

## 10. GEOCHEMISTRY AND CARBONATE PETROLOGY OF SELECTED SEDIMENT SAMPLES FROM DEEP SEA DRILLING PROJECT LEG 54, EASTERN PACIFIC

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### ABSTRACT

Thirty selected samples of pelagic and hydrothermal sediments retrieved on DSDP Leg 54 were chemically analyzed for major and minor oxide concentrations. Additionally, 11 samples of lithified carbonate sediments were petrologically studied.

The pelagic sediments, which are described as foraminiferal biomicrite, were found to be generally higher in Fe and Zn, similar in Co content, and lower in Cu content, than the average Pacific pelagic sediments. Mineralogically, these samples are composed principally of calcite with minor amounts of quartz and clays.

Hydrothermal sediments from Site 424 are divisible into three classes: (1) silica-rich, iron-poor smectites; (2) silica-poor, iron-rich mixtures of smectites and oxides; and (3) silica-poor, iron-rich materials, comprising mainly amorphous manganese oxides. Thus, two chemically distinct hydrothermal phases are recognizable: Class 1, iron-rich smectites, and Class 3, Mn-rich oxides and oxyhydroxides.

Dolomite and pyrite were identified in X-ray diffraction studies of samples from Site 427.

### INTRODUCTION

During Leg 54, the D/V *Glomar Challenger* recovered sediments from three discrete geologic environments (Figure 1): (1) from the flanks of the active, rapidly spreading East Pacific Rise (EPR) crest (Sites 419, 420, 421, 422, 423, 428, and 429); (2) from an area of known high heat flow and probable hydrothermal affinity near the Galapagos Spreading Center (Site 424); and (3) from the topographic low created by the active Siqueiros transform fault (Site 427). An additional site, Site 425, was placed on the northern flank of the Galapagos Rift.

The general geochemistry of sediments along the EPR has been previously discussed by Cronan and Garret (1973), Cronan (1976), Boström et al. (1976), Boström et al. (1973), and many others. The present study was undertaken: (1) to determine if similarities exist between hydrothermal deposits near the Galapagos Rift and other sediments previously described as hydrothermal (Hoffert et al., 1978); (2) to establish quantitative relationships among trace metals without recalculating them to a theoretical "carbonate free" value; (3) to provide a general description of sediment adjacent to spreading centers and transform faults of the Central East Pacific; and (4) to describe the petrology of lithified portions of the carbonate sediments which occur as lumps or nodules in the cores obtained on Leg 54.

### CHEMICAL RESULTS AND DISCUSSIONS

#### Analytical Procedure

Between one and nine representative samples were selected per site for chemical studies, but several of the sites include more than one hole (Table 1a and b). In addition, 11 lithified samples were taken for petrographic studies (Table 2). Additional lithologic descriptions of the sediments are given in the appropriate Site Reports of this volume. Conventional atomic absorption analysis techniques were used to determine Fe, Mn, Au, Co, Zn, and Mo. Ca, K, P, Ti, Zn, Y, Rb, Nb, and Sr were determined by X-ray fluorescence spectroscopy, using compressed powder pellets. USGS and other international standards were used to calibrate both methods, and the overall precisions are estimated as better than  $\pm 5$  per cent. Detection limits for Zr, Y, Rb, and Nb are 10 ppm, 5 ppm, 1 ppm, and 1 ppm, respectively.

The large errors possible when calculating "carbonate free" values and other compensatory techniques (such as norm calculations) which are not yet proven reliable, led the authors to choose representation of all chemical data in its original, bulk sample form. No recalculations or other data manipulations have been performed. Chemical data for 30 sediment samples are presented in Table 1.

#### Fe and Mn Relationships

Fe concentrations range between 2 per cent and 26 per cent throughout the sample group. Most values fall between 5 per cent and 10 per cent Fe. Mn values are

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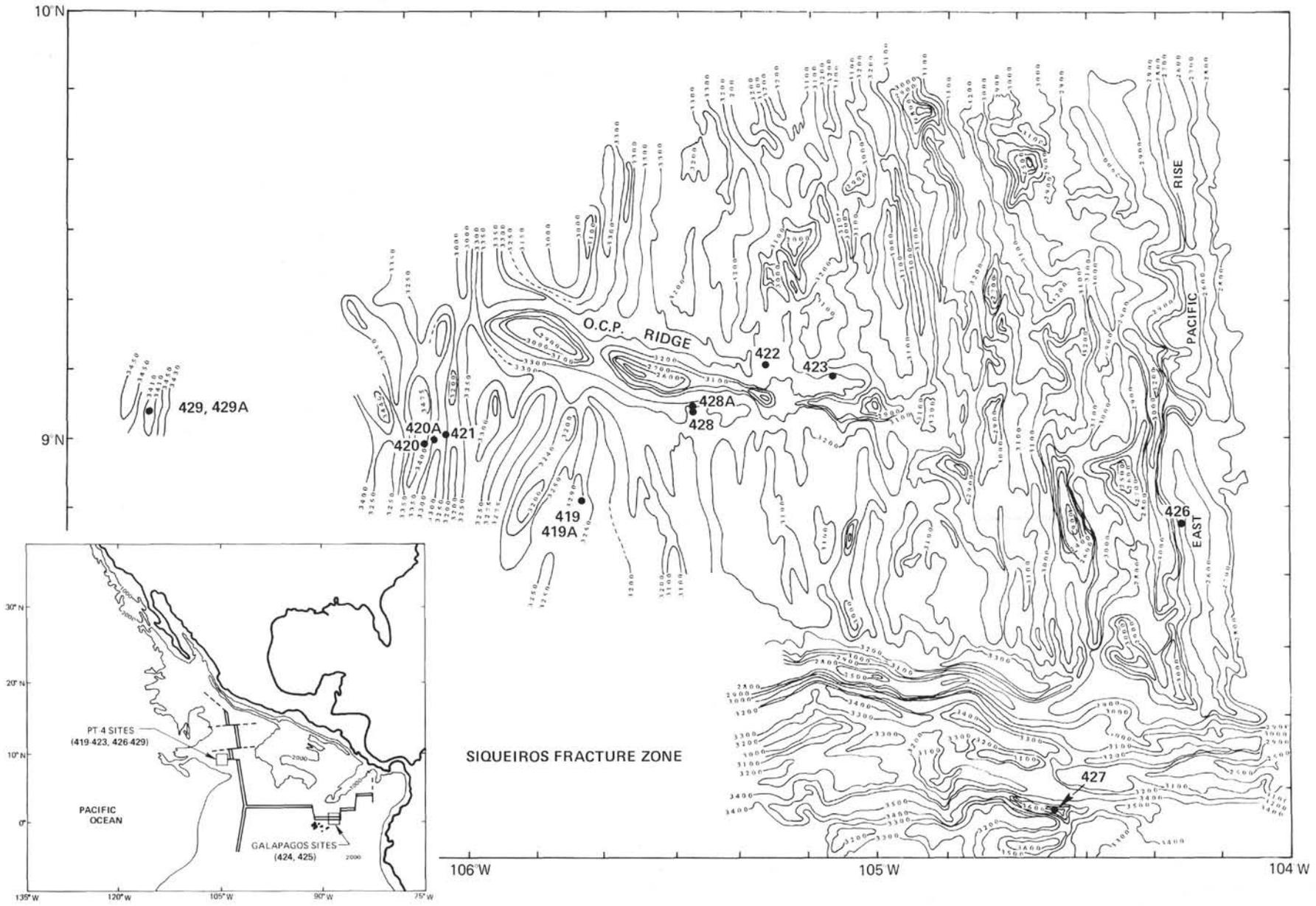


Figure 1. Location of Deep Sea Drilling Project sites for Leg 54.

TABLE 1a  
Concentration of Trace Metals (ppm) in Sediments by  
Atomic Absorption Analyses<sup>a</sup>

Sample (Interval in cm)	Fe	Mn	Cu	Co	Zn	Mo
<b>Hole 419</b>						
1,CC, 2-4a	76,786	3,233	177.8	48.5	327.4	56.6
2-3, 53-55a	74,306	2,890	156.4	90.8	214.7	—
3-1, 91-93a	85,728	4,082	187.8	102.6	240.9	—
4-2, 92-94b	93,006	2,232	177.8	339.0	421.6	—
4-5, 13-15b	99,777	97,781	123.7	43.9	355.2	55.9
5,CC, 1-2a	69,115	1,580	79.0	67.1	177.8	—
<b>Hole 419A</b>						
1-3, 132-34a	50,615	1,539	178.2	145.8	465.7	76.9
<b>Hole 420</b>						
1-1, 10-12c	71,557	20,445	188.1	163.6	462.1	57.3
1-1, 129-31a	66,203	6,041	132.4	74.5	211.0	57.9
2-3, 70-72a	105,460	29,449	254.7	127.4	350.2	59.7
9-1, 10-12d	36,012	136,044	172.1	96.0	208.1	48.0
10-2, 41-43e	80,749	8,882	205.9	64.6	298.8	72.7
11-2, 15-17e	47,985	2,319	96.0	104.0	44.0	—
12-2, 50-52f	50,225	2,652	64.3	92.4	136.6	—
13-4, 130-32f	60,562	2,423	310.9	56.5	165.5	72.7
<b>Hole 420A</b>						
1-1, 24-26c	92,638	14,822	263.5	74.1	275.9	49.4
<b>Hole 424</b>						
1-1, 2-4g*	99,396	286,260	151.1	31.8	83.5	373.7
1-1, 97-99 g,a	165,235	40,069	190.0	28.9	400.7	90.9
2-1, 50-52g	240,077	1,601	112.1	16.0	36.0	64.0
2-4, 29-31 g,a	259,465	4,982	99.6	37.4	49.8	62.3
2-4, 130-32a	134,922	1,827	116.2	58.1	78.9	49.8
3-1, 27-29g	211,081	38,598	172.9	40.2	80.4	120.6
4-6, 83-85a,g	21,495	4,547	190.2	53.7	86.9	41.3
<b>Hole 424A</b>						
1-1, 77-79g*	115,435	71,735	119.6	28.9	630.8	239.1
<b>Hole 424B</b>						
1-2, 67-69g,a*	49,968	1,839	123.9	28.0	103.9	60.0
<b>Hole 425</b>						
1-1, 13-15a	34,430	2,187	206.6	36.5	243.0	44.6
<b>Hole 427</b>						
2-1, 30-32a	49,793	258,923	175.2	191.2	235.0	39.8
3-3, 81-83b	175,139	21,994	228.1	350.4	297.3	154.8
8-1, 18-20a	51,415	11,928	205.7	172.8	246.8	49.4
<b>Hole 429</b>						
1-1, 90-92a	57,283	6,547	188.2	57.3	155.5	57.3

\*Tabulated values of sediment from the Mounds Hydrothermal Field are derived from bulk samples and may represent mixtures of carbonate ooze, silica-poor and silica-rich hydrothermal deposits as defined in this paper. Samples analyzed for this *Initial Reports* volume maintain the integrity of shipboard sampling. Analyses of hand-separated, carbonate-free portions of the sediment are reported in the Site 424 Report.

Note: a = Foraminifer-nannofossil ooze. f = Nannofossil ooze.  
 b = Radiolarian-nannofossil ooze. g = Mixture of Mn oxide fragments and green clay.  
 c = Brown calcareous clay.  
 d = Lithified siliceous nannofossil ooze. h = Calcareous siliceous ooze.  
 e = Siliceous nannofossil ooze.

generally lower, with the major portion of samples having values between 1 per cent and 7 per cent. The spectrum of Mn concentrations runs from 1.5 per cent to 29 per cent. Fe generally correlates positively with Mn. In only three specimens does Mn become more concentrated than Fe (Samples 420-9-1, 10-12 cm; 424-1-1, 2-4 cm; and 427-2-1, 30-32 cm).

TABLE 1b  
Concentration (ppm) of Selected Elements in Sediments  
by XRF Analyses

Sample (Interval in cm)	CaO	K <sub>2</sub> O	P <sub>2</sub> O <sub>5</sub>	TiO <sub>2</sub>	Zr	Y	Rb	Nb	Sr
<b>Hole 419</b>									
1,CC, 2-4	28.73	1.31	0.40	0.23	64	53	16	4	708
2-3, 53-55	36.00	1.23	0.43	0.22	50	45	21	3	817
3-1, 91-93	31.64	1.16	0.50	0.28	68	49	23	3	728
4-2, 92-94	10.03	1.50	0.22	0.27	41	37	20	0	305
4-5, 13-15	20.16	1.55	0.23	0.19	63	41	28	3	510
5,CC, 1-2	37.30	1.35	0.31	0.14	47	37	22	1	761
<b>Hole 419A</b>									
1-3, 132-134	27.37	1.53	0.42	0.25	70	68	26	3	690
<b>Hole 420</b>									
1-1, 10-2	28.84	1.03	0.55	0.27	72	50	18	4	873
1-1, 129-131	32.06	1.20	0.40	0.21	57	47	23	2	712
2-3, 70-72	12.16	1.49	0.56	0.45	100	74	34	4	664
9-1, 10-12	19.69	0.83	0.33	0.16	32	33	14	1	474
10-2, 41-43	11.50	1.53	0.27	0.30	88	69	34	4	509
11-2, 15-17	26.05	2.98	0.25	0.17	75	25	64	2	773
12-2, 50-52	43.46	1.07	0.40	0.12	35	41	17	2	982
13-4, 130-132	41.80	1.35	0.40	0.14	43	45	22	1	1050
<b>Hole 420A</b>									
1-1, 24-26	27.52	1.17	0.53	0.29	68	50	22	1	801
<b>Hole 424</b>									
1-1, 2-4	2.19	1.27	0.22	0.07	2	6	12	0	259
1-1, 97-99	0.74	2.39	0.13	0.04	1	1	51	0	75
2-1, 50-52	0.34	3.46	0.07	0.04	1	0	70	2	27
2-4, 29-31	1.29	3.58	0.10	0.05	2	3	65	0	52
2-4, 130-132	14.62	2.06	0.13	0.13	18	15	37	1	366
3-1, 20-29	0.73	3.20	0.10	0.04	2	2	57	0	61
4-6, 83-85	1.01	0.61	0.52	0.09	14	11	8	0	975
<b>Hole 424A</b>									
1-1, 77-79 (duplicate)	7.53 7.47	1.59 1.45	0.17 0.17	0.17 0.16	15 17	9 9	31 33	0 0	270 276
<b>Hole 424B</b>									
1-2, 67-69	9.82	2.89	0.08	0.18	47	20	71	2	360
<b>Hole 425</b>									
1-1, 13-15	37.37	0.77	0.29	0.14	28	20	9	1	856
<b>Hole 427</b>									
2-1, 30-32	20.02	0.18	0.99	0.10	10	11	1	1	198
3-3, 81-83	4.20	0.89	0.26	0.23	57	43	17	0	258
8-1, 18-20	13.04	0.79	0.21	0.18	50	36	14	2	462
<b>Hole 429</b>									
1-1, 90-92	43.10	0.82	0.47	0.12	36	41	10	1	1058

Reversals of Fe/Mn ratios (i.e., when Mn% > Fe%) relate an atypical segregation of these cations in the geochemical cycle. Such concentration of Mn may lead to deposition of Mn oxide ore deposits. It has been explained in the past (Natland, 1973; Dymond et al., 1976) that abnormally high concentrations of Fe and Mn oxides in sediments other than Fe/Mn nodules may indicate hydrothermal deposition. The extreme concentration of Mn to the exclusion of Fe in diagenetic fluids or connate brines is inherently difficult, since the two elements so closely follow one another in sedimentary geochemical cycles (Stanton, 1972; Krauskopf, 1967). With this factor in mind, we see such Fe/Mn ratio reversals as at least suggesting the effects of previously heated, circulating fluids on the sediments. Such fluids may have a geochemical buffer or magmatic component favoring

TABLE 2  
Lithified Sediment  
Specimens Used in  
Carbonate Petro-  
logic Study

Sample (Interval in cm)
420-9-1, 10-12
420-10-3, 78-80
420-11-1, 10-12
424-3-2, 3-5
424-3-3, 77-79
423-4-2, 51-53
423-3-4, 130-132
424A-2-1, 78-80
424A-4-1, 35-37
427-2-1, 30-32
427-2-6, 74-76

the precipitation of Fe at depth and the continued migration of Mn to be deposited at the surface (Krauskopf, 1957).

#### Zr and Y Relationships

The high concentrations of Zr and Y correlate positively with the content of volcanic glass in the sediments. Since no detrital minerals containing Zr and Y were observed in polished thin section or X-ray diffraction studies, we infer that these pneumatophyle cations are trapped in the silicate glass. Upon hydration of the glass, leaching of trapped constituents is possible. In such cases the Fe-Mn oxides coating sediment grains may adsorb these positively charged particles.

In sediment from Site 420, Zr exhibits concentrations of 72, 100, 88, and 75 ppm, while Y values of 50, 60, and 74 ppm are recorded. At other sites the highest Zr values never exceed 65 ppm and Y does not exceed 55 ppm. Hydrated volcanic glass comprises about 50 per cent of the pyroclastic component in the Site 420 sediments. Fe coatings on many carbonate grains, as well as Fe-Mn oxide masses, are common throughout Site 420. The Zr and Y are believed to be associated with these oxides, probably as adsorbed ions or interstitially trapped constituents.

#### ELEMENTAL VARIATIONS AND DESCRIPTIVE GEOCHEMISTRY OF SITE 424

The anomalous distribution of cations and oxides in Site 424 is indicative of a nonsedimentary origin. A variety of contributing factors suggest a hydrothermal origin. The Zr, Y, Nb, Co, and TiO<sub>2</sub> contents of the Hole 424 sediments are generally much lower than those of the other sample sites. Sr, Mo, and Zn concentrations fluctuate strongly, perhaps as a response to pulses of hydrothermal activity, some of which were richer in Mo and/or Zn than in Sr. The similar ionic radius and

charge of Sr and Ca allow diadochy between these cations. Sr correlates with CaO, whose concentration is directly related to the total calcite content. Thus, the greater volumes of hydrothermal silicates and oxides may dilute the normal calcite bearing sediments, and the Sr becomes concomitantly lower. In Hole 424, Sr deviates strongly from Ca in the stratigraphically lowest sample from the core, implying a nonsedimentary affiliation of the enriched Sr.

The concentration of Zr, Y, Nb, and Co may reflect the nature of the fluids giving rise to hydrothermal deposition at Hole 424. Since Nb, Zr, and Y are pneumatophyle elements often concentrated in residual fluids of basaltic magmas (Gerasimovsky, 1974), any abnormal concentration of these elements implies a magmatic-hydrothermal affiliation. The relative low contents of these cations in Site 424 samples therefore indicate that fluids have mineralized these sediments were not directly derived from residual brines of a magmatic system. The hydrogeological setting, then, must be one of downward percolating sea water that becomes heated and rises along appropriate fracture patterns (Lonsdale, 1977).

Most of the sediments analyzed from Site 424 are hydrothermally derived. Only Sample 424-2-4, 130-132 cm is an unaltered, calcite-bearing, pelagic sediment. Samples 424-1-1, 2-4 cm; 424-2-4, 29-31 cm; 424-4-6, 83-85 cm; and 424B-1-2, 67-69 cm consist of mixtures, apparently created by drilling disturbance and contamination during coring, of hydrothermal and pelagic sediments.

Analyses of the noncarbonate portion (oxide crusts and clays) of the sediment at Hole 424 suggest a hydrothermal affiliation. Three classes of sediment types were discovered by these analyses; they are reported here together with their average analysis results (15 analyses each):

- Class 1 (Silica-rich, iron-rich green clays): SiO<sub>2</sub>: 44%; Mn: 0.06%; Fe: 19%; Co: 28 ppm; Cu: 10 ppm; Ni: 25 ppm; U: 0.5 ppm; Zn: 40 ppm.
- Class 2 (Silica-poor, iron-rich clay-oxide mixtures): SiO<sub>2</sub>: 1.1%; Mn: 34.0%; Fe: 7.2%; Co: 21 ppm; Cu: 20 ppm; Ni: 70 ppm; U: 11 ppm; Zn: 95 ppm.
- Class 3 (Silica-poor, iron-poor oxide crusts): SiO<sub>2</sub>: 0.8%; Mn: 46%; Fe: 0.2%; Co: 11 ppm; Cu: 42 ppm; Ni: 88 ppm; U: 14 ppm; Zn: 161 ppm.

The three classes of sediments are not distinct chemical entities, because Class 2 material (comprising black to dark brown nodules and crusts) appears to be intermediate between the other two classes which approximate chemical end members. Its microscopic study disclosed that these deposits consist of an intimate physical mixture of Class 1 material and opaque coatings and granules. The materials were separated by hand under a binocular microscope, and the components were ex-

amed by X-ray diffraction. The results are tabulated as follows:

*Class 1 grains:* Mixed layered clay, major peak at 11.0Å on Mg-saturation and 17.0Å on Mg-saturation and glycolation.

*Opaque granules and crusts coating Class 1 grains:* Todorokite, birnessite, minor manganite, amorphous Fe-Mn (?) oxides.

The coated clay particles were found to be chemically identical to Class 1 sediments, and the oxides were defined as Class 3 sediments. Average whole-rock analyses of Class 3 and Class 1 sediments are as follows:

	SiO <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub>	CaO	MgO	
Class 3 (oxides):	0.93%	0.26%	0.23%	1.8%	2.0%	
Class 1 (clays):	46%	28%	0.34%	0.3%	4.2%	
	TiO <sub>2</sub>	MnO	Na <sub>2</sub> O	K <sub>2</sub> O	Ni	
Class 3:	0.01%	56.5%	3.9%	0.5%	89 ppm	
Class 1:	0.02%	0.08%	1.4%	3.0%	18 ppm	
	Cu	Zn	Cr	Co	Sr	V
Class 3:	42 ppm	160 ppm	15 ppm	11 ppm	392 ppm	18 ppm
Class 1:	15 ppm	35 ppm	36 ppm	23 ppm	24 ppm	23 ppm
	Ba	P <sub>2</sub> O <sub>5</sub>	Zr			
Class 3:	2090 ppm	—	28 ppm			
Class 1:	59 ppm	0.08%	6 ppm			

The green clays comprising layers intercalated with pelagic sediments in Hole 424B were analyzed and proved to be identical to the Class 1 sediments.

These samples are obviously different from average pelagic sediment as described by Turekian and Wedepohl (1961) or the Pacific surface sediments described by Cronan (1969). The silica-rich material, Class 1, comprising green smectite, is chemically very similar to the hydrothermal deposit near transform fault A in the FAMOUS area as described by Hoffert et al. (1978). The silica-poor material, Class 3, is low in Co, Cu, Ni, and Fe relative to reported concentrations of these elements in typical Fe-Mn nodules of the East Pacific (Cronan, 1973; and Cronan and Tooms, 1969). The U contents of the silica-poor sediments are similar, however, to both Pacific and Atlantic nodules of diagenetic origin (Schrader, unpublished research). The data are somewhat conflicting, but the authors feel that the association of this material with the "Mounds Area" (Lonsdale, 1977; Site Report, this volume), the intimate intercalation of the two noncarbonate materials, and the low transition-element contents of these sediments imply a hydrothermal origin for both classes of noncarbonate material. If this deduction is correct, then Leg 54 has retrieved and identified a new mode of sea-floor hydrothermal sedimentation which is silica-poor, Fe-poor, and Mn-rich.

#### ELEMENTAL AND OXIDE RELATIONSHIPS

Additional variations in trace metal concentrations can be observed in depth versus concentration diagrams. Figures 2, 3, 4, and 5 display CaO, Sr, and P<sub>2</sub>O<sub>5</sub> variations with depth below the sediment/water interface. In general, the CaO and Sr curves are similar ow-

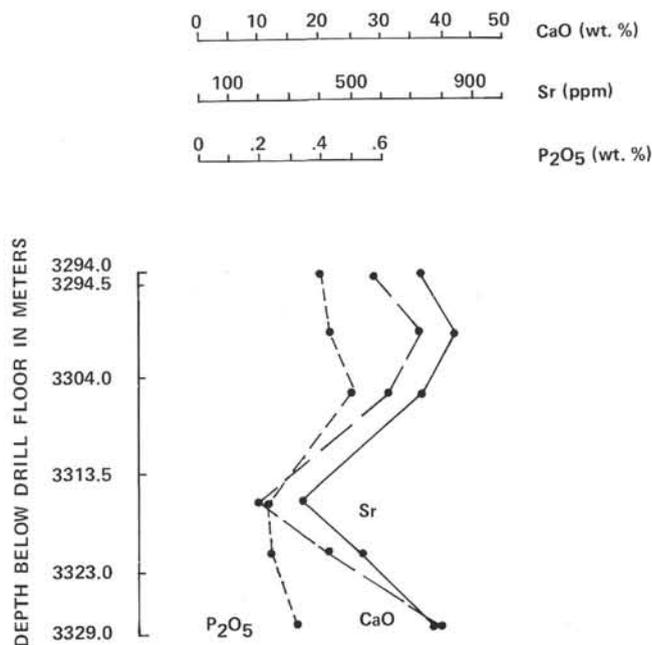


Figure 2. Depth versus CaO, Sr, and P<sub>2</sub>O<sub>5</sub> concentrations in sediment from Site 419.

ing to the Sr affinity for the calcite lattice. Only in the deepest sample in Hole 424 does Sr strongly deviate from CaO. Since this site is strongly influenced by hydrothermal fluids, we must assume that this deviation is the result of a geochemical separation of these cations by hydrothermal processes.

P<sub>2</sub>O<sub>5</sub> can be seen to fluctuate more or less independently of CaO (Figures 2, 3, 4, and 5). The P<sub>2</sub>O<sub>5</sub> contents of surface or near-surface sediments is consistently higher than the lowest sample in each core. The lower P<sub>2</sub>O<sub>5</sub> values in the surface sediments reflect either a heavier deposition of possible skeletal debris in recent times or a diagenetic solution and removal of the phosphate-bearing compounds near the basalt/sediment interface. The only exception to this relationship is seen again at Site 424, where the deepest sample is strongly enriched in P<sub>2</sub>O<sub>5</sub>. The effect of hydrothermal solutions is a possible cause. Downward percolating seawater may have dissolved phosphatic material in sediments and P-bearing phases in basalts. These solutions, when encountering porous and reactive sediment above basalt (during their ascent), may have deposited a portion of their chemical burden in the form of P<sub>2</sub>O<sub>5</sub> and Sr. It is also possible that these elevated concentrations of Sr and P<sub>2</sub>O<sub>5</sub> represent heightened dissolution of CaCO<sub>3</sub>, perhaps by hydrothermal fluids, and are thus residually concentrated ichthyolite debris.

The relationship between Fe/Mn and Co is displayed in Figure 6. Schrader et al. (1976) discussed the relationship of base metals to Fe and Mn oxides. They found that in the case studied, base metals were preferentially concentrated in the Mn oxides. The same relationship is observable in the samples of the present study, although it is complicated by the presence of two apparent trends. As can be seen in Figure 6, the entire field of data can be

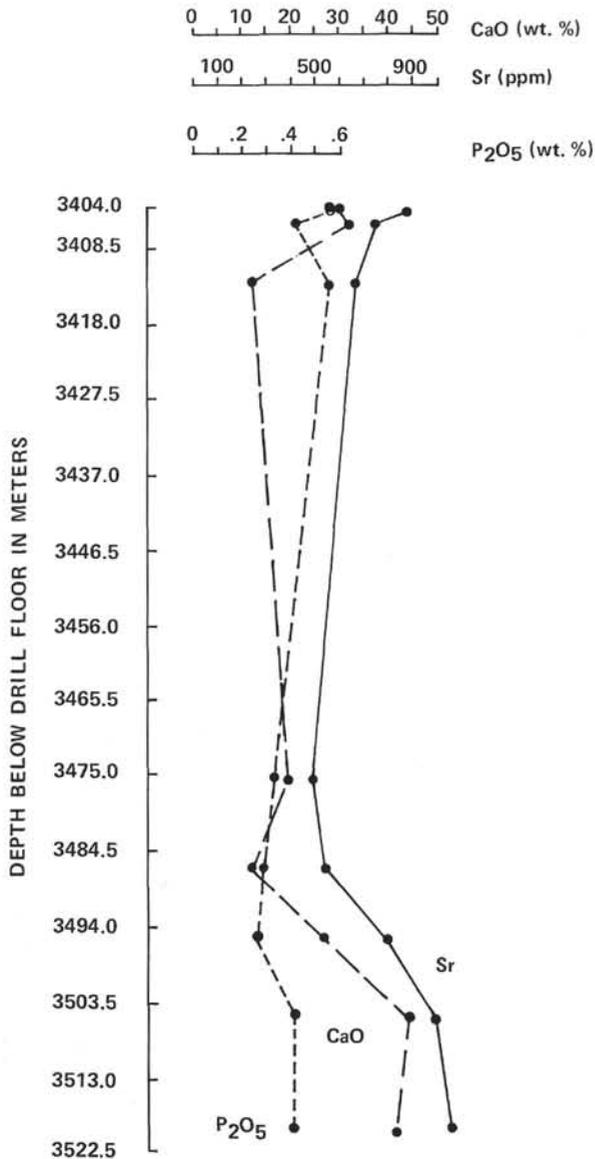


Figure 3. Depth versus CaO, Sr, and P<sub>2</sub>O<sub>5</sub> concentrations in sediment from Site 420.

described by a hyperbolic curve. If, however, only the data points with Co concentrations below 150 ppm and Fe/Mn ratios below 35 were considered, then the curve describing these points would become less well defined and the relationship obscure. Apparently, high Fe concentrations correlate with lower Co values, and the higher Mn values correspond to increased Co levels. However, in the range of Fe/Mn ratios of 2 to 40 no trend is actually discernible.

The typical linear relationship of K to Rb is observable in Figure 7. The coherent relationship between the elements as described by Ahrens et al., (1952) is evident. The upper half of the trend is completely dominated by the samples from Hole 424. We attribute this to a hydrothermal component contributing both elements for fixation in smectites as substitutional ions within lattices and as sorbed ions on oxide and smectite surfaces.

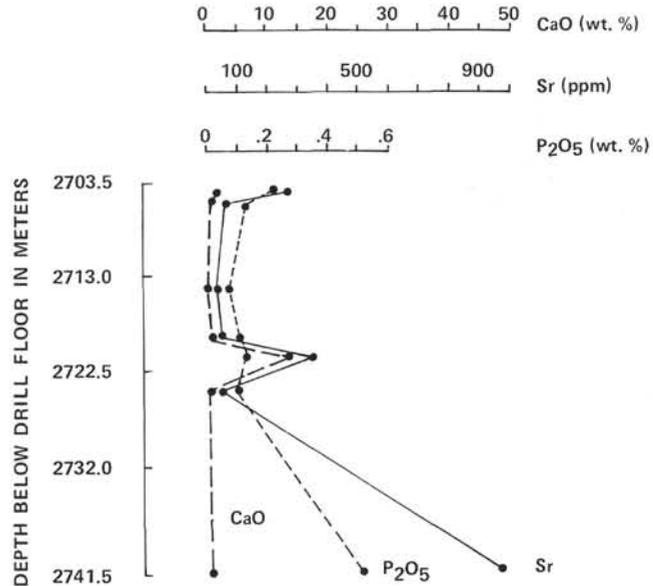


Figure 4. Depth versus CaO, Sr, and P<sub>2</sub>O<sub>5</sub> concentrations in sediment from Site 424.

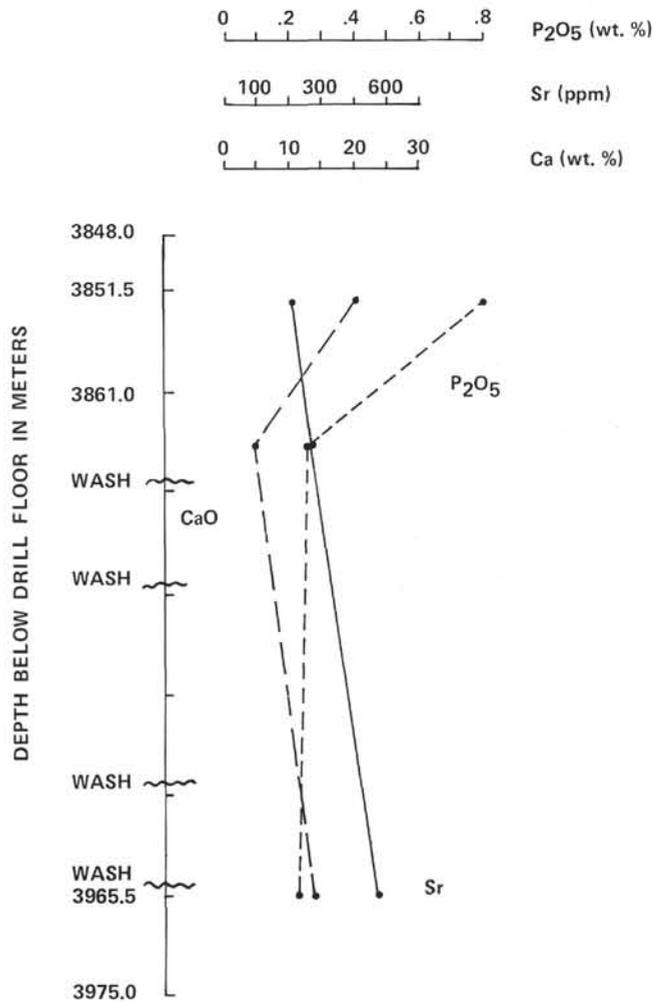


Figure 5. Depth versus CaO, Sr, and P<sub>2</sub>O<sub>5</sub> concentrations in sediment from Site 427.

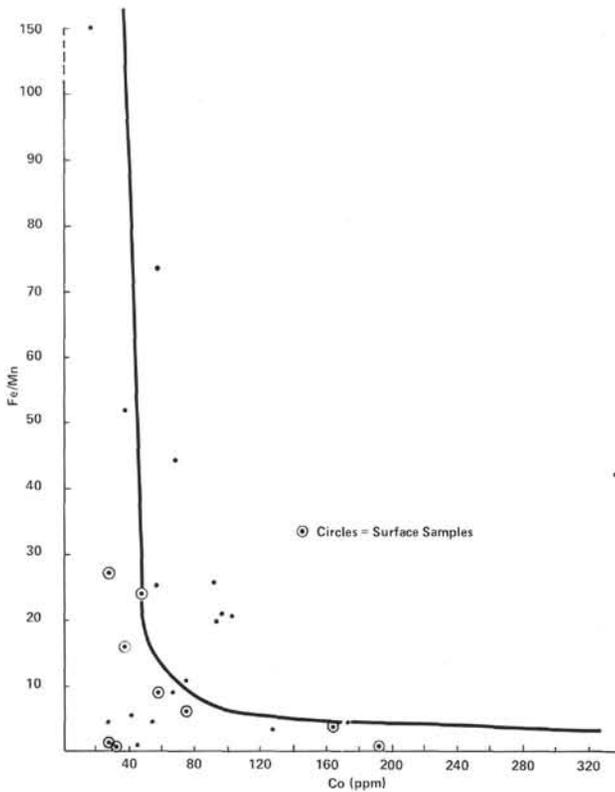


Figure 6. *Fe/Mn versus Co(ppm) for all analyzed sediment samples. The curve is a best-fit, regular geometrical approximation of the data.*

Future work is planned to determine the nature of the enrichment of these cations.

In a similar graph, Figure 8 displays the fairly incoherent scatter of points relating Sr to Rb. It is interesting to note, however, that the three surface sediments that plot in a nearly linear fashion in the lower third of the graph are all from the "Mounds Hydrothermal Field." Again, the low CaO content of the hydrothermal sediments predicts that Sr will also be depleted. In fact, the four points with Sr contents less than 100 ppm are all samples from Hole 424. Perhaps, then, the shaded portion of the graph may approximate a field occupied by deposits of hydrothermal affiliation at least in the Galapagos region. It is also interesting to note that the only other point falling in this field is Sample 427-2-1, 30-32 cm. We have previously postulated the hydrothermal affiliation of this sediment as due to its Fe/Mn reversal. Alteration of silicate phases and hydrothermal sulfide veining are reported in the basement basalts of Site 427 by Schrader and Furbish (Mineralogy and geochemistry of ore minerals, etc., this volume).

#### BULK X-RAY DIFFRACTION MINERAL IDENTIFICATION

The most intense peak for each mineral phase identified in the sediment cores is presented in Table 3.

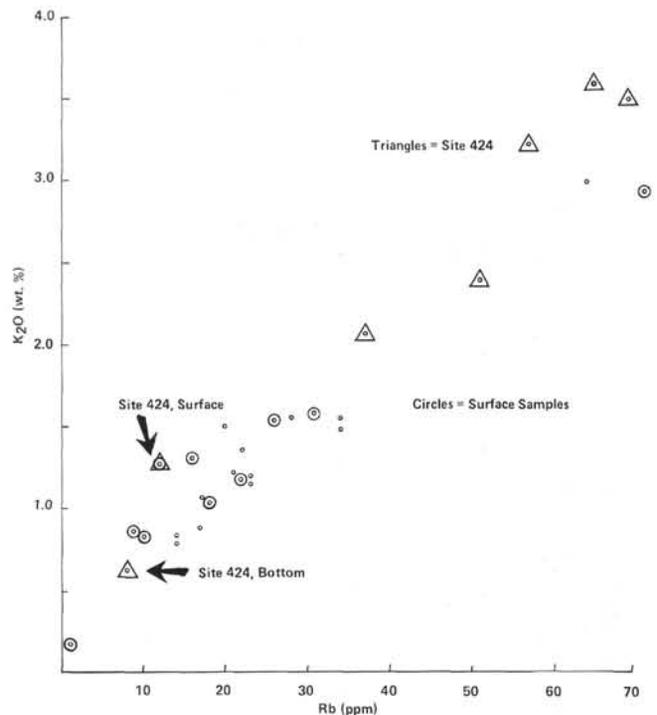


Figure 7. *K<sub>2</sub>O(wt. %) versus Rb(ppm) for all analyzed sediment samples.*

Calcite is by far the dominant constituent, decreasing in relative abundance in Hole 424 in the Mounds Hydrothermal Field. Saponite is nearly ubiquitous throughout the samples, showing no relative increase in intensity or crystallinity at Hole 424. Chlorite is generally absent, although it does appear in the upper two samples from Hole 424 and the surface sample from Hole 424A.

Two minerals occur in Hole 427 samples that are not seen in other cores: dolomite and pyrite. Dolomite occurs in the surface sample from Hole 427 and corresponds to a decrease in Rb, Sr, and K<sub>2</sub>O relative to underlying sediment. These relative depletions and the low intensity of the calcite peaks indicate that the ordered dolomite lattice is less capable of holding these cations in substitutional sites and that the volume of calcite present is insufficient to accommodate the trace quantities found in other samples. The high P<sub>2</sub>O<sub>5</sub> content (0.79 wt.%) is reflected in the occurrence of colophane as a grain coating and minor matrix constituent of the lithic nodules found in this portion of the core.

The presence of pyrite in Sample 427-3-3, 81-83 cm is megascopically noticeable in the core as disseminated black flecks in an apparently unaltered carbonate ooze. The pyrite is thought to be diagenetic and the result of H<sub>2</sub>S fixation and reduction of Fe<sup>+3</sup> ions in the pore waters; it is accompanied by an increase in Co, Cu, Fe, Zn, and Mo relative to the surrounding sediments. These elements apparently are incorporated in the poorly crystalline pyrite, since no sulfides or other minerals containing these cations as major constituents are present in the sample.

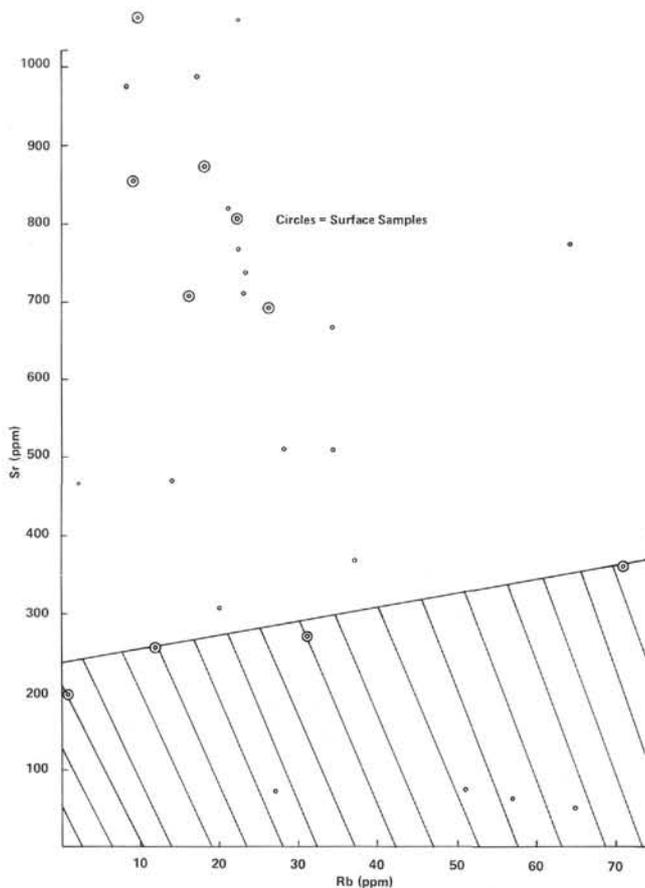


Figure 8. *Sr(ppm) versus Rb(ppm) for all analyzed sediment samples. Shaded area represents field dominated by hydrothermally affiliated samples.*

## CARBONATE PETROLOGY OF LITHIC NODULES

### Sample Descriptions

Eleven thin sections of carbonate oozes directly overlying basalts of the EPR region were examined (Table 2). The majority are foraminiferal biomicrite (Folk, 1962) or foraminifer wackestone (Dunham, 1962). The foraminifers are predominantly *Globorotalia* spp. and *Globogerina* spp.; other fossils include biserial foraminifers, diatoms, radiolarians, and unidentified minute fragments. The matrix is light tan to dark brown, high-magnesium calcite, with a crystal size usually less than 5  $\mu\text{m}$ . Bioclasts are rarely in contact, at most in point contact, separated by the micrite. Some foraminifer tests are completely filled in with sediment, although incomplete sediment infilling of the chambers is the rule. Partially filled tests display a systematic flooring, the result of carbonate mud filtering in under the influence of gravity, allowing for the orientation of the samples. Numerous other samples contain unfilled tests, which display an incipient internal rim of blunt and short (< 10  $\mu\text{m}$ ) magnesium calcite druse. These secondary crystals parallel the sweeping extinction of the shell wall when rotated under polarized transmitted light with crossed nicols, and appear to be overgrowths in optical

TABLE 3  
X-Ray Diffraction Mineral Identification of Unwashed Sediment

Sample (Interval in cm)	Relative Value of the Most Intense X-Ray Peaks						
	Calcite	Quartz	Halite	Smectite			Pyrite
				Saponite	Chlorite	Dolomite	
<b>Hole 419</b>							
1-CC, 2-4	60	8	3	7	—	—	—
2-3, 53-55	70	7	3	6	—	—	—
3-1, 91-93	87	12	8	9	11	—	—
4-2, 92-94	30	9	17	10	0.5	—	—
4-5, 13-15	41	7	—	8	—	—	—
5-CC, 1-2	95	5	4	6	—	—	—
<b>Hole 419A</b>							
1-3, 132-134	82	12	5	10	—	—	—
<b>Hole 420</b>							
1-1, 10-12	82	10	6	7	—	—	—
2-3, 70-72	28	12	5	7	—	—	—
9-1, 10-12	55	8	6	7	—	—	—
10-2, 41-43	31	9	5	10	—	—	—
11-2, 15-17	100	6	—	7	—	—	—
12-2, 50-52	100	—	5	5	—	—	—
13-4, 130-132	120	5	4	5	—	—	—
<b>Hole 420A</b>							
1-1, 24-26	68	11	—	8	—	—	—
<b>Hole 424</b>							
1-1, 97-99	—	—	5	9	9	—	—
1-2, 67-69	40	—	6	12	10	—	—
2-1, 50-52	—	—	—	6	—	—	—
2-4, 29-31	6	—	—	10	—	—	—
2-4, 130-132	35	6	4	9	—	—	—
3-1, 27-29	—	—	—	6	—	—	—
4-6, 83-85	40	5	7	4	—	—	—
<b>Hole 424A</b>							
1-1, 77-79	20	7	29	8	10	—	—
<b>Hole 425</b>							
1-1, 13-15	115	—	11	8	—	—	—
<b>Hole 427</b>							
2-1, 30-32	13	3	—	—	—	46	—
3-3, 81-83	41	—	8	9	5	—	12
8-1, 18-20	43	—	11	12	7	—	—
<b>Hole 429</b>							
1-1, 90-92	115	5	4	6	—	—	—

continuity with the tests. Two foraminifer chambers display a small grouping of radiating acicular crystals up to 20  $\mu\text{m}$  long. Although resembling "whisker calcite," these also may represent crystallization by noncarbonate minerals.

In contrast, broken fragments make up a majority of the bioclasts in some samples, and are "floating" within the matrix. Still other samples almost completely lack bioclastic material, and have a clotted or pelleted appearance. These might be termed pelletoidal packstones (Dunham, 1962). Regardless of bioclastic make-up, most samples display mottling of the micrite, owing to bioturbation. Many still retain open burrows, some of which have organically stained walls, although one burrow with a darkened border was filled in with cream-colored carbonate mud. Numerous samples have patches and spherules which are opaque in transmitted light, but orange to reddish brown in reflected light. These are believed to be ferromanganese oxides. Patches of an unidentified yellow material (translucent under transmitted light) occur in lesser amounts. Many thin sections display rare anhedral quartz grains and elongate shards, which may be original or replaced microfossil fragments.

Only one sample contains calcite filling a fracture. Nowhere can the underlying volcanic material be seen to be worked up into the carbonates.

## Discussion

If preserved in the rock record, these samples would portray an heterogeneous suite of fine-grained carbonates. Variations are observed in porosity, mottling, dissolution/recrystallization, presence of noncarbonate minerals, pelleted versus nonpelleted matrix, both the amount and types of bioclasts, and whole versus broken tests. The accompanying volcanic rocks do not exert a uniform influence on recrystallization; even when in direct contact with the basalts, no change in the overlying carbonate fabric is visible. However, the presence of noncarbonate phases and stains indicates that geochemical and/or biochemical reactions have taken place.

An interesting aspect is the great variation in paragenetic sequences displayed by these samples. There is no grading of fossils or apparent working of the sediments, yet some samples consist wholly of broken tests while others are an admixture of whole and broken bioclasts. This leads to variations in porosity because the whole tests are rarely completely filled. Even those chambers which are ruptured upon compaction remain relatively unfilled. Fragmentation may have arisen through diverse means, such as chemical dissolution and disarticulation before or after sedimentation, or by physical processes, such as reworking of the sediments by benthic organisms. Most tests appear to retain the original shell wall architecture, although some display patches of recrystallization which go to extinction under crossed nicols. Internal cementation by an incipient primary pore-filling druse is present only within those chambers that do not display micrite infilling. This sediment flooring appears to have been an early process, preventing any internal cementation in those tests where present. No tests display complete filling by pore-filling cement.

A great variability in diagenetic pathways may be inferred from this thin section analysis. Even within those samples directly in contact with volcanic rocks, there has been no extensive or uniform recrystallization. However, the presence of noncarbonate materials indicates some diagenetic influence owing to biochemical and/or geochemical reactions. Of special interest is the heterogeneity displayed by these samples, although deposited within and diagenetically controlled by relatively equivalent environments.

## SUMMARY AND CONCLUSIONS

To summarize chemical relationships between the sediments reported here and to compare the present study with previous work, Table 4 is provided. Obviously, major variations exist both within the sediments of the present study and between these sediments and the previously reported metal concentrations of Pacific sediments.

Sites 419, 420, and 427 are generally higher in Fe, Zn, and Sr than previously reported Pacific clays (Table 4; B and C) and the average of pelagic clays (Table 4; A).

TABLE 4  
Average of Selected Trace Metal Compositions  
in Pacific Sediments (ppm)

Leg 54, Sites/Previous Studies	Fe(%)	Co	Cu	Zn	Sr
419	8.31	115(71)	150	290	638
420	6.48	96	178	242	755
424	16.17	38	147	117(69)	259(140)
427	9.21(5.06)	238	203	260	306
A) Pelagic clay <sup>a</sup>	6.50	74	250	165	180
B) 19 Brown Pacific clays <sup>b</sup>	5.39	55	239	154	228
C) Surface Pacific pelagic clays <sup>c</sup>	5.06	101	323	—	—
D) 7 EPR sediments <sup>d</sup>	18.00	105	730	380	—
E) 11 Ferruginous sediments from Sites 159, 160, and 162 <sup>e</sup>	17.50	83	917	358	—
Crustal abundances <sup>f</sup>	5.63	25	55	70	375

<sup>a</sup> = Turekian and Wedepohl, 1961.

<sup>b</sup> = Burnett, 1971.

<sup>c</sup> = Cronan, 1969.

<sup>d</sup> = Bostrom and Peterson, 1969.

<sup>e</sup> = Cronan and Garret, 1973.

<sup>f</sup> = Taylor, 1964.

Note: Values in parentheses are averages excluding one very high anomalous concentration.

The Co contents of the sediments from these sites are similar to averages A, B, and C, while their Cu concentrations are lower than these averaged values. The increased Fe and transition elements at Site 427 may be due to hydrothermal components of the sediment.

The sediments of Site 424 are similar to ferruginous deposits (D and E in Table 4) of the EPR in their Fe content. The low transition-element concentrations of the Mounds area deposits correlate with other documented occurrences of hydrothermal deposits (Hoffert, 1978). Although Fe-rich sediments of the East Pacific have been postulated as hydrothermal in origin (D and E, Table 4), it is evident that they were not deposited from fluids similar in composition to those responsible for topographic build-up in the Mounds Hydrothermal Field.

On the whole, the authors feel that any or all of the sediments studied may have a component directly related to hydrothermal deposition. The common recrystallization and dissolution of carbonate tests in the lithic nodules studied may be a chemical response to these circulating fluids. Perhaps the fact that the Fe contents of most of the sediments studied are higher than those of older sediments reflects diagenetic adjustment of the metal with time. The fingerprint of slight or subtle hydrothermal effects may thus be lost with minor redistribution of the previously deposited elements.

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