# 14. IRON-RICH BASAL SEDIMENTS FROM THE INDIAN OCEAN: SITE 245, DEEP SEA DRILLING PROJECT

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#### ABSTRACT

Basal beds of black manganiferous sediment (early Paleocene) were recovered from the southwest Indian Ocean in the southern Madagascar Basin. Thirty samples were selected from the lowest 26 meters of core, representing about  $3 \times 10^6$  years of accumulation and spreading. Concentrations of Ca, Al, Si, Fe, Mn, K, Ti, Sr, Cu, and Zn were examined. These sediments are chemically similar to basal sediments in the Atlantic and Pacific oceans, as well as to those presently being deposited on the East Pacific Rise, but they have a noticeably lower metal content. Over the examined period of sediment deposition, iron and manganese accumulation rates decreased significantly. Interbedded ash layers have a distinctive chemical signature and are sometimes enriched with heavy metals. The ash layers have a much higher Ti/Al ratio than the surrounding sediment, which makes the origin of these ashes somewhat uncertain.

#### INTRODUCTION

Sediments near the basaltic "basement" that presently are far from any active ridge or spreading center and are covered by hundreds of meters of normal pelagic sediments often resemble active-ridge sediments in many ways. This has been shown in the Atlantic and Pacific oceans (Boström, 1970; von der Borch and Rex, 1970; von der Borch et al., 1971; Cronan et al., 1972; Boström et al., 1972a). Such results can best be understood in terms of the concept of sea floor spreading and, at the same time, offer direct evidence supporting this hypothesis. To date, similar information has not been available from the Indian Ocean.

During the course of drilling in the southern Madagascar Basin northwest of the southwest Indian Ridge, evidence of basal iron-rich sediment was found. Holes 245 and 245A, drilled in August 1972 at 31°32.02'S, 52°18.11'E in 4857 meters of water, covered the entire stratigraphic column. The lowest sedimentary unit had many sharply defined ash layers and a basal bed of black manganiferous clayey nanno ooze underlain by a relatively young diabasic sill (Vallier, this volume).

The purpose of this report is to provide a general description and some preliminary chemical analyses of this iron-rich deposit. Emphasis was placed on obtaining a high sample density (30 samples in the lowest 26 meters of sediment) in order to give data concerning, on the one hand, the normal variability of composition with time (about  $3 \times 10^6$  years) and, on the other hand, the kinds of large-scale changes caused by different input events. In this way, it was hoped that the different components could be separated and their chemical signatures identified, i.e., changes in the input rates of metal-rich sediments will relate

to the steadiness and duration of ridge crest emanations, if this is, in fact, the source at this location (Natland, 1973).

Long cores reaching to basement offer a particularly attractive way to study both variations in ridge activity with time and, also, changes in the influence of ridge emanations with distance from the ridge. Samples taken at various places up the core should closely resemble a suite of surface cores taken at increasing distances from the ridge, such as those examined by Boström and Peterson (1966), Bender et al. (1971), Boström et al. (1972b), and Piper (1973). The deep samples differ from such a surface suite by being older-they represent the conditions that existed near the ridge previously, and, thus, differences between old and recent crestal sediments will be due to a change in the kind of crestal activity, to increasing distance, or to diagenesis. Long cores are also a very efficient way to obtain material for examination, for one core can be sampled almost as closely spaced as desired, yielding the equivalent of a very large number of surface cores. Moreover, samples can be taken at particularly interesting locations.

The manganiferous sediments of Hole 245 are among the oldest yet examined, being at least early Paleocene (Danian) in age, and thus serve as a reference point for the kinds of compositional changes that have occurred in such sediments, as a function of time, since deposition. Data from even older Upper Cretaceous (Campanian) sediments from the Atlantic have been reported by Boström et al. (1972a).

#### METHODS

Each sample (about 2 g) was dried at 105°C, ground to pass 200 mesh, pressed into pellets containing 0.75-g

sediment mixed with 0.25g chromatographic cellulose, and examined, using X-ray fluorescence, for Ca, Al, Si, Fe, Mn, K, Ti, Sr, Cu, and Zn. Al, Si, and K were determined with a conventional unit and the other elements by X-ray fluorescence, using energy spectrometry for detection. In addition, calcium carbonate was determined by the thermal decomposition method (LECO) (Figure 1).

No attempt was made to remove sea salts from the sediments. The contribution of such salts to the total composition is negligible, and it was felt that the risk of changing composition, because of possible leaching, was too great. The amount of any element present due to pore fluids can be estimated from extrapolated pore water data of Gieskes (this volume) and the water content. Water content is described elsewhere in this volume. In brief, it varied linearly from 15 percent at 370 meters to 40 percent at 70 meters and from there up to about 65 percent at the sediment surface on a steeper gradient.

The precision of the data, given as the relative standard deviation of an individual determination (Table 1), was determined on separately prepared replicate samples and includes errors due to sample preparation and sample inhomogeneity, as well as measurement errors. The accuracy, given as estimated limit of relative error (Table 1), represents the sum of estimated bias due to possible differences between the sample matrix and the standards plus three times the relative standard deviation. This represents maximum estimated error from the true value. Relative errors from sample to sample will be defined better by the precision, since matrix differences are quite small between nearly all samples.

Bias was estimated by using as standards a series of samples of USGS diabase W-1 diluted with 0 to 80 percent  $CaCO_3$  (J. T. Baker, Utrex grade) and spiked with 2 percent Mn. A similar set of basalt (BCR-1) and a granite (G-2), plus calcium carbonate, were measured as unknowns, and deviations from expected values were determined. Carbonate-rich diabase and basalt spanned the compositional ranges probable in these samples, while the granite represented a "worst-case" variation unlikely to be encountered and hence defined as outside error limits due to matrix variations.

# Sediment Description

Hole 245 was drilled and intermittently cored to a depth of 396.5 meters, which included 7.5 meters of basalt. Hole 245A was drilled to sample the 20 to 150 meter interval. Four major lithologic units are summarized here and described in detail elsewhere in this volume (Chapter 7). Unit I (63 m), mostly of middle Miocene and late Eocene age, consists of brown silt-rich clay and brown silty clay. Unit II (63 m), of late and middle Eocene age, is a brown nanno-bearing clay with interbeds of nanno ooze and silty clay. Unit III (83 m), late early Eocene in age, is composed of orange to pinkish-gray nanno ooze. Unit IV (180 m), early Eocene and Paleocene in age, is a nanno chalk with silicified chalk and chert beds in the upper part, devitrified volcanic ash layers in the lower part, and a basal bed of black manganiferous clayey nanno ooze. Leclaire (this volume) notes that these Fe/Mn deposits appear not as coatings but as amorphous agglomerates of very fine grains, suggesting very fast formation of these oxides. A diabasic sill of an age of 27  $\pm 3$  m.y. occurs at 389 meters. No sediment was recovered between 382 and 389 meters, but the paleontological age of the sediment at 382 meters was at least early Paleocene (Danian, ca. 63 m.y.). The magnetically predicted age of basement was Late Cretaceous, ca. 68 m.y. (Schlich, this volume). Thus, the sill intersects the sediment column not more than 50 meters above true basement, assuming a uniform sedimentation rate of 1 cm/1000 y.

This sediment column fits a model (Chapter 7, this volume) which is consistent with the sea floor spreading hypothesis, involving lateral spreading and subsidence below the carbonate compensation depth.

#### RESULTS

The compositional changes observed (Tables 1 and 2, Figure 2) cover the sediment accumulated during a period of 3 m.y. (approximately), based on an estimated sedimentation rate of 10 m/m.y. (Chapter 7, this volume). Lines have been drawn between samples in Figure 2 only to guide the eye, and they do not imply knowledge of intervening layers.

If the XRF data are converted to CaCO<sub>3</sub> (assuming all Ca to be present as calcium carbonate) and these data are plotted against the LECO calcium carbonate values, an almost linear relationship is obtained (Figure 1). The ratio of the two CaCO<sub>3</sub> values is not equal to unity, the XRF yielding higher values in almost all cases. (Note that the accuracy is about 2% for both methods.) The difference, i.e., the higher XRF values, is due to the calcium associated with the noncarbonate fraction of the sediment. The experimental inaccuracies do not allow us to present meaningful figures on noncarbonate calcium in the tables, but it appears that this calcium usually constitutes less than 3 percent of the noncarbonate fraction. Sayles and Bischoff (1973) found similar values in East Pacific Rise deposits.

# DISCUSSION

There are three main regions in the cored interval. The lowest third (Samples 22-29) is enriched in Fe and Mn and contains 50 to 55 percent  $CaCO_3$ . The middle third includes four samples taken from visually distinct devitrified ash layers (Samples 9, 10, 16, and 18). The upper third (Samples 1-8) has about 70 percent  $CaCO_3$  and distinctly less Fe and Mn than the lowest third. The entire layer is predominantly Al-poor and Fe- and Mn-rich, characteristics of sediments influenced by active ridge crests.

Sample 30 was from the core catcher and does not resemble nearby samples, but seems more like samples from the upper third. It is probable that this is a contaminated sample, and in the discussion following it has not been considered as part of the lowest third. It has been observed in previous studies that core catcher samples are often nonrepresentative.

#### Mineralogy

Preliminary smear slides (Chapter 7, this volume), summarized in Tables 3 and 4, indicate that at least three of



Figure 1. Relation between "calcium carbonate" obtained from X-ray fluorescence data (assuming all Ca to be in calcium carbonate) and calcium carbonate obtained from thermal decomposition measurements (LECO).

Sample No.	Core, Section, Interval (in cm)	Depth in Core (m)	Ca (Wt %)	Al (Wt %)	Si (Wt %)	Fe (Wt %)	Mn (Wt %)	K (Wt %)	Ti (Wt %)	Sr (ppm)	Cu (ppm)	Zn (ppm)
1	13-5, 19-20	356.2	30.8	1.00	4.00	2.07	0.51	0.45	0.11	530	40	70
2	13-5, 149-150	357.5	27.6	1.30	8.96	2.86	0.66	0.65	0.17	500	90	90
3	13-6, 104-105	358.5	30.9	0.83	5.43	1.92	0.52	0.34	0.12	490		_
4	14-1, 118-119	360.2	20.4	2.26	11.90	4.97	1.10	0.90	0.25	380	100	80
5	14-2, 109-110	361.6	29.8	0.98	6.28	2.42	0.62	0.47	0.12	480	-	-
6	14-3, 77-78	362.8	29.6	1.02	6.40	2.46	0.60	0.50	0.14	470	-	-
7	14-4, 64-65	364.1	24.6	1.37	8.86	2.58	0.55	0.66	0.23	400	-	-
8	14-5, 58-59	365.6	30.8	1.07	5.06	1.88	0.55	0.43	0.09	450	100	
9 (ash)	14-6, 3-4	366.5	3.6	7.15	26.00	4.78	0.08	0.64	0.52	250	110	240
10 (ash)	14-6, 65-66	367.2	4.3	6.83	25.58	4.17	0.24	0.45	0.44	260	170	240
11	14-6,97-98	367.5	29.5	1.11	6.70	2.22	0.52	0.45	0.13	430	10	50
12	14, CC	368.0	22.8	1.38	9.50	4.65	1.43	0.81	0.20	540	110	120
13	15-1, 113-114	369.1	27.8	1.29	7.76	2.46	0.58	0.52	0.13	420	40	90
14	15-2, 1-2	369.5	26.3	1.40	8.85	2.80	0.65	0.63	0.17	390	100	90
15	15-2, 49-50	370.0	26.6	1.34	8.21	3.01	0.70	0.58	0.15	410	60	80
16 (ash)	15-2,84-85	370.3	14.2	4.27	18.08	4.03	0.68	0.44	0.25	360	110	160
17	15-2, 98-99	370.5	26.6	1.47	8.22	2.84	0.66	0.49	0.19	410	30	80
18 (ash)	15-2, 135-136	370.9	16.3	2.18	7.95	2.02	7.7	0.63	0.69	800	80	80
19	15-2, 149-150	371.0	27.3	1.43	8.18	2.90	0.76	0.53	0.16	390	40	80
20	15-3, 39-40	371.4	26.7	1.40	8.18	2.70	0.96	0.47	0.22	390	<10	60
21	15-3,80-81	371.8	27.7	1.19	7.44	2.62	0.74	0.45	0.20	390	<10	40
22	15-3, 145-146	372.5	23.0	1.94	11.10	4.92	1.36	0.77	0.23	440	70	80
23	15, CC	375.5	22.2	1.83	11.25	4.57	1.41	0.78	0.23	490	120	140
24	16-1, 11-12	380.1	22.9	1.43	9.40	4.56	1.41	0.75	0.21	490	100	110
15	16-1, 56-57	380.6	20.1	1.68	11.60	5.83	1.69	0.82	0.23	530	110	140
26	16-1, 56-58	380.6	18.7	2.19	14.17	6.20	1.72	1.08	0.30	530	80	110
27	16-1,83-84	380.8	20.9	1.71	11.05	5.19	1.70	0.74	0.26	550	100	130
28	16-1, 129-130	381.3	22.0	2.05	12.26	4.93	1.34	0.75	0.21	510	70	90
29	16-1, 143-144	381.4	17.3	2.86	16.03	5.89	1.58	0.70	0.30	560	90	130
30	16, CC	381.8	28.6	1.22	7.07	2.36	0.66	0.52	0.15	420	40	50
Basement,	basalt	389.0										
Relative st	andard <sup>a</sup> deviation (%)		1.4	2.0	1.5	2.3	0.6	0.9	4.2	0.9	11	8
Estimated	limit of error, relative	: (%)	4	12	10	10	10	15	20	30	50	50

 TABLE 1

 Chemical Composition of Sediments Obtained at Site 245 in the Indian Ocean (on a Whole-Sediment Basis)

<sup>a</sup>Determined on separately prepared replicate samples randomly interspersed in the order of analysis; includes errors in sample preparation as well as measurement. Sample 11 was prepared in duplicate, Sample 14 in triplicate, and Sample 26 in quadruplicate; the compositions given are the means of the replicated measurements.

Sample No.	CaCO <sub>3</sub> in Sample <sup>a</sup> (Wt %)	Al (%)	Si (%)	Fe (%)	Mn (%)	K (%)	Ti (%)	Sr (ppm)	Cu (ppm)	Zn (ppm)	$\frac{Sr}{Ca} \times 10^4$	$\frac{Al}{K}$	$\frac{Al}{Ti}$	100Al (Al+Fe+Mn)	<u>100 Mn</u> (Al+Fe+Mn)	100Fe (Al+Fe+Mn)	$\frac{SiO_2}{Al_2O_3}$
1	75	4.0	16.0	8.3	2.0	1.80	0.44	2120	160	280	17	2.2	9.3	28	14	57	4.5
2	70	4.3	30.0	9.5	2.2	2.17	0.57	1670	300	300	18	2.0	7.8	27	14	59	7.8
3	75	3.3	21.9	7.7	2.1	1.36	0.48	1960	—	-	16	2.4	6.9	25	16	59	7.4
4	48	4.4	22.9	9.5	2.1	1.73	0.48	730	190	155	19	2.5	9.2	27	13	60	5.9
5	74	3.8	24.6	9.5	2.4	1.84	0.47	1900		-	16	2.1	8.2	24	15	60	7.2
6	71	3.5	22.0	8.5	2.1	1.72	0.48	1620			16	2.0	7.4	25	15	60	7.1
7	63	3.7	24.0	7.0	1.5	1.78	0.62	1080		-	16	2.1	5.9	30	12	57	7.3
8	70	3.6	16.9	6.3	1.8	1.43	0.30	1500	-	-	15	2.5	11.9	31	16	54	5.3
9	4	7.5	27.0	5.0	0.1	0.67	0.54	260	115	250	69	11.2	13.8	60	0.7	40	4.1
10	5	7.2	26.9	4.4	0.3	0.47	0.46	270	180	250	60	15.3	15.9	61	2	37	4.2
11	71	3.8	23.1	7.7	1.8	1.55	0.45	1480	35	170	15	2.5	8.6	29	14	58	6.8
12	54	3.0	20.6	10.1	3.1	1.76	0.44	1180	240	260	23	1.7	7.0	18	19	62	7.8
13	69	4.1	24.8	8.0	1.9	1.68	0.42	1350	130	290	15	2.5	12.8	30	13	57	6.8
14	65	4.0	25.2	8.0	1.9	1.80	0.49	1110	290	260	15	2.2	8.3	29	13	58	7.1
15	65	3.8	23.4	8.6	2.0	1.66	0.43	1170	170	230	16	2.3	8.9	27	14	60	6.9
16	29	6.0	25.4	5.8	1.0	0.62	0.35	510	155	225	25	9.7	16.5	48	8	45	4.8
17	66	4.3	24.2	8.4	1.9	1.44	0.56	1200	90	240	15	3.0	7.7	30	13	57	5.6
18	36	3.4	12.4	4.5	12.0	0.99	1.08	1250	125	125	49	3.5	3.1	18	64	17	4.1
19	65	4.1	23.4	8.3	2.2	1.52	0.46	1110	115	230	14	3.1	2.7	28	15	57	6.5
20	64	3.9	22.7	7.5	2.7	1.30	0.61	1080	<30	170	15	3.0	6.4	28	19	53	6.6
21	68	3.7	23.2	8.2	2.3	1.41	0.63	1220	<30	125	14	2.7	5.9	26	16	58	7.1
22	56	4.4	25.2	11.2	3.1	1.75	0.52	1000	160	180	19	2.5	8.3	24	17	60	6.5
23	52	3.8	23.4	9.5	2.9	1.63	0.48	1020	250	290	22	2.3	8.1	23	18	59	6.9
24	56	3.3	21.4	10.4	3.2	1.70	0.48	1110	230	250	21	1.9	7.0	19	19	62	7.4
25	47	3.2	21.9	11.0	3.2	1.55	0.43	1000	210	260	26	1.7	6.1	18	18	63	7.8
26	41	3.7	24.0	10.5	2.9	1.83	0.51	930	135	185	28	2.0	7.2	22	17	61	7.3
27	49	3.4	21.6	10.2	3.2	1.45	0.51	1080	200	250	26	2.3	6.5	20	20	60	7.3
28	53	4.3	26.1	10.5	2.9	1.60	0.45	1080	150	190	23	2.7	9.9	25	16	59	6.8
29	37	4.5	25.4	9.4	2.5	1.11	0.48	890	140	210	32	4.1	9.3	28	15	57	6.3
30	71	4.2	24.4	8.1	2.3	1.79	0.52	1450	140	170	15	2.3	8.1	29	16	56	6.5

TABLE 2 Chemical Composition of Sediments Obtained at Site 245 in the Indian Ocean (Carbonate-Free Basis) and Selected Ratios on a Whole-Sediment Basis

<sup>a</sup>Assuming all Ca present as CaCO<sub>3</sub>.



Figure 2. Site 245: Sediment composition on a carbonate-free basis and selected ratios on a whole-sediment basis.

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RON-RICH BASAL SEDIMENT	FROM THE	INDIAN OC	CEAN, SITE 245
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TABLE 3 Smear Slide Studies of Samples from High-Ash Layers

Sample 9 (14-6, 3-4)	Smear 6-4, 6-6 (devitrified volcanic ash)
Clay	70%
Opaques	20 (Fe-Mn oxides)
Calcareous nannos	10
Sample 16 (15-2, 84-85)	Smear 2-84 (devitrified volcanic ash)
Clay	90%
Forams	3
Calcareous nannos	5
Microcrystalline carbo	nate 3
Rhombs	1

 TABLE 4

 X-Ray Studies of Samples from High-Ash Layers

	Calcite	Quartz	Plagioclase	Montmorillonite
Sample 16 (1	5-2, 84-85);	X-ray 2-83	3	
Bulk	25.1	0.9		74.0
2-20µ	_	3.7	5.2	91.0
$< 2\mu$	-	5.000		100.0
Sample 10 (1	4-6, 65-66);	X-ray 6-64	4	
Bulk	-	1.2	1990 - 1990 - 1990 - 1990 - 1990 - 1990 - 1990 - 1990 - 1990 - 1990 - 1990 - 1990 - 1990 - 1990 - 1990 - 1990 -	98.8
2-20µ	-	0.7	-	99.3
$< 2\mu$		-		100.0

Note: Bulk X-ray studies (after removal of CaCO<sub>3</sub>) on nonash layers gave the following qualitative data:

Sample 5 (14-2, 100-110); montmorillonite, palygorskite, mica, clinoptillolite.

Sample 13 (15-1, 113-114); montmorillonite.

Sample 27 (16-1, 83-84); montmorillonite.

the four high-ash samples were mostly montmorillonite. In the surrounding sediments, montmorillonite is also the dominant mineral in the noncarbonate fraction, though some quartz, plagioclase, clinoptilolite, and palygorskite can be contributors. More detailed mineralogical studies on all samples have been planned.

# Ash Layers

The ash layers show the presence of devitrified glass shards and generally contain only small amounts of calcium carbonate. Vallier (this volume) reports many more ash layers in the 20 meters of core above the segment reported on in this report.

Most ash layers were fairly thin. Samples 9 and 10 did not come from one thick ash layer, as might be assumed from Figure 2, but from two distinct layers about 7 cm thick, separated by 55 cm of sediment without visual ash layers. Sample 18 has some somewhat unusual characteristics, and we suspect that we may have ground up a manganese nodule in the sample preparation.

The  $SiO_2/Al_2O_3$  ratio in these ash layers is about equal to 4, a value which is still twice that expected in pure montmorillonite. Some plagioclase is also present, as well as some (detrital?) quartz. No precise quantitative data are available yet on the mineralogy of these particular samples, but it should be remarked that the  $SiO_2/Al_2O_3$  ratio is often high for unaltered volcanic ashes, cf. for instance the analyses for ashes in Hole 178 (Pratt et al., 1973) which show high ratios (>4). The Al/Ti ratios in the ash layers (Samples 9, 10, and 16) are significantly higher than in the sediments above and below them. In fact, the Al/Ti ratios are characteristic of those found in the continental crust. Yet we believe that the source of these ashes is ridge crest volcanism or associated island arc volcanism. Fe, Mn, and K values are significantly lower (except, of course, in Sample 18) in the ash layers than in the surrounding sediments. However, the Al/K ratio is significantly higher and the Al/Fe ratio significantly lower in the ash layers.

We found it of some interest to investigate the Sr/Ca ratio in the various samples and found that this ratio is very high in the ash layers. Whereas in the upper third of the core interval the Sr/Ca ratio is about  $18 \times 10^{-4}$ , in the ash layers values of more than  $50 \times 10^{-4}$  are found. Much of this strontium in the upper portion is associated with the calcium carbonate fraction. In fact, Manheim and Sayles (in press) estimate that recrystallized carbonate calcite should contain about 0.05 percent strontium (cf., Katz et al., 1972), whereas we obtain an average value of 0.07 percent. Gieskes (this volume) found that the interstitial Sr++ concentrations increased linearly with depth in this hole, which is evidence of a recrystallization process of calcium carbonate. Some of this mobilized Sr++ may be taken up in the montmorillonites, thus raising the Sr/Ca ratio in the ash layers. One could, therefore, consider the Sr/Ca ratio to be a diagnostic parameter of the presence of small admixtures of volcanic ash to the lowest third of the core interval. The slightly higher Sr/Ca ratio and also the slightly lower CaCO3 content would tend to support this view. The decreased SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratios and increased Al/Ti ratio in Samples 24-29 would also indicate higher volcanic ash contributions to the sediment.

# Other Sediments

The upper and the lower third of the cored interval is characterized by uniform contents in Si, Al, K, and a fairly constant Al/Ti ratio. The latter ratio is similar to those found in the surface sediments in this same geographic area (Boström et al., 1972b). This is rather interesting because the nature of the clay mineral changes considerably in this hole (Matti et al., this volume). Boström et al. (1972b) noted that the Al/Ti ratio shows a regional distribution related not to oceanic ridges but, rather, to latitude.

The  $SiO_2/Al_2O_3$  ratio of about 7 is quite high, which does suggest the presence of appreciable amounts of amorphous silica (no opaline skeletal material was observed) or of low aluminum silicates (e.g., palygorskite or Na-feldspar). More detailed mineralogical work has been planned.

Of interest is the rather low Al/K ratio in these sediments. Such low ratios are often observed in active-ridge sediments (Sayles and Bischoff, 1973). Only small amounts of K-feldspar have been detected in these sediments, but one possible explanation may be the uptake of  $K^+$  ions from seawater or interstitial waters in possible mixed-layer clay minerals. However, no significant change was found in interstitial  $K^+$  values in the overlying sediment column.

# Fe, Mn, and Al

The ratios with respect to (Al + Fe + Mn) are very close to those found by Boström et al. (1972a) as characteristic

of basal metalliferous sediments in the Atlantic Ocean (Table 5). The data suggest (Figure 2) that Al and Mn behave differently from Fe, for their ratios change sensibly and gradually in the first 26 meters of the core, whereas Fe/(Al + Fe + Mn) is more or less constant. This implies that Fe and Mn may arrive in the sediments via different paths, as has also been discussed by Bender et al. (1971) and Cronan and Garrett (1973). It is interesting to note that these ratios do not change much, whereas the actual percent Fe drops 10 percent (11.5 to 9) and the percent Mn drops 25 percent (3.2 to 2.4) toward the top of the cored interval. The ratios appear to be more useful identifiers for ridge crest inputs than are the actual amounts, while the actual amounts may better describe the rates of input. In view of the fact that about 7 meters of sediments are missing above the diabasic sill, and also because of the unknown thickness of sediment below this sill to actual basement, we can only speculate that actual contents in Mn and Fe will continue to rise to values substantially higher than those found in this study (cf., Table 6, and Boström and Fisher, 1971; Boström et al., 1972b).

It is difficult to assess the probable distance over which ridge crest activity had an influence on the sediments.

TABLE 5 Comparison of Mn and Fe Enrichment in Basal Metalliferous Sediments of the Indian and Atlantic Oceans

		Characteristic Values of the Ratio				
R	atio	Atlantic Ocean Boström et al. (1972a)	Indian Ocean (this study)			
$\frac{100 \text{ Al}}{(\text{Al} + \text{Fe} + \text{Mn})}$	near ridge crest far from ridge crest	<20 >60	20			
$\frac{100 \text{ Fe}}{(\text{Al} + \text{Fe} + \text{Mn})}$	near ridge crest far from ridge crest	>60 <40	60			
$\frac{100 \text{ Mn}}{(\text{Al} + \text{Fe} + \text{Mn})}$	near ridge crest far from ridge crest	>16 0-2	18			

Although spreading rates are roughly known, spreading has changed direction in this particular region (Schlich, this volume; McKenzie and Sclater, 1973). The genesis of a diabasic sill in this region of intense interaction between the southwestward trend of basement and the relatively young ocean floor spreading in the northwest direction from the southwest Indian Ridge again complicates interpretations. As distance above basement may be considerable, it is worthwhile to speculate about the possible source of the high iron in the sediments. Cronan and Garrett (1973) concluded that most of the iron did not seem to be associated with the carbonate or ferromanganese oxide phases in the Pacific basal sediments. Sayles and Bischoff (1973) found that much of the iron in their samples from the East Pacific Rise was associated with the clay fraction in the form of nontronites. Although hydrothermal leaching of basalts (Corliss, 1971) has been suggested as the major source of this iron, we submit that the iron may originally have been associated with the volcanic glass and ash deposited in these sediments, either interspersed in the carbonate ooze or as distinct ash layers. Later diagenetic alteration associated with devitrification processes may have mobilized some of this iron. Further chemical and mineralogical analysis of the samples should clarify this concept.

The manganese occurs mostly in the form of dispersed manganese oxides. This observation led Leclaire (this volume) to suggest that deposition occurred rapidly. Perhaps the association between rapidly depositing biogenous calcium carbonate and intermixed volcanic ash led to favorable conditions for rapid precipitation of  $MnO_2$  phases from seawater (Michard, 1969; Cronan and Garrett, 1973).

#### CONCLUSIONS

Studies of the iron-manganese-rich deposit in the lowest part of Hole 245 drilled during DSDP Leg 25 have revealed a close correlation between these deposits and other iron-manganese-rich deposits reported on active ocean ridges. The present studies suggest that the provenance of the iron, and perhaps the manganese, is indeed associated

TABLE 6
Comparison of Some Metal Concentrations in Metalliferous Sediments from Deep Cores in th
Pacific and Indian Oceans, in Surface Metalliferous Sediments from the East Pacific Rise,
and in Normal Pelagic Clays from the Indian and Pacific Oceans (CaCO <sub>3</sub> -Free Basis)

	Age	Fe	Mn	Cu	Zn	Ti
Average of 11 ferruginous sediments from the DSDP Leg 16, Pacific Ocean (Cronan et al., 1972)	Early Miocene to middle Eocene	17.5	4.5	920	360	-
East Pacific Rise, surface (Boström and Peterson, 1969)	Recent	18.0	6.0	730	380	0.02
Indian Ocean, DSDP, Leg 25 (This study)	Early Paleocene	11	3.2	200	250	0.5
Average deep-sea clay (Turekian and Wedepohl, 1969)	Recent	6.5	0.7	5760	1777	0.5
Average surface Pacific pelagic clay (Cronan, 1969)	Recent	5.1	0.5	320	ίΞ.	
Average deep-sea surface Indian Ocean clay (Marchig, 1972)	Recent	6.5	0.6		-	0.7

with volcanic activity on active ridge crests but that the source may be associated with the deposition of volcanic ash and glass, rather than with "hydrothermal" emanations. The distinct ash layers analyzed in this study have a very different chemical signature, compared to the surrounding sediments. The latter are characterized by low contents in Al and high contents in Fe and Mn, as well as by low Al/K and Al/Ti ratios.  $SiO_2/Al_2O_3$  ratios are high in the carbonate portions of the core interval, suggesting the presence of amorphous silica (not biogenous), quartz, and low alumino-silicates (e.g., palygorskite). Sediments found near ridge crests are often characterized by such high  $SiO_2/Al_2O_3$  and low Al/K ratios. Mineralogical studies, as well as further chemical studies, are in progress, and these will clarify some of the observations made in this study.

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