50. CHEMICAL COMPOSITION AND METAL ACCUMULATION RATES OF METALLIFEROUS SEDIMENTS FROM SITES 319, 320, AND 321

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ABSTRACT

Chemical analyses of 22 elements in 27 samples from DSDP Leg 34 cores clarify some of the sedimentological processes operating on the Nazca plate. All sediments analyzed have high transition metal to aluminum ratios typical of metalliferous sediments found near spreading centers. Distinctive compositional differences exist between surficial sediments and basal sediments of Site 319. The elemental abundance patterns and metal accumulation rate data for these two contrasting parts of the core suggest that the basal sediments are dominated by hydrothermal sources of metals, while the hydrogenous precipitation is important in the near-surface sediments. Hole 320B and Site 321 exhibit many of the same compositional patterns; however, the younger sediments of Site 321 reflect an increasingly important detrital sediment component.

INTRODUCTION

Two areas of the Nazca plate, the East Pacific Rise Crest (EPR) and the Bauer Deep, have Recent sediments with anomalously high concentrations of various transition metals. The EPR sediments have been extensively studied, and on the basis of their unique chemistry (Boström, 1973 and references contained therein), accumulation rates (Bender et al., 1971), and lead isotopic composition (Bender et al., 1971; Dymond et al., 1973), these metalliferous sediments are thought to form from hydrothermal solutions resulting from mid-ocean ridge volcanism. Sediments from the Bauer Deep have been less extensively studied than the Rise Crest sediments and their origin is less certain. Although the Bauer Deep sediments are chemically similar to EPR sediments, some clear compositional distinctions can be made (Dymond et al., 1973). In addition, the metal accumulation rates are much lower in the Bauer Deep than on the EPR crest (Dymond and Veeh, in press). Nonetheless, lead isotopic data of Bauer Deep sediments indicate a magmatic origin.

Leg 34 of the Deep Sea Drilling Project recovered sediments from three locations on the Nazca plate. These sites are located on crust formed by volcanism along the now extinct Galapagos Rise, and one of the sites (319) is within the Bauer Deep. These sites, consequently, offer the possibility of (1) looking for evidence of metalliferous sediments deposited on the Galapagos Rise; (2) comparing possible hydrothermal products in basal sediments of different ages formed on the Galapagos Rise; and (3) investigating the time variations of the composition of metalliferous sediments in the Bauer Deep over the past 16 m.y.

ANALYTICAL PROCEDURES

The chemical compositions of the sediments were determined by instrumental neutron activation (INAA) and atomic absorption spectrophotometry (AAS). All sediments were dried at 110°C overnight before weighing for the analysis. For the INAA analyses, the samples were irradiated with USGS standard rocks in the rotating rack of the Oregon State 1 megawatt TRIGA research reactor. The samples were counted on an 8% efficient Ge(Li) detector with 0.9 kev resolution at 122 kev and 2.0 kev resolution at 1333 kev. Data accumulation and reduction were done with a computerized multichannel analyzer system. Each sample was counted twice, once 5 to 12 days after irradiation for Na, La, and Sm and after 18 days for the remaining elements. The general procedure is discussed in Gordon et al. (1968).

AAS measurements were made on samples dissolved in Teflon-lined bombs using HF, HNO₃, and HCl heated to 125°C. H₃BO₃ was added to neutralize the HF and to dissolve insoluble fluorides. CsCl was added to both standards and unknowns to depress ionization effects caused by the presence of Na in the samples. Standard solutions, prepared from pure metals, were matched with respect to pH and anion content. The precision of these analyses varies from less than 1% for the major elements and trace elements with concentrations greater than 200 ppm to approximately 20% for trace elements in the CaCO₃-rich samples. Comparison with reported data on USGS standard rocks suggest there are no systematic errors. We have analyzed Fe and Ba by both INAA and AAS. In most cases the iron analyses agree to better than 5% and the Ba analyses agree to within 15%.

Salt content of each sample was determined by measuring the water content of the bulk sample and assuming a constant salinity of $35^{\circ}/_{00}$ for the interstitial waters. The CaCO₃ content of each sample was determined by measuring the total calcium content of the sediment and solving a mass balance equation of the form:

$$Ca_T = Ca_c S + Ca_N N + Ca_c C \tag{1}$$

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where:

- Ca_t = the wt% of Ca in the total sample Ca_s = the wt% of Ca in the salt fraction of the sample, which equals 1.14% for sea salts S = the weight fraction of salt in the sample Ca_N = the wt% of Ca in the noncarbonate fraction
- N = the weight fraction of noncarbonate phases
- Ca_c = the wt% of Ca in CaCO₃, which equals 40.04%

C = the weight fraction of CaCO₃ in the sediment The measured variables in this expression are CaT and S. By definition, the sediments is composed of only salt, noncarbonate and CaCO₃ phases. Therefore, S + N + C= 1, which when combined with Eq. 1 results in one equation with two unknowns, CaN and C:

$$Ca_T = 1.14S + Ca_N - Ca_N S - Ca_N C$$

+ 40.04 C (2)

By assuming a value for the percent Ca in the noncarbonate fraction (Ca_N), this equation can be solved for C, the percent of CaCO₃. Fortunately, for the sediments of the Nazca plate, Ca is a relatively minor element of the noncarbonate fraction. We have measured the Ca content of 12 samples which had been leached with buffered acetic acid or which by visual inspection were naturally free of CaCO₃. The Ca content of these noncarbonate samples is $0.73 \pm 0.12\%$, and we have chosen this value for Ca_N of Eq. 2. With appropriate rearranging, the final equation results:

$$C = \frac{\text{Ca}_T - 0.41 \, S - 0.73}{39.31} \times 100 \tag{3}$$

Figure 1 shows the effects of errors in our assumption that $Ca_N = 0.73\%$. It can be seen that if our estimate of Ca_N is 100% too high or low, large percentage errors in



Figure 1. Errors introduced into the $CaCO_3$ determination by errors in the estimate of Ca_N of Equation 1.

our CaCO₃ determination result for sediments with less than 10% CaCO₃. The important point, however, is that the errors due to poor estimates of Ca_N drop very rapidly with higher CaCO₃ contents and reach values of approximately 1% in error for sediments with 90% CaCO₃. Our experience with other methods of determining CaCO₃ (Leco-combustion and acid leaching) suggests that for high CaCO₃ contents there may be no more accurate means of measuring CaCO₃ in these sediments. It should be emphasized that as the percent of CaCO₃ in a sediment approached 100%, small errors in the CaCO₃ are magnified greatly into the determination of the carbonate-free correction factor. Our CaCO₃ estimate theoretically has the greatest precision near 100% CaCO₃, and errors in the Ca_N assumption result in relatively constant errors in the carbonate-free correction factor (<9% error for 100% underestimate and <5% for 100% overestimation between 10 and 100% CaCO₃).

DATA

Twenty-seven samples were analyzed for 22 elements (Table 1) from Leg 34 sites. At Site 319, the Bauer Deep site, samples were taken at relatively equal intervals over the entire length of the core. At Site 320 six samples spaced over the lower 50 meters of core were analyzed. Two samples, 319-1 and 319-2, included in the Site 319 data are not from the DSDP core but were sampled by

TABLE 1 Samples Analyzed

Sample Code	Sample (Interval in cm)	Depth Below Ocean Floor (m)
319-1	Y73-3-13 MG3, 5-10 ^a	0.08
319-2	Y73-3-13 MG3, 25-30 ^a	0.28
319-3	319-1-2, 60-62	2.11
319-4	319-1-3, 80-82	3.81
319-5	319-1-6, 23-25	7.74
319-6	319-2-4, 40-42	14.41
319-7	319-3-3, 80-82	22.81
319-8	319-4-1 and 2, 8-10, 104-106	30.00
319-9	319-5-2 and 3, 6-8, 40-42	40.00
319-10	319-6-4 and 5, 20-22, 122-124	53.50
319-11	319-7-3, 129-131	61.30
319-12	319-7-6, 69-71	65.20
319-13	319-8-5, 114-116	73.65
319-14	319-9-2, 124-126	78.75
319-15	319-10-2, 86-88	87.87
319-16	319-11-2, 80-82	97.31
319-17	319-11-5, 57-59	101.58
319-18	319-11-6, 40-43	102.92
319-19	319-12-3, 86-93	106.89
320-1	320B-2-3, 140-142	149.91
320-2	320B-2-5, 89-91	152.40
321-1	321-9-1, 30-32	68.31
321-2	321-9-6, 50-52	76.01
321-3	321-11-2, 80-82	89.31
321-4	321-13-1, 133-135	116.84
321-5	321-13-2, 84-86	117.85
321-6	321-13-3, 125-127	119.76

^aLocation is 12°59.0'S, 101°33.05'W, 4303 meters depth.

gravity coring in the same location by an Oregon State cruise YALOC-73. These samples provide a surface sampling of the site not possible by the DSDP coring.

Metal accumulation rates (Table 2) have been calculated using the compositional data in Table 3, shipboard bulk density measurements, and paleontological age control (Quilty, this volume; Quilty et al., this volume).

DISCUSSION

We have based much of the discussion of the metalliferous sediments of this site on an acceptance of the hypothesis that a marine hydrothermal system is the essential mechanism for their formation. There are many aspects of marine hydrothermal systems which are unknown and need refinement. For example, we have only crude ideas about which elements have a magmatic source and which a seawater source; we know little about the composition of the hydrothermal fluids; and we are only beginning to understand the important rock-water reactions which produce metal enrichments in the hydrothermal fluid and change the rock compositions. Nonetheless, the chemistry of the sediments (high transition metal to Al ratios); the high accumulation rates of these sediments on mid-ocean ridges; the magmatic lead isotopic composition of the sediments; and geophysical data (primarily heat-flow patterns) strongly point to hydrothermal processes for their origin. Thus, for the sake of brevity, we have not considered alternative hypotheses of origin in our discussion (low temperature weathering for example).

Hole 319

Chemical Composition

Compared to typical pelagic sediments, the chemical composition of the sediments analyzed in this study are anomalous with regard to their unusually low aluminum and high iron values (Figure 2). However, the sediments from Site 319 are very similar to other metalliferous sediments in surface samples from the Nazca plate (Figures 2 and 3). The upper 20 meters of Hole 319 are similar to surficial Bauer Deep sediments, while the basal sediments strongly resemble surficial EPR sediments (Figures 2 and 3). The elements Ca, Zn, Mn, and Fe are strongly correlated with each other and in general have the highest abundances in the basal sediments (Figure 4). Since the bottom 40 meters of the core were deposited between 16 to 13 m.y. ago as this site was near the crest of the Galapagos Rise, it is tempting to ascribe the origin of these elements primarily to

TABLE 2 Metal Accumulation Rates

Sample	Sedimentation Rate ^a (cm/10 ³ yr)	Density ^b (g/cc)	Fe	Accum (mg/ Mn	ulation cm ² /10 Si	Rates 3 yr) Al	Ni
319-1	0.11	1.14	2.9	0.86	3.1	0.64	0.022
319-2	0.11	1.15	3.0	1.1	3.2	0.58	0.021
319-3	0.11	0.18	3.5	1.2	3.8	0.73	0.019
319-4	0.11	1.17	3.9	0.92	4.0	0.65	0.018
319-5	0.11	1.14	4.0	0.90	3.8	0.61	0.015
319-6	0.44	1.32	13	2.6	15	1.0	0.020
319-7	0.44	1.30	9.2	2.1	9.2	0.53	0.012
319-8	0.44	1.56	16	3.4	6.2	1.0	0.021
319-9	3.2	1.62	32	7.1	10	1.8	0.060
319-1 0	3.2	1.67	25	4.8	10	1.8	0.059
319-11	3.2	1.69	52	12	20	3.8	0.089
319-12	3.2	1.68	34	7.9	17	2.6	0.052
319-13	3.2	1.72	85	23	25	4.7	0.21
319-14	3.2	1.69	221	70	46	8.3	0.57
319-15	3.2	1.74	86	25	23	3.7	0.22
319-16	3.2	1.79	172	53	33	6.0	0.48
319-17	3.2	1.68	181	54	37	6.4	0.43
319-18	3.2	1.68	107	33	21	3.4	0.27
320-1	0.67	1.68	15	7.0	8.0	0.78	0.052
320-2	0.67	1.68	17	7.9	8.3	0.82	0.048
321-1	0.28	1.60	11	3.2	18	6.3	0.050
321-2	0.28	1.63	29	6.1	14	4.7	0.074
321-3	0.62	1.63	5.5	1.3	3.5	1.1	0.017
321-4	0.62	1.67	22	12	6.3	1.8	0.12
321-5	0.62	1.67	40	21	7.2	1.9	0.20
321-6	0.62	1.67	23	5.9	3.8	6.1	0.077

^aSedimentation rates from paleontological data in Leg 34 Hole Summaries and Bukry, personal communication.

^bDensity from data in Leg 34 Hole Summaries. In most cases these values are from measurements on nearby samples; however, in a few cases there were no measurements available for close samples. The density estimates in these cases are typical values for sediments with similar CaCO₃ contents.

	319-1	319-2	319-3	319-4	319-5	319-6	319-7	319-8	319-9	319-10	319-11	319-12	319-13	319-14
Depth in core (m)	0.08	0.28	2.11	3.81	7.74	14.41	22.81	30.00	40.00	53.50	61.30	65.20	73.65	78.75
Major elements (%)														
Fe (AASC)	16.45	16.68	16.25	17.50	18.20	16.86	17.90	26.00	21.00	13.50	18.50	24.20	26.00	32.30
Fe (INAA)	_	-	18.80	19.30	21.30	17.30	20.30	26.00	22.00	13.90	18.50	26.70	30.00	32.10
Mn	4.94	6.05	5.39	4.14	4.15	3.46	4.06	5.60	5.00	2.60	4.24	5.69	7.00	10.20
Si	17.51	17.36	17.33	17.67	17.60	19.33	18.00	10.20	7.00	5.40	7.00	12.30	7.70	6.70
Al	3.65	3.15	3.35	2.94	2.80	1.14	1.03	1.63	1.20	0.95	1.35	1.87	1.40	1.2
Ba (AASC)	2.36	2.37	2.27	2.19	2.24	1.62	1.25	1.16	1.20	1.18	1.16	1.90	1.01	0.64
Ba (INAA)	_		2.31	2.58	2.59	1.39	1.12	.98	1.10	1.03	1.03	1.60	1.03	0.5
Trace elements (ppm)														
Sc	_	_	29.30	25.40	26.30	10.89	10.70	11.80	15.00	10.10	12.30	19.10	14.00	9.60
Cr	-	-	40.00	36.00	40.00	18.80	39.00	18.00	_	_	24.00	45.00	27.00	25.00
Со	_	_	319.00	236.00	249.00	100.00	108.00	169.00	160.00	114.00	139.00	197.00	180.00	136.00
Ni	1259.00	1161.00	874.00	797.00	690.00	261.00	225.00	350.00	400.00	310.00	310.00	570.00	630.00	830.00
Cu	1360.00	1167.00	1172.00	1184.00	1190.80	1044.00	1220.00	1530.00	1500.00	1120.00	1210.00	1880.00	1800.00	1650.00
Zn	472.50	503.70	442.00	450.00	461.00	418.00	372.00	500.00	600.00	363.00	380.00	540.00	670.00	704.00
Sb	_	-	12.60	10.90	11.80	4.43	3.60	7.30	11.00	4.20	6.20	16.40	11.60	7.9
La	_	_	282.00	281.00	293.00	126.80	142.00	174.00	_	167.00	175.00	245.00	220.00	151.0
Ce	_	-	—	_	_	_	_	51.00	50.00	31.50	_	66.00	53.00	
Nd	_	_	222.00	238.00	236.00	109.80	119.00	136.00	100.00	113.00	133.00	174.00	140.00	119.0
Sm		_	40.00	40.20	41.80	17.70	21.00	27.00	_	19.30	24.10	34.00	32.00	19.9
Eu	—		11.20	10.79	11.30	5.08	6.08	7.20	8.00	6.10	7.10	9.50	8.50	5.7
Тb	_		5.90	5.93	6.30	2.61	2.77	4.90	5.00	3.90	3.42	7.30	5.80	2.7
Yb	_	_	34.00	30.20	32.00	12.20	12.60	24.00	31.00	22.00	15.50	32.00	28.00	11.6
Lu	—		7.50	6.49	6.70	2.39	2.56	3.30	4.00	2.85	3.00	4.70	3.90	2.3
Hf	_	_	4.95	4.34	4.49	_	_	2.30	_	_	_	_	2.50	2.0
Th			_	_	_	_	_	2.00	_	_	_	1.98	1.70	_
Salt, CaCO ₃ corrections														
Correction factor	1.53	1.28	1.23	1.21	1.35	2.78	4.92	6.17	24.08	19.40	12.42	25.04	11.80	4.7
Ca ^a (%)	9.31	3.32	2.70	2.51	6.39	23.42	30.32	32.60	37.80	37.39	36.15	37.74	36.10	30.8
CaCO ₃ (%)	21.70	6.43	4.88	4.39	14.29	57.66	75.24	80.92	94.27	93.24	90.09	94.12	90.02	76.6
Water (%)	78.71	81.49	79.40	78.92	76.61	64.63	55.86	45.05	31.04	31.45	34.59	34.97	30.16	39.98
Salt (%)	12.94	15.41	13.49	13.10	11.46	6.40	4.43	2.87	1.58	1.61	1.85	1.88	1.51	2.3
						0110		2107	1.00	1101	1100	2100		

TABLE 3 Carbonate and Salt Corrected Chemical Compositions

^aUncorrected.

	319-15	319-16	319-17	319-18	319-19	320-1	320-2	321-1	321-2	321-3	321-4	321-5	321-6
Depth in core (m)	87.87	97.31	101.58	102.92	106.89	149.91	152.40	68.31	76.01	89.31	116.84	117.85	119.76
Major elements (%)	10.00	20.00	20.00	20.00	22.00	17.10	22 (0	15 40	26.00	24.00	27.00	27.04	14.20
Fe (AASC)	18.80	29.00	29.00	28.00	22.00	17.10	23.60	15.40	26.90	24.00	27.00	27.94	14.20
Fe (INAA)	19.60	29.00	31.10	29.00	19.00	18.70	24.60	15.50	26.60	26.00	27.00	29.60	14.90
Mn	5.40	8.90	8.70	8.50	5.10	7.90	10.80	3.37	5.70	5.80	13.80	14.76	3.70
Si	5.00	5.50	5.84	5.40	9.00	8.90	11.40	19.00	12.60	15.00	7.60	4.99	23.80
Al	0.80	1.00	1.03	0.89	1.30	0.88	1.12	6.73	4.37	4.70	2.10	1.33	4.00
Ba (AASC)	0.54	0.52	0.54	0.74	0.74	0.50	0.61	0.19	0.11	0.57	0.35	0.35	0.06
Ba (INAA)	0.50	0.45	0.42	0.64	0.61	0.44	0.62	0.15	0.10	0.54	0.34	0.32	0.07
Trace elements (ppm)	7.60	0.70	0.00	0.00	7 10	5.20	6.10	04.10	17.10	22.00	11.00	7.70	26.00
Sc	7.60	8.70	8.20	8.60	7.10	5.20	6.10	24.10	17.10	23.00	11.60	7.76	26.90
Cr	12.90	17.10	33.00	28.00	22.00	_	23.00	40.00	31.00	_	27.00	19.20	17.30
Со	94.00	127.00	133.00	122.00	74.00	62.00	84.00	224.00	185.00	230.00	123.00	101.20	54.00
Ni	480.00	800.00	690.00	700.00	490.00	580.00	650.00	530.00	690.00	700.00	1430.00	1390.00	480.00
Cu	1070.00	1490.00	1410.00	1400.00	1300.00	1030.00	1290.00	927.00	1190.00	1500.00	1420.00	1439.00	500.00
Zn	470.00	670.00	630.00	570.00	510.00	550.00	730.00	418.00	650.00	730.00	870.00	885.40	390.00
Sb	5.60	7.70	8.20	7.20	5.20	2.56	3.50	9.10	13.90	7.50	8.80	7.70	1.16
La	112.00	137.00	137.00	150.00	84.00	76.00	85.00	208.00	206.00	220.00	180.00	168.00	33.00
Ce	27.00	34.00	_	_	_	_	27.00	116.00	_	110.00	48.00	_	17.40
Nd	83.00	85.00	113.00	122.00	76.00	54.00	86.00	161.00	132.00	180.00	141.00	140.10	30.00
Sm	17.20	18.20	18.40	20.00	12.00	10.60	13.40	35.90	33.70	40.00	29.00	22.70	7.20
Eu	4.50	5.20	5.11	5.20	3.40	3.24	3.80	9.50	8.30	12.00	7.70	6.52	2.03
Tb	2.90	3.50	2.56	2.70	1.50	1.41	2.31	6.30	5.20	6.60	4.90	2.78	1.37
Yb	14.00	17.00	11.00	12.00	7.40	6.20	12.20	27.00	24.00	31.00	28.00	11.70	5.60
Lu	2.10	2.40	2.23	2.40	1.50	1.31	1.75	3.89	3.20	4.30	3.10	2.25	0.77
Hf	1.15	1.75	_				—	4.99	2.87	_	2.10	0.81	2.93
Th	0.62	1.11	—		-	-	_	7.90	4.10	4.40	1.83		-
Salt, CaCO ₃ corrections													
Correction factor	8.72	6.26	5.99	9.06	8.64	8.30	10.12	2.44	2.24	29.55	7.38	4.44	3.62
Ca ^a (%)	35.00	33.00	32.90	35.00	34.80	34.59	35.40	22.60	21.30	38.10	33.80	30.34	28.10
CaCO ₃ (%)	87.16	82.18	81.76	87.06	86.56	86.12	88.28	55.54	52.24	94.95	84.07	75.31	69.63
Water (%)	28.07	34.54	30.59	35.21	34.71	34.34	34.44	49.76	46.91	32.27	40.45	38.36	44.12
Salt (%)	1.37	1.85	1.54	1.90	1.86	1.83	1.84	3.47	3.09	1.67	2.38	2.18	2.76

 TABLE 3 – Continued



Figure 2. Al-Fe-Mn plot of 319, 320B, and 321 data.

hydrothermal processes accompanying mid-ocean ridge volcanism. Several of the elements, including Si, Al, Ni, Co, Ba, Sb, Sc, and the rare earth elements (REE), are dramatically enriched in the upper 20 meters of the core (Figures 5, 6, and 7). Since these surficial sediments were deposited after the site moved well away from the Galapagos Rise and into the Bauer Deep, it is tempting to suggest that they have a seawater origin rather than a hydrothermal origin. This possibility is supported by the REE abundance pattern which is very similar to the seawater pattern (Figure 8). As will be discussed in more detail below, there are other possible interpretations of these data. The point we wish to make here is that the contrasting elemental abundance patterns are not unique to this core. They have been observed in surface samples recovered from the EPR and the Bauer Deep (Dymond et al., 1973; Bischoff and Sayles, 1972) and must be accounted for in any model for the origin of Nazca plate metalliferous sediments.

Calcium carbonate content varies from approximately 80% near the bottom of Site 319 to a maximum of approximately 90% at 50 meters and then decreases to a few percent in the upper 10 meters. These CaCO₃ variations mark the movement of Site 319 from its position on the crest of the Galapagos Rise to its present location below the calcite compensation depth (CCD). The maximum CaCO₃ content at 50 meters can be the result of a rapid decrease in the accumulation of the metalliferous components away from the spreading center (Table 2), and a relatively constant accumulation of carbonate at depths shallower than the lysocline.

Metal Accumulation Rates

If we consider metal accumulation rates of Site 319, a rather different picture than that exhibited by concentration data emerges (Table 2 and Figure 9). Accumulation rates of Mn, Fe, and Ni are high in sediments less than a million years younger than basement ; an expected result for sediments formed by hydrothermal processes accompanying mid-ocean ridge volcanism. Aluminum and silicon accumulation rates, however, also reach a maximum near basement in spite of the fact that both elements have maximum concentrations in the youngest sediments at this site. This is possible because sedimentation rates increase by a factor of 30 from surface to near basement in this core. Any elements which do not show approximately this same concentration enrichment from bottom to top will have higher accumulation rates in the lower part of the core. The compositional differences between near-surface and nearbasement sediments at this site are possible because the accumulation rates of Mn and Fe decrease by a factor of 50 from basement to near-surface, while Si, Al, Ni, and other minor element accumulation rates decrease by a factor of approximately 10 or less.

Most studies of marine sediments have concluded that Al and nonbiogenous Si concentrations are primarily controlled by accumulation of detrital phases. This concept is undoubtedly true in many regions of the ocean; however, we suggest that on the Nazca plate these elements may be dominated by hydrothermal sources. An alternative hypothesis is that the high accumulation rates of Si and Al in the basal sediments result from detrital, volcanogenic phases which are easily weathered from the numerous exposed outcrops on mid-ocean ridges. If detrital phases were to account for all the aluminum in the Hole 319 sediments, there would have to be approximately 10% volcanogenic detritus in the basal sediments and 30%-50% detrital phases in the near-surface sediments. Detrital phases are extremely rare in these sediments. An occasional sample has volcanic glass or rock fragments; however, both X-ray diffraction and microscopic examination of these sediments suggest that this component comprises generally less than 1% of the sediment mass (Dasch et al., 1971).

Si-Al ratios also indicate a nonbasaltic source for these elements in the sediment. With the exception of Samples 319-6 and 319-7, the Si-Al ratios do not deviate greatly from a value of six (Figure 10). If detrital phases



Figure 3. Cu-Ni-Zn plot of 319, 320B, and 321 data.



Figure 4. Carbonate and salt corrected sediment compositions of Site 319 versus depth from sediment surface.

were accounting for the Si and Al in both near-bottom and near-surface sediments, generally lower and more variable Si/Al values would be expected. Volcanogenic detritus with Si/Al equal to approximately three might be expected in basal sediments; however, near-surface sediments, as a result of extremely slow sedimentation rates, might contain some continental detritus with higher Si/Al values. We shall discuss the significance of the high Si and Si/Al values in Sample 319-6 and 319-7 below.

Hydrothermal addition of Si to the sediments is a reasonable process. The solubility of Si in water increases rapidly with increasing temperature (Morey et al., 1962), and circulating seawater through cooling basalt would undoubtedly leach silica (Corliss, 1971). Relatively high concentrations of silica are observed in seawater hydrothermal systems (Tomasson and Kristmannsdottir, 1972; Brewer and Spencer, 1969).

The addition of aluminum by hydrothermal processes is more conjectural. Aluminum is rarely measured in hydrothermal solutions and is known to have very low solubility in aqueous solutions (Garrels and Christ, 1965). A possible mechanism for releasing aluminum into a seawater hydrothermal system is the albitization of feldspars. This reaction is important in greenschist metamorphism, a common metamorphic facies in the oceanic crust (Melson et al., 1968).

Another interesting relationship in this report is that of Fe and Si. From the metal accumulation rate data (Table 2), it is apparent that these elements are very closely correlated in the upper part of Site 319 sediments. In the upper 23 meters of sediment (approximately the last 10 m.y. of deposition), the Si and Fe accumulation rates are equal. Deeper in the core, however, Fe accumulates more rapidly than Si and near basement is approximately five times higher in concentration. It is probable that both Fe and Si are fixed primarily in the form of an Fe-smectite in the upper 20 meters of the core. Eklund (1973) found smectite to be the most important Fe-bearing phase in the Bauer Deep and from microprobe analyses of individual smectite grains determined an Fe/Si value of 0.91 ± 0.20 for this phase. Deeper in the core some of the Si may be in the form of smectite as this phase is known to be present in surface samples from the EPR Crest (Kendrick, 1973). Presumably, in the basal sediments the excess iron over that required to form Fe-smectites must largely be in the form of amorphous iron hydroxides and oxides.

Models of Sedimentation

Several hypotheses can be proposed to account for the vertical change in composition of the metalliferous sediments at Site 319. If the change in composition



Figure 5. Carbonate and salt corrected sediment compositions of Site 319 versus depth from sediment surface.



Figure 6. Carbonate and salt corrected sediment compositions of Site 319 versus depth from sediment surface.

results from an increase in the distance of the site from the hydrothermal source, the composition may reflect (1) adsorption of elements from seawater during transport of solid phases or addition of new solid phases (for example, Fe-Mn micronodules) by precipitation from seawater, or (2) fractionation of elements due to different rates of precipitation so that, for example, iron may precipitate rapidly and be concentrated in sediments near the source, while manganese and silica precipitate more slowly and thus further from the source. The change in composition may also result from initiation of volcanic activity and associated hydrothermal activity which produce hydrothermal products of a different composition.

If the first of these mechanisms is operating, the surface Bauer Deep sediments will consist of authigenic phases precipitated directly from seawater or primary hydrothermal phases transported from the EPR that have adsorbed elements from seawater or a mixture of these two. There is support for this model in some of the chemical trends in the data. The sediments become relatively more enriched through time in the trace metals, Ni and Co, relative to iron and manganese. Ferromanganese nodules, which may represent the authigenic precipitation, typically have higher Ni and Co contents than crestal EPR sediments. Also, Figure 3 suggests that the surface Bauer Deep sediments lie on a compositional tieline between metalliferous sediments from the EPR crest and Nazca plate nodules.

The metal accumulation rate data (Table 2 and Figure 11) are compatible with this model as well. Data on manganese accumulation rates in nodules and sediments (Bender et al., 1970) suggest that hydrogenous manganese accumultaion in the Pacific is approximately $1 \text{ mg/cm}^2/1000 \text{ yr}$. The low rates of manganese and the minor transition metal accumulation in the Bauer Deep suggest that authigenic precipitation could provide a significant fraction of the total accumulation of metals.

The second hypothesis, that fractionation of elements may occur during the precipitation process, is based on the concept that different metals precipitate at different rates from hydrothermal solutions entering seawater. Boström (1970) has favored this as an explanation for the decrease in Fe/Mn and Fe/Co values away from the EPR. He suggests, on the basis of stability relationships of Fe, Mn, Ni, and Co (Pourbaix et al., 1963), that the order of precipitation is Fe, Mn, Ni, and Co in oxygenated seawater. We might also add Si as a relatively mobile element which, because of its relatively high solubility, may enter the dissolved silica load of seawater. Evidence that fractionation of elements takes place in marine hydrothermal systems can be inferred by the dramatic fractionation of Fe and Mn observed in a few deep-sea deposits thought to be of hydrothermal origin. Bonatti and Joensuu (1966) and Piper et al. (in press) have reported on extremely Fe-rich deposits which have uranium isotopic compositions (Veeh and Boström, 1971) and rare earth abundances suggestive of a hydrothermal origin. The deposits described in these studies have very low abundances of the trace transition elements and in one case an anomalously enriched manganese deposit is associated with the iron deposits. Another example of Fe and Mn fractionation may be the highly manganese enriched crusts recovered from the Mid-Atlantic Ridge (Scott et al., 1974). A hydrothermal origin for these crusts is indicated by the U-Th disequilibrium and their unusual composition compared to other Fe-Mn nodules. These rather dramatic fractionation effects, however, are rather rare and the Fe/Mn ratio is relatively constant for all of the Nazca plate metalliferous sediments (Fe/Mn = 3.5 ± 1.8). Furthermore, it may be simplistic to think that formation of oxides and hydroxides of the trace transition metals (Cu, Ni, Zn, and Co) is the cause of their removal to the sediments. These elements are more likely removed by coprecipitation and adsorption with the more major



Figure 7. Carbonate and salt corrected sediment compositions of Site 319 versus depth from sediment surface.

phases. Thus, differences in the stability relationships of the different transition metals are not the likely explanation for the compositional differences of near-surface and near-bottom sediments of Site 319. It may be more feasible, however, that a silicate phase (smectite) precipitating from a hydrothermal solution could have a different grain size than the precipitated iron and manganese phases, and would be subject to transport to a greater or lesser degree.

The third hypothesis would account for the differences between the near-surface and near-basement compositions of Site 319 only if a new hydrothermal system and resulting fluids released to seawater had a different chemical composition than the original Galapagos Rise system. Mid-plate volcanism could result from the rearrangement of plate motions which occurred with the jump of spreading from the Galapagos Rise to the EPR. Alternatively, volcanism on the newly formed EPR could be the source of hydrothermal products in the near-surface sediments of this site. Anderson and Halunen (1974) have argued on the basis of a bimodal heat-flow distribution in the Bauer Deep for a local hydrothermal source of Bauer Deep metalliferous sediments. Both possibilities seem somewhat untenable at the present time. Presently there is no evidence of mid-late volcanism in the Bauer Deep region. The ages of basement and the overlying sediments of Site 319 are concordant (Hogan and Dymond, this volume) and suggest the basalts were emplaced on the Galapagos Rise. The bimodal heat-flow distribution itself is questionable, since it is largely indicated by the presence of only 2 or 3 heat-flow measurements in the Bauer Deep with values between 3 and 5 heat-flow units (Anderson and Halunen, 1974). In addition, there is no evidence that the EPR hydrothermal system is producing sediments with a composition similar to near-surface Bauer Deep sediments. Sediments recovered from the crestal EPR strongly resemble the near-basement sediments of Site 319 and are distinctly different than the surface Bauer sediments (Figures 2 and 3).

Although hydrothermal activity from the EPR is not a probable explanation for the dramatic compositional differences of near surface and basal sediments from Site 319, there is evidence that the formation of the EPR is reflected in subtle ways in the sediments. Site 319 is located approximately 300 km east of a topographic scarp (Bauer Scarp) which appears to mark the boundary between the more recent crust produced by the EPR and older crust produced by the Galapagos spreading center (Rea, in preparation). Site 319 is nearly 600 km from the Galapagos spreading center. Thus, at the time the EPR was beginning to form, the nearest source of volcanism and hydrothermally produced products was the EPR. Would this closer new source of volcanism result in a detectable increase in hydrothermal products at this site? Rea (in preparation) estimates that the initiation of spreading at the EPR began approximately 8 m.y. ago. Figure 9 and Table 2 suggest that at 8 m.y., represented by Sample 319-6, the accumulation rate of metals is higher than in samples above or below this depth. Furthermore, in Figure 11 we see that for Site 319 the relatively smooth almost exponential decrease in manganese accumulation rate is perturbed at this age depth of the core. Because Site 319 is 300 km from the probable location of the incipient



Figure 8. Carbonate and salt corrected rare earth compositions of Leg 34 sediments normalized to the chondritic rare earth abundances of Haskin et al. (1967). The normalized seawater pattern uses data of Hogdahl et al. (1968).

EPR, a large perturbation in the metal accumulation rate with the initiation of spreading would not be expected. This distance (equivalent to 3-4 m.y.) would mean only a 2-3 times increase in rate over the expected rate due to volcanism on the Galapagos Rise (Figure 11).

Due to the scatter in the accumulation rate data through time for Site 319, this interpretation is speculative. There are subtle, chemical variations in Samples 319-6 and 319-7, however, which we further speculate are due to the beginning of hydrothermal activity on the EPR. For example, Fe/Ni values, which are always higher for ridge-crest sedimentation compared to the Bauer Deep (Dymond et al., 1973) reach a maximum in Samples 319-6, 319-7, and 319-8. More dramatic compositional differences are exhibited by the Si/Al values for 319-6 and 319-7. As discussed above and exhibited by Figure 9, the Si/Al value for Site 319 does not vary greatly except for 319-6 (Si/Al = 16.8) and 319-7 (Si/Al = 17.5). These high Si/Al might be thought to be the result of a sharp increase in biogenous opal content in this portion of the core. Examination of acetic-acidleached smear slides of these two samples, however,



Figure 9. Accumulation rates of Fe, Mn, Si, and Al versus age above basement. Because of the small age difference of the five deepest samples in the core, they have been averaged and are shown as a single point.

reveals no biogenous opal. The noncarbonate sediment fraction of these samples is primarily translucent yellowbrown, equal-dimensional grains, probably a smectite. Thus, the variations in the Si/Al ratio in these sediments may result from the existence of different temperature conditions in a newly developing hydrothermal system such as existed when the EPR was beginning. For example, at temperatures <125°C silica in hydrothermal solutions will not be supersaturated with respect to amorphous silica (Morey et al., 1962; Jones and Pytkowicz, 1973) when cooled to seawater temperatures and may enter the dissolved silica budget of seawater. At higher temperatures silica will be supersaturated in cooled hydrothermal solutions and may be initially deposited as amorphous silica which is diagenetically altered to smectites. There may be other explanations for the chemical variations exhibited by these two samples, but it is an intriguing possibility that the timing of the EPR spreading might be discernible in long sediment cores from near the Bauer Scarp.

CONCLUSIONS

The clear compositional distinctions between the near-basement and near-surface sediments from Site 319 probably result from the superposition of authigenic metal deposition over metal deposition from marine hydrothermal systems. The sharp decrease in the rate of



Figure 10. Carbonate and salt corrected silicon versus aluminum concentrations.



Figure 11. Summary of available Nazca plate manganese accumulation rates plotted against age above basement.

metal deposition through time observed at this site results from movement of the site away from the

hydrothermal system inferred to operate on the Galapagos Rise. The relatively constant addition of trace elements by adsorption onto hydrothermally produced phases and authigenic precipitation from seawater becomes an important addition to the sediments deposited far from the spreading center where the sedimentation rate is approximately 0.1 cm/1000 yr. Because of the extremely low inputs of continental detritus to this region, the hydrothermal addition of Fe, Mn, and probably Si and the authigenic addition of Ni, Co, Ba, and REE to the sediment dominates the inorganic metal deposition at this site.

There is some evidence in the elemental abundance patterns and the metal accumulation rates for the initiation of sea-floor spreading on the EPR at 8-10 m.y. ago.

Site 320

The two near-basement samples analyzed from Site 320 show high Fe and Mn and low Al values (Figure 2) typical of metalliferous sediments from near spreading centers. The samples are relatively enriched in Mn compared to the other samples analyzed in this study (Fe/Mn \sim 2, compared to \sim 3.5 for near-bottom Site 319, also see Figure 2). In other respects, such as the relatively high Fe/Ni and Fe/Co values, low Ba concentration, these samples strongly resemble the near-basement sediments of Site 319, which suggests a hydrothermal source of metals.

The metal accumulation rates calculated for these samples are approximately 10 times lower than those calculated for near-basement sediments at Site 319 (Table 2, Figure 11). The reasons for this observation are uncertain; however, similar variability in measured metal accumulation rates have been observed for recent sediments deposited on the EPR (Dymond and Veeh, in press, and Figure 11). Sediment ponding, proximity to hydrothermal vents, and variations in spreading rate are some of the factors which could cause variations in the metal accumulation rate. Nonetheless, the Fe and Mn accumulation rates for these samples are 5 to 10 times greater than the near-surface sediments from Site 319 and other Pacific pelagic sediments (Table 3 and Bender et al., 1970). This observation and the chemical composition point to a hydrothermal origin for these sediments as well.

Site 321

The six samples analyzed from Site 321 (Table 3) are from the bottom 60 meters of core in the early Miocene to late Eocene sediments described as nanno-ooze interbedded with zeolite-bearing, iron-rich nanno ooze (Unit 4) in the site survey (this volume). All samples from this part of the core have low Al and high Fe concentrations similar to other metalliferous sediments from the Nazca plate (Figure 2). The two youngest samples from the core and the three oldest samples are from the two sections of the core which have a high percentage of ferruginous particles ("RSO" = 10%-25%in Core 9; "RSO" = 15%-35% in Core 13, Chapter 5, this volume). The carbonate contents (Table 3) indicate a similar trend to the values observed in Site 319 samples, with the maximum CaCO₃ content at 35 meters above basement (321-3). These changes presumably reflect movement of Site 321 to the east, away from the hydrothermal source of metals on the Galapagos Rise Crest. The reduced carbonate values of the zeolitebearing sediments from Core 9 (321-1 and 321-2) may be an eastern analog to the Bauer Deep. For this site, however, the sediments may be expected to reveal an increasing continental detrital component with movement of the plate toward the continent.

The strong correlation between Fe, Mn, Zn, and Cu (Figure 12) and the relative enrichment of Si, Al, Co, Sc, Sb, Th, and REE in the younger sediments (Table 3, Figures 12, 13, 14, and 15) are features of the data shared by both Site 319 and 321. In contrast, two of the basal sediments from this site (321-4 and 321-5) are enriched in Mn relative to Fe compared to other sediments from the Nazca plate (Figure 2). Also 321-4, 321-5, 321-6 do not have the enrichment of Cu relative to Ni that other basal sediments and crestal EPR sediments exhibit (Figure 3). The Si/Al values for Site 321 are approximately 3, except for 321-6, and contrast with the higher values observed in Site 319 samples. Barium and nickel are not greatly enriched in the uppermost two samples analyzed (321-1 and 321-2) as they are in surface Bauer Deep samples (Figures 14 and 15). The significance of these chemical distinctions between the two sites in unclear and may result from such factors as: time variations on the Galapagos Rise hydrothermal system, a greater influence of continental detritus in this area, and east-west variations in productivity and the quantity of metals transported to the sediments by biological vectors.

Some of these factors are evident in the metal accumulation rate data for Site 321 (Table 2, Figure 11). The metals accumulated in the lower 10 meters of the core at rates in excess of those expected by authigenic precipitation; however, at rates approximately five times lower than those determined in Site 319. Also the clear maximum in Si and Al accumulation rates, observed in Site 319 basal sediments, is lacking in this core. The metal accumulation rates in the two youngest samples analyzed are more than three times higher than the nearsurface Bauer Deep sediments. This may result from local ponding effects or may indicate that continental detritus is a contributor of Si and Al and other metals in the younger samples analyzed. It is possible that sediments from Unit 3, which is lower in CaCO3 and accumulated at very slow rates, is a more proper analog to Bauer Basin sedimentation. However, no sediments from this unit were analyzed.

In summary, the composition of the basal sediments from Site 321 and the rapid rate of metal accumulation suggests that these samples have a hydrothermal origin.



Figure 12. Carbonate and salt corrected sediment composition data for Site 321.



Figure 13. Carbonate and salt corrected sediment composition data for Site 321.



Figure 14. Carbonate and salt corrected sediment composition data for Site 321.



Figure 15. Carbonate and salt corrected sediment composition data for Site 321.

A smooth decrease in metal accumulation is not as evident at this site as it was at Site 319. This may result from a smaller influence of authigenic sedimentation in this location as a result of the greater proximity to South America and the absence of the Galapagos Rise as a barrier to bottom-transported sediments.

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