	15.23	49.2	112	5.9	27	10.8	19.41	35.5	<b>B</b>
1/-2, 144-150	155	7.47	2.17	28.0	46	900	14.60	51.0	96	17.0	28	9.5	19.51	35.5	Basalt contact
4-6. 144-150	85	7 44	2.14	28.4	58	866	14.40	40.1	104	14.5	26	10.9	19.51	35.8	
6-2, 140-150	165	1.44	2.00	27.6	217	618	14.90	49.5	85	6.7	28	9.0	10.44	35.5	No good-chunks etc.
Hole 471															
3-3, 144-150	23.5	8.01	6.15	24.4		295	10.45	49.3	92	51	30.9	11.0	19.4	35.5	
8-5, 144-150	74	7.33	5.31	23.5		960	11.82	49.6	110	10	29.6	9.2	19.6	35.5	
13-6, 144-150	123	7.26	4.58	24.0		1129	12.14	50.2	100	10	38.2	8.2	19.5	35.2	12 M 12 M 12 M
38-1, 138-150	355	7.90	0.70			02	24.50	11.9	(20)	10	100	1.0	18.8	31.9	Mostly cuttings
50-3 140-150	412	8.04	0.72	1.0		93	29.45	10.2	030	10	190	1.5	18.0	31.9	
57-4, 140-150	538	7 71	-	_		118	43 6	11.4	776		294	17	19.3	32.4	
63-2, 140-150	592	_		2.2		120	50.2	12.6	804	13	294	1.6	18.9	32.7	
70-3, 140-150	660	8.03	-			120	64.6	12.9	454	7	-	2.4	19.0	33.6	
75-2, 140-150	705	7.95	-	-			78.1	8.3	$\overline{f} : \xrightarrow{1} C$		340		19.3	34.4	
Hole 472															
2-4, 144-150	11.5	7.28	2.73	27.9	226	438	11.75	51.5	80	125.1	26	7.9	19.1	34.2	
7-2, 144-150	56	7.48	3.10	28.1	47	830	12.95	51.2	87	54.2	26	6.7	19.2	35.2	
12-1, 144-150	102	7.49	2.63	-	48	718	13.01	50.8	97	22.6	26	6.2	19.1	35.2	
Hole 473															
2-4, 144-150	6.5	7.73	10.22	20.1	838	510	10.10	49.4	73	54.5	27	7.9	19.2	34.9	
7-2, 144-150	51	7.60	16.84	5.8	1190	495	10.61	42.5	71	43.9	47	5.1	19.3	34.1	
13-3, 144-150	156	7.67	10.17	9.6	1410	238	12.82	42.6	84	37.2	88	3.0	19.2	34.1	
24-1, 144-150	202	7.47	6.17	2.4	1480	577	16 55	35.8	15	38 1	102	1.2	19.1	32.7	
				200				0010							

Note: - indicates no data available.

with depth. The dissolved magnesium profile indicates uptake of this element in the sediments, as does the dissolved potassium profile. We postulate that these changes in magnesium and potassium are associated with the alteration of volcanic matter in these siliceous sediments. Again, studies of the oxygen isotopic composition of the pore waters and the strontium isotopic composition of the dissolved strontium should help to unravel this problem. In Site 474 of Leg 64 a good correlation between changes in magnesium, calcium, and <sup>87</sup>Sr/<sup>86</sup>Sr was found (Gieskes et al., in press).

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Figure 5. Interstitial water chemistry, Site 470 and Mohole Site (calcium and magnesium).

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Figure 6. Interstitial water chemistry, Site 471. (Lithology: 1-clay and ooze; 2-porcellanite; 3-claystone; 4-diabase.)



Figure 7. Interstitial water chemistry, Site 473. (Lithology: 1-clay; 2-claystone; 3-diabase; basalt.)